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Quang Minh DO

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ETUDE DES MATÉRIAUX COMPOSITES DE MATRICES POLYMÈRES ISSUS DE RESSOURCES RENOUVELABLES ET FIBRES DE BAMBOU

Thèse dirigée par **Thi Hoang LAN TIGHZERT**

JURY

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Etude des matériaux composites de matrices polymères issus de ressources renouvelables et fibres de bambou

Résumé

Dans cette étude, les matériaux composites formés à partir de poly 3-hydroxybutyrate-co-4-hydroxybutyrate (P34HB) / fibres de bambou et de polybutylènesuccinate (PBS) / fibres bambou ont été préparés en mélangeur interne et par moulage par compression. La résistance à la traction et à la flexion, le module d’élasticité et les propriétés thermiques ont été étudiés. Il a été constaté que le module est significativement amélioré et l'utilisation de fibres traitées permettra d’améliorer les propriétés globales des matériaux composites, par rapport à celles des fibres non traitées. L'étude a révélé que la modification des fibres par l’acide acétique, suivie d’une silanisation, améliore l'adhésion, ce qui entraîne une augmentation des propriétés mécaniques. En outre, le taux de fibres de 20% est considéré comme la bonne composition pour garantir de bonnes propriétés mécaniques et thermiques, ainsi qu’une réduction de l'absorption d’eau. La morphologie des composites observée en microscopie électronique à balayage (MEB) confirme ces résultats.

Mots clés: PBS, P34HB, fibres de bambou, composites.

Introduction générale

Chaque année, avec le développement de la science et de la technologie, un grand nombre de polymères et de produits dérivés des polymères sont produits. Cependant, la plupart des polymères sont synthétisés à partir de combustibles fossiles. Ces polymères ne sont pas biodégradables et en l'absence de méthode de traitement, ils deviennent des déchets nocifs pour l'environnement.

Par ailleurs, la pénurie de pétrole et de combustibles fossiles constitue des problèmes depuis de nombreuses années qui soulèvent l'inquiétude dans le monde entier. Elle affecte également considérablement l'industrie chimique. Par exemple, une statistique en 2012 a montré que la production annuelle de plastiques est de 200 millions de tonnes [1] qui sont, à l'heure actuelle principalement dérivés du pétrole. Ainsi, avec l'épuisement des ressources de pétrole brut, la fabrication de plastiques classiques devient de plus en plus chère. Par conséquent, il est nécessaire de trouver une alternative pour remplacer les ressources fossiles. Ce sont les matières premières renouvelables et respectueuses de l'environnement. Une bonne approche est de produire des agro-polymères utilisant l'amidon, les sucres, ou la cellulose pour remplacer les plastiques conventionnels. D'ailleurs, dérivés de matériaux naturels et durables, ces agro-polymères sont généralement biodégradables, ce qui en fait un processus plus respectueux de l'environnement [1]. En outre, nous pensons tirer profit des fibres naturelles abondantes et disponibles. Avec les ressources abondantes de fibres et de nouveaux agro-polymères nous nous attendons à produire des composites à moindre coût et respectueux de l'environnement.

L'avantage des fibres naturelles par rapport aux matériaux inorganiques tels que les fibres de verre est qu'elles impliquent un coût réduit. Les propriétés comprennent également une faible densité, un rapport élevé de la résistance spécifique sur la densité, une faible abrasivité, une bonne biodégradabilité et une origine renouvelable [3]. En outre, leur flexibilité facilite leur emploi, et leur rigidité très spécifique les rend attractives pour les fabricants [6]. De plus, les fibres naturelles peuvent être employées comment renforts pour de nombreux thermoplastiques. Récemment, les propriétés mécaniques des thermoplastiques renforcés de fibres végétales ont atteint un niveau aussi bon, ou meilleur que celui de certains thermodurcissables. Il en résulte que ces composites thermoplastiques sont de plus en plus utilisés [4]. Les composites de haute performance obtenus par le mélange des polymères avec des fibres naturelles peuvent être extrudés, injectés et moulés en utilisant les machines de production existantes déjà sur le marché [2, 5]. Les plastiques renforcés par des fibres naturelles utilisant des polymères biodégradables comme matrices sont les matériaux respectueux de l'environnement qui peuvent être compostés à la fin de leur cycle de vie.

Cependant, les composites renforcés par des fibres naturelles présentent quelques inconvénients. Par exemple, les propriétés physiques globales sont moins bonnes que celles des thermoplastiques renforcés aux fibres de verre. Ainsi, la température de fabrication reste faible en raison d'une dégradation possible du matériau lignocellulosique et/ou des émissions de produits volatils susceptibles d’affecter les propriétés du composite. Les températures de fabrication sont donc limitées à environ 200°C, bien qu'il soit possible d'utiliser des températures plus élevées pendant de courtes périodes. Les matrices thermoplastiques les plus populaires utilisées dans les composites renforcés de fibres naturelles sont PE, PP, PVC, PHA, etc. Généralement, pour la production de composites reposant sur des matrices thermoplastiques renforcées de fibres naturelles, la température de traitement est habituellement maintenue en dessous de 200°C [2].

L'un des inconvénients majeurs à considérer est l'absorption d'humidité relativement élevée des fibres naturelles. Elle peut conduire à un gonflement des fibres et affecter de manière significative la stabilité dimensionnelle des matériaux composites employant des fibres naturelles. Ces problèmes ne peuvent pas être ignorés. Cette absorption d'humidité par les fibres est réduite dans le composite en raison de l'encapsulation par le polymère. Si nécessaire, l'absorption d'humidité des fibres peut être réduite de manière significative par l'acétylation de certains des groupes hydroxyle présents sur la fibre.

Le problème majeur associé à l'intégration des fibres naturelles dans les thermoplastiques de grande diffusion est l'incompatibilité chimique entre les fibres hydrophiles et la matrice hydrophobe. Cette incompatibilité induit une mauvaise adhérence et une réduction de la capacité de la matrice à transférer les contraintes sur les fibres. En général, pour améliorer la compatibilité polymère-fibres, il est possible de rendre les fibres moins hydrophiles ou rendre le polymère moins hydrophobe. L'une des méthodes les plus employées pour améliorer l'adhérence consiste à utiliser des agents de couplage. Ces substances chimiques contiennent des groupes polaires et apolaires dans leur structure et qui sont employées pour former un pontage entre les fibres et la matrice. Des compatibilisants peuvent être utilisés pour améliorer l'adhérence entre les fibres et la matrice, mais cela conduira à l'augmentation du coût des fibres.

Dans cette étude, nous essayons de trouver les conditions optimales pour la production d'un nouveau matériau présentant de bonnes propriétés mécaniques d’une part et un coût réduit d’autre part [7].

Chapitre 1: Etude bibliographique

Dans ce chapitre, les propriétés des fibres naturelles et des matrices polymère : poly[3 -hydroxybutyrate - co - 4-butyrate hydroxy] (P34HB) et polybutylène succinate (PBS) sont décrites.

I.1. Fibres de bambou

Le bambou est cultivé dans de différents continents dans le monde. Il existe de différentes variétés. Cependant, les compositions des fibres de bambou sont similaires. Elles sont constituées de cellulose, d’hémicellulose et de lignine. En outre, la fibre de bambou contient également de la cire, de la pectine et d'autres substances. Le bambou est très abondant dans la nature et constitue un renfort de choix pour produire des matériaux à faible coût. D'un autre côté, les fibres de bambou montrent un caractère hydrophile similaire aux autres fibres naturelles et il est donc difficile de les rendre compatibles avec les polymères hydrophobes. Par conséquent, il existe de nombreux traitements physiques et chimiques des fibres de bambou améliorant leur compatibilité. Les méthodes physiques les plus employées sont : le traitement plasma, la modification par effet corona. Les traitements chimiques sont probablement plus simples et sont étudiés pour optimiser l'interface entre les fibres et la matrice. Les méthodes chimiques les plus largement utilisées sont les suivantes: le traitement alcalin, le traitement par acétylation, le traitement au silane, les traitements enzymatiques et les traitements avec un agent de couplage. Les traitements révèlent des surfaces de fibres plus lisses. Ces modifications sont confirmées par MEB (microscopie électronique à balayage). En outre, par rapport à d'autres fibres végétales, les fibres de bambou présentent une meilleure résistance mécanique.

I.2. Poly[3-hydroxybutyrate-co-4-hydroxybutyrate] (P34HB)

Le P34HB est un copolymère de 3-hydroxybutyrate et de 4-hydroxybutyrate. L’intérêt principal du P34HB est l’amélioration des propriétés de poly(3-hydroxybutyrate) (P3HB). La présence du 4-hydroxybutyrate diminue la cristallinité du copolymère et ajoute typiquement des propriétés d’élasticité et de flexibilité. De plus, le P34HB permet d’élargir la fenêtre d’utilisation plus étroite du P3HB. Parmi les PHA (polyhydroxyalcanoate) disponibles dans le commerce, le P34HB possède les meilleures propriétés mécaniques de résistance à la traction et d’allongement à la rupture.

I.3. Poly(butylènesuccinate) (PBS)

Le PBS est un polymère biodégradable ayant de bonnes propriétés. Il est produit par estérification et selon le mécanisme de réaction et le catalyseur utilisé, la masse molaire varie. Le PBS peut être décomposé via la coupure de la liaison ester. En outre, le PBS montre une excellente faculté au recyclage. D'une manière générale, les bonnes propriétés du PBS font de ce dernier un bon candidat en tant que matrice de matériaux composites.

Chapitre 2: Fibres de bambou

I. Données générales sur les fibres de bambou

Les plants de bambou ont été cultivés dans la province Hoa Binh, Vietnam. Les plants ont été découpés en plusieurs parties et immergés dans une solution très diluée de NaOH. Les fibres de bambou ont finalement été extraites par explosion à la vapeur.

La composition des fibres de bambou a été déterminée. La cellulose est présente à hauteur de 57,75%, la teneur de la lignine est de 25,64% et l'humidité est présente à hauteur de 8,5%. Après traitement à la vapeur, les dimensions des fibres ont pour valeurs moyennes environ 0,2 mm de diamètre et 10 cm de longueur. La longueur est ensuite ramenée à 2mm.

II. Modifications des fibres de bambou

Les fibres de bambou ont été modifiées et traitées par une solution alcaline, un mélange d'acide acétique et d'anhydride acétique et un silane en vue d'améliorer la compatibilité avec le polymère hydrophobe. Quel que soit le traitement, les fibres ont été finalement séchées à l'étuve à 80°C.

Pour tous les traitements, les fibres sont préalablement traitées avec une solution de NaOH à 0,1 N. La solution est placée sous agitation pendant 3 jours à température ambiante. Les fibres de bambou sont ensuite lavées à l'eau distillée jusqu'à ce que le pH atteigne la valeur de 7,0. Le traitement alcalin a pour objectif de modifier la surface de la fibre. Après ce traitement, une partie de la cire, de la lignine et de la pectine est éliminée.

Dans cette étude, la réaction d'acétylation est utilisée pour modifier la surface de la fibre. Comme cela est mentionné ci-dessus, les fibres ont été prétraitées par une solution de NaOH à 0,1 N. Les fibres sont introduites dans un ballon tricol, puis immergées et agitées dans un mélange de réactifs d'acide acétique et d'anhydride acétique (50/50 en volume). Le traitement requiert la présence de quelques gouttelettes d'acide sulfurique comme catalyseur. Le processus a été maintenu 3 heures à 70°C. Le pourcentage d'acétylation est évalué à 18,68%, alors que le degré de substitution (DS) est égal à 0,86. Après le traitement, le poids de la fibre gagne 11,5%.

Le traitement par le silane a également été utilisé pour modifier la surface de la fibre. Dans cette expérience, le 3-aminopropyltriméthoxysilane est hydrolysé dans un mélange éthanol / eau distillée 60/40 (en masse) durant 2 heures, en présence d'acide acétique comme catalyseur. L'acide acétique a été ajouté goutte à goutte jusqu'à obtenir un pH de 4. Enfin, les fibres ont été immergées pendant 3 heures puis ont été lavées jusqu'à obtenir un pH de 7.

Une troisième méthode combinant les deux précédentes a été proposée. L’objectif est de profiter des avantages des 2 traitements précédents. La méthode se déroule en deux temps. Les fibres sont tout d'abord traitées par acétylation, puis dans un second temps par silanisation.

Les effets des traitements ont été confirmés par des analyses utilisant l’IR-FT (spectroscopie infrarouge à transformée de Fourier), l’ATG (analyse thermogravimétrique) et la microscopie électronique à balayage (MEB). L'apparition des pics associés au groupe carbonyle dans les analyses par spectroscopie infrarouge confirme le succès du traitement par acétylation. Cependant, il est plus difficile de déceler l'effet du traitement au silane par ce même type d’analyse, car les pics du silane sont semblables à celles des fibres. L’analyse ATG, d'autre part, montre les variations des propriétés thermiques des fibres après chaque modification. Les images obtenues par microscopie électronique à balayage montrent également la modification de la surface des fibres.

Les propriétés mécaniques ont également été étudiées. Le module d'Young des fibres est compris entre 12 et 15,78 GPa. La résistance à la traction varie de 314,64 à 379,88 MPa, tandis que la déformation à la rupture varie entre 2,94 et 3,19%. Les traitements améliorent également la résistance à l'absorption d'eau des fibres. De plus de 22% de reprise d’humidité pour les fibres non traitées, elle passe à environ de 15% après 120 heures, quel que soit le type de traitement.

Chapitre 3: Composites à base de matrice P34HB et de fibres de bambou

I. Préparation

Les principaux facteurs qui régissent les propriétés des composites renforcés par des fibres sont la dispersion des fibres, la distribution de longueur de fibres, l'adhérence entre les fibres et la matrice. Dans cette étude, les fibres sont découpées à une longueur 2 mm pour faire en sorte de bien les mélanger avec le polymère. Les fibres, traitées ou non traitées, sont ajoutées au P34HB présent dans le mélangeur et déjà à l'état fondu (son point de fusion est de 167°C). La température du mélangeur interne est portée à 155°C (les frictions font augmenter la température de la matière au-delà de celle de fusion du polymère), la vitesse des rotors est de 100 tours par minute et le temps de mélange est de 5 minutes. Les teneurs en fibres sont fixées à 10, 20 et 30% en masse, dans le composite.

Les mélanges, en mélangeur interne, de fibres et de polymères obtenus sont disposés dans un moule métallique de 25x25 cm. L'ensemble est ensuite placé sous une presse de 25T. Ces échantillons sont pressés sous 5000 kg durant 10 minutes, à 180°C. L'épaisseur du matériau composite est ajustée par la dimension du cadre inséré entre les plaques métalliques supérieure et inférieure du moule.

II. Propriétés thermomécaniques des composites

Les analyses DMA (Analyse Mécanique Dynamique), DSC (Calorimétrie Différentielle à Balayage) et ATG (Analyse Thermogravimétrique) ont été utilisées pour étudier les propriétés mécaniques et thermiques des composites.

Via l'analyse DMA, le module de conservation augmente avec l'augmentation du taux de fibre sur toute la plage de température. C'est une indication claire du renforcement par l'ajout de fibres. En outre, le module de perte suit la même tendance mais dans une moindre importance. Les pics s'élargissent avec l'augmentation du taux de fibre signifiant que l'adhésion entre les fibres et la matrice est plus faible et hétérogène. Tanδ est défini comme étant le rapport du module de perte sur le module de conservation. La hauteur de tanδ diminue avec l'augmentation de la quantité de fibres de bambou et rend compte d'une augmentation plus importante du module de conservation comparativement à celle du module de perte. L'effet de l'augmentation de la quantité de fibres qui influe le module de conservation est plus important que celui lié à la qualité de l'interface entre la fibre et la matrice.

L'analyse DSC a été utilisée pour déterminer l'évolution des températures de fusion et de cristallisations du polymère et des composites. En outre, par DSC, il est possible de calculer et d'évaluer les changements du degré de cristallinité.

La chaleur de fusion diminue lors de l'augmentation du taux de fibres. Le degré de cristallinité, dans la plupart des cas, diminue avec l'augmentation du taux de fibre. Seuls les composites renforcés par des fibres de bambou modifiées par la méthode combinant successivement les deux traitements (acétylation et silanisation) montrent une augmentation de la cristallinité en augmentant le taux de fibres. Dans ce cas, l'augmentation du degré de cristallinité est provoquée par un effet de nucléation due aux fibres.

Les analyses ATG ont été réalisées pour les fibres, le polymère et les composites. Ces derniers se dégradent plus lentement que le polymère. Les courbes d'ATG des composites sont toujours situées entre celles des fibres seules et de la matrice. Les courbes d'ATG montrent que les composites renforcés par les fibres traitées se dégradent à des températures légèrement plus élevées.

III. Propriétés mécaniques

Les propriétés mécaniques des composites ont été caractérisées par des essais de traction et de flexion. Les modules de traction et de flexion ont été significativement améliorés en raison de la présence de fibres de bambou traitées, par rapport au polymère seul et au composite renforcé par les fibres non traitées. La résistance à la traction diminue avec l'incorporation de fibres traitées ou non. Par exemple, la résistance à la traction du composite P34HB/fibres de bambou a diminué de 4,4 MPa en passant de 17,4 MPa pour le polymère seul à 13 MPa pour le polymère renforcé par 20% de fibres traitées par la méthode combinant acétylation et silanisation. La résistance à la flexion suit la même tendance. Globalement, la présence de fibres traitées augmente le module de manière significative, mais réduit la résistance à la traction. Enfin, les composites renforcés par des fibres traitées montrent les propriétés bien meilleures que les composites renforcés par des fibres non traitées.

IV. Propriétés d'absorption

L'absorption d'eau est une propriété importante des composites biodégradables renforcés de fibres végétales. La mesure a prouvé que pour les fibres selon le type de traitement considéré, l'absorption d'eau est différente. Un composite renforcé par des fibres non traitées absorbe beaucoup plus d'eau (12,95% après 20 jours pour 20% de fibres) que celui renforcé par des fibres modifiées (environ 8,5% en 20 jours) avec la même teneur en fibres. Il est également montré que les 3 types de fibres modifiées ont une capacité d'absorption d'eau très similaire. Comparativement, le P34HB absorbe 2,76% en 20 jours et indiquant qu'il est beaucoup plus hydrophobe que les fibres de bambou. Les résultats montrent que simultanément le polymère P34HB est plus hydrophobe et que le traitement des fibres a une action sur la reprise d'eau des fibres dans composite. En d'autres termes, les traitements et la qualité hydrophobe du

P34HB rendent les fibres de bambou plus difficiles à absorber de l’eau à l'intérieur du composite.

Chapitre 4: Composites à base de matrice PBS et fibres de bambou

Le PBS a également été choisi comme matrice des composites. Nous nous attendions à ce que le PBS soit plus compatible avec les fibres de bambou que le P34HB. Cependant, si les composites issus du PBS montrent des résultats de la résistance à la traction similaires, les résultats sur les modules sont plus faibles.

Les composites de PBS et de fibres de bambou ont également été préparés en utilisant le mélangeur interne à 140°C. Les paramètres de vitesse et de temps de mélange sont identiques à ceux employés pour le P34HB. Le moulage par compression est réalisé à 130°C en 5 minutes et sous une pression de 1000 kg avec le même moule que pour le P34HB.

Les propriétés thermiques des matériaux composites ont été étudiées par les analyses DSC et ATG. Les composites à base de différents types de fibres de bambou ont été étudiés. La DSC révèle que la température de fusion du PBS est de 116,8°C, tandis que les composites montrent toujours 2 températures de fusion. Ce phénomène est dû probablement à une réorganisation cristalline durant le chauffage. La cristallinité diminue parce que les fibres agissent comme des charges dans le matériau composite. L’analyse ATG révèle que les composites sont plus stables avec la température que le polymère seul.

Les propriétés mécaniques ont été examinées en utilisant les tests de traction et de flexion. Dans les deux cas, les composites montrent l'amélioration significative du module alors que la résistance à la traction ne montre pas d’amélioration par rapport au polymère seul. Cela signifie que les fibres de bambou peuvent également contribuer aux propriétés mécaniques. Les traitements montrent leurs avantages via l’amélioration des propriétés mécaniques lorsque l’on compare les composites contenant des fibres traitées et non traitées. Et de tous les traitements, le procédé combinant les méthodes d’acétylation et de silanisation est le meilleur.

Le PBS a une faible température de mise en œuvre et après sa température de fusion, il devient très fluide. Par conséquent, garantir la dispersion des fibres dans la matrice PBS devient plus délicat avec notre procédé. Par la méthode de moulage par compression, il est également plus difficile d'ajuster l'épaisseur de la plaque du composite, car le PBS est très fluide à haute température. Enfin, au refroidissement, il devient rapidement fragile et cassant, ce qui limite une fois de plus son emploi via notre procédé.

Matériels et méthodes

I. Matériaux

Les fibres de bambou ont été obtenues à l'Université de Sciences et de Technologies de Hanoi (USTH). Les fibres sont issues de plants de bambou provenant des récoltes de la province de Hoa Binh, Vietnam. Transférés à l'Université de Hanoi, les plants de bambou ont été découpés en morceaux plus petits et ont été immergés dans une solution alcaline diluée. Enfin les fibres ont été extraites par la méthode d'explosion à la vapeur. Les fibres sont ensuite coupées à moins de 2 mm de longueur avant les traitements chimiques.

Le P34HB et le PBS sont les polymères thermoplastiques qui ont été utilisés en tant que matrice :

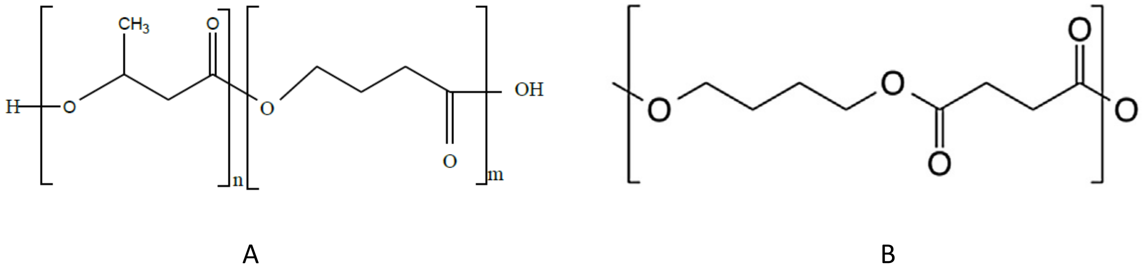


Figure 1: Structure du P34HB (A) et du PBS (B)

II. Essais et méthodes de caractérisation

II.1. Traitement alcalin des fibres

Les fibres de bambou découpées à 2 mm de longueur ont d'abord été traitées avec une solution d'hydroxyde sodium NaOH 0,1 N, pendant 3 jours. Les fibres ont ensuite été lavées avec de l'eau distillée jusqu'à ce que le pH atteigne une valeur de 7.

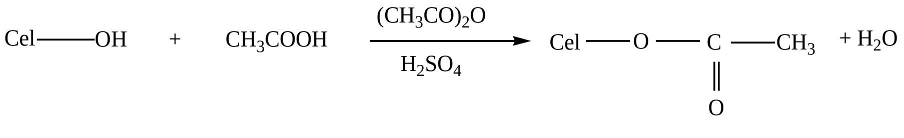
Le traitement des fibres par NaOH améliore sa capacité au mouillage et par conséquent réduit sa porosité. Cette étape donne lieu à des composites ayant des propriétés améliorées, notamment celle liée à la reprise d'humidité. Le traitement alcalin est censé précéder toute procédure de modification de surface des fibres de bambou. Il conduit à l'augmentation de la quantité de cellulose amorphe au détriment de la cellulose cristalline. La modification importante apparaissant ici est la suppression de la liaison hydrogène dans la structure en réseau de la cellulose [8,9].

II.2.Traitement des fibres par acétylation

L’acétylation des fibres naturelles est une méthode d'estérification déjà bien étudiée et détaillée. Dans ce procédé, les groupes acétyle, réagissent avec les groupes hydroxyle des parois cellulaires des fibres. Il en résulte des fibres bien plus hydrophobes qui améliorent la stabilité de ces dernières contre l'humidité. En remplaçant certains des groupes hydroxyle présents sur la paroi cellulaire des fibres par des groupes ester, nous nous attendons à réduire le caractère hygroscopique de la partie lignocellulosique [10, 11,12].

Dans cette méthode, il est nécessaire que les fibres soient trempées dans de l'anhydride acétique. Cependant, l'anhydride acétique n’est pas un bon agent gonflant des fibres [10]. Par conséquent, dans cette étude, les fibres pré-traitées par la solution alcaline, ont tout d'abord été trempées dans de l'acide acétique pendant 30 minutes, puis le même volume d'anhydride acétique y a été ajouté progressivement. Précisément, 5 grammes de fibres de bambou ont été immergés dans 280 ml du mélange acide acétique / anhydride acétique (50/50 v/v). Quatre gouttes d'acide sulfurique à 98% ont également été utilisées comme catalyseur pour accélérer la réaction.

Le mélange a été maintenu pendant 3 heures à 70°C. Le processus est décrit dans l’équation chimique suivante:



$$\mathrm{Cel{-}OH} + CH_3COOH \xrightarrow[H_2SO_4]{(CH_3CO)_2O} \mathrm{Cel{-}O{-}\underset{\underset{O}{\|}}{C}{-}CH_3} + H_2O$$

Figure 2 : Equation générale de réaction des groupes hydroxyle des fibres.

Les fibres ont ensuite été lavées avec une solution de NaOH diluée, puis avec de l'eau distillée jusqu’à obtenir un pH de 7.

II.3. Calcul du degré d'acétylation

Dans un ballon en verre, 100 mg de fibres traitées par acétylation ont été mises en suspension dans 40 ml d'un mélange eau distillée / éthanol de proportion 25/75 (en volume). Le ballon est chauffé à 50°C - 60°C dans un bain-marie pendant 30 minutes pour assurer le gonflement des fibres. Puis, 40 ml d'une solution de NaOH à 0,5 N ont été ajoutés dans le ballon contenant les fibres. Le mélange a été à nouveau chauffé à 50°C - 60°C dans un bain-marie pendant 15 min. Puis le ballon est bouché hermétiquement et maintenu à la température ambiante pendant 72 heures. Des essais à blanc ont également été préparés suivant la même procédure [13, 14, 15].

L'excès de NaOH (le volume qui ne réagit pas avec les groupes acétyle) a ensuite été titré avec de l'acide chlorhydrique HCl 0,5 N en utilisant la phénolphtaléine comme indicateur du virage. Le mélange est sous agitation pour assurer une réaction totale de l'excès de NaOH, ce qui est mis en évidence par l'apparition d'une couleur rose pâle.

Le pourcentage d'acétylation est déterminé par l'équation suivante :

$$\%\text{Acetyl} = \frac{(\text{D}-\text{C})\text{N}_{\text{HCl}}0.04305}{\text{mb}} \text{ x } 100 \qquad \text{(eq.1)}$$

mb est la masse de fibre de bambou (en g) employée pour le dosage, C'est le volume d'HCl en ml nécessaire pour le titrage de l'échantillon et D est le volume d'HCl requis pour le titrage du blanc également en ml. N est la concentration de la solution d'HCl.

Le degré de substitution (DS) est également un paramètre important à déterminer. Le degré de substitution est calculé comme suit :

$$\% \text{ Acétylation} = \frac{43.\text{DS}}{162+42.\text{DS}} \text{ x } 100 \qquad \text{(eq.2)}$$

La masse de l'ester d'acétyle est de 43 grammes, le nombre d'esters d'acétyle par unité de glucose anhydre est le DS, la masse de l'unité de glucose anhydre est de 162 grammes, la masse supplémentaire de l'estérification avec de l'acétate est de 42 grammes [14, 15].

II.4. Traitement des fibres par silanisation

Le 3-aminopropyltriméthoxysilane à 97% fourni par Aldrich, a été dissous dans un mélange d'eau distillée / éthanol de proportion 40/60 (en masse). La solution a été ajustée à l'aide d'acide acétique jusqu'à obtenir une valeur de pH égale à 4, puis elle est placée sous agitation en continu pendant 2 heures. Dans l'étape suivante, les fibres (prétraitées selon le paragraphe II.1) sont immergées dans ce mélange pendant 12 heures. La quantité de silane est de 10% en masse des fibres. Un test à 5% a permis d'obtenir les mêmes résultats [16, 17, 18]. Enfin, les fibres ont été lavées avec de l'eau distillée jusqu'à obtenir une valeur de pH égale à 7, puis elles ont été exposées à l'air pendant 12 heures avant de passer à l'étuve à 80°C pendant 12 heures.

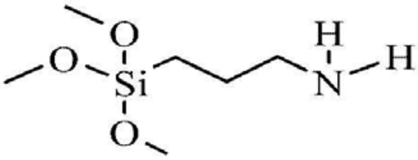


Figure 3 : Formule du 3-aminopropyltriméthoxysilane

II.5. Traitement des fibres par la combinaison acétylation- silanisation

Une autre méthode qui combine le traitement par acétylation et silanisation a également été proposée. Cette méthode a pour ambition d'exploiter les avantages des 2 traitements séparés en agissant sur un plus grand nombre de sites hydroxyle. Les fibres sont tout d'abord traitées par acétylation et dans une seconde étape ces fibres subissent la silanisation.

III. Méthodes de caractérisation

III.1. La préparation des composites

Les fibres de bambou ont été découpées à une longueur de 2 mm et traitées par diverses méthodes. Les fibres non découpées ne sont pas appropriées à l'emploi via le procédé de mélange direct. Les fibres, après modification(s), ont été séchées à 60°C avant la réalisation des mélanges par compression.

Le P34HB et le PBS et ont d'abord été séchés à 70°C et 60°C respectivement, pendant 12 heures. Puis ils ont été chargés dans le mélangeur interne. Le P34HB a été mélangé pendant 3 minutes à 160°C à la vitesse de 100 tours par minute tandis que la température utilisée pour le PBS est de 140°C toujours à 100 tours par minute. Les teneurs en fibres retenues sont de

10%; 20% et 30% en masse. Au-delà de ces pourcentages de fibres, il devient difficile de mélanger les fibres et le polymère.

Les fibres préalablement séchées ont été ensuite introduites dans le mélangeur interne et mélangées avec le polymère à l'état fondu pendant 5 minutes à la même vitesse de 100 rpm. Dans l'étape finale, les mélanges de P34HB (ou PBS) et de fibres obtenus ont été placés sur la plaque métallique du moule. L'épaisseur de la plaque de composite est ajustée en utilisant un cadre de l'épaisseur choisie. Une deuxième plaque métallique recouvrant le cadre et le mélange a été déposée dessus créant ainsi le moule. Ce dernier a été placé à l'intérieur de la presse. La température de la presse a été ajustée à 180°C pour le P34HB et 130°C pour le PBS. La pression est de 5000 kg pour le P34HB et 1000 kg pour le PBS sur une surface de 25 cmx25cm. La pression est maintenue 10 minutes pour le P34HB et 3 minutes pour le PBS.

La plaque de composite obtenue est ensuite découpée en éprouvettes via un découpoir conçu pour obtenir des formes rectangulaires suivant la norme ISO 178 :2010 (2,2-2,5 mm d'épaisseur, 13 mm de largeur et 60 mm en longueur), ou de type altère suivant la norme ISO 527-2 (75mm de longueur, 12,5 mm de largeur et 0,3 mm d'épaisseur)

III.2. Essais de traction

Les essais de traction sont menés sur un appareil MTS Adamel Lhomargy - DY35XL équipé d'une cellule de charge de 500N qui est reliée à un ordinateur piloté par un logiciel d'essais dédié (MTS version 4). Une vitesse de traverse de 10 mm / minute est appliquée pour tous les échantillons. Pour chaque type d'échantillon, au moins 30 répliques sont analysées pour garantir la fiabilité des résultats.

III.3. Essais de flexion

Les tests de flexion ont été réalisés sur un appareil INSTRON, avec une vitesse de la tête transversale de 10 mm / minute. Chaque test a été réalisé selon la norme ISO 178: 2010. Dans cet essai, les échantillons ont été découpés en forme rectangulaire et la dimension est de 2,2 mm d'épaisseur et 13 mm de largeur. La longueur de portée entre appuis est de 40 mm.

Pour un échantillon rectangulaire sous charge dans une configuration de flexion à trois points, la résistance à la flexion est calculée selon l'équation suivante [20]:

$$\sigma = \frac{3FL}{2bd^2} \qquad \text{(eq.3)}$$

Le module de flexion est déterminé selon l'équation suivante :

$$E = \frac{mL^3}{4bd^3} \qquad \text{(eq.4)}$$

F est la charge en newton (force) au niveau du point de rupture, L est la longueur de la travée de soutien, m est la pente de la courbe charge-déplacement, b est la largeur de l'éprouvette et d est l'épaisseur.

III.4. Absorption d'eau

Les variations W de masse par sorption d'eau ont été calculées selon l'équation suivante :

$$W = \frac{m_2 - m_1}{m_1} 100\% \qquad \text{(eq.5)}$$

m_1 est la masse avant immersion et m_2 est la masse à l'équilibre après immersion.

Les fibres sont placées dans un dessiccateur contenant une solution aqueuse saturée de KNO_3. L'humidité enregistrée après 1 jour est de 91%. Dans la dernière mesure, les fibres sont retirées du dessiccateur et pesées. Le rapport entre le gain de masse et la masse initiale est l'absorption d'humidité.

Pour déterminer l'absorption d'eau des composites, les éprouvettes rectangulaires de taille 60x13x2,2mm ont été placées dans un bécher rempli d'eau distillée. Les dispositifs sont maintenus dans des étuves régulées à des températures spécifiques. La méthode de calcul est identique à celle des fibres.

III.5. Microscopie électronique à balayage (MEB)

La morphologie a été étudiée par observation des surfaces fracturées via un microscope électronique à balayage. Les fragments de composites ont été obtenus en brisant l'échantillon dans de l'azote liquide. L'étude morphologique des échantillons a été réalisée avec un microscope électronique ayant un dispositif à l'hexaborure de lanthane (LaB_6) (JEOL JSM-5400LV) fonctionnant à 0-30kV. Pour éviter les effets de charge, les échantillons ont été revêtus d'une couche conductrice d'or (épaisseur ~ 10 nm). Une tension d'accélération de 20 kV a été utilisée pour recueillir des microphotographies MEB.

III.6. IR-FT (spectroscopie infrarouge à transformée de Fourier)

Les expériences en spectroscopie infrarouge ont été effectuées sur un appareil Shimadzu FTIR- 8400 S en vue de confirmer l'effet produit par les méthodes de modification appliquées aux fibres.

III.7. ATG (analyse thermique gravimétrique)

Un appareil ATG 209F3 (NEZSCH) a été utilisé pour caractériser les propriétés de dégradation thermique du P34HB. La température a été augmentée de la température ambiante à 650 °C, à la vitesse de 10°C / minute.

III.8. DSC (calorimétrie différentielle à balayage)

Les propriétés thermiques du copolymère P34HB et des composites sont caractérisées moyennant un appareil de DSC NETZSCH 204F1. Les échantillons sont chauffés sous atmosphère d'azote de la température ambiante à 185°C à la vitesse de 10°C/min de chauffage.

III.9. DMA (analyse mécanique dynamique)

Dans ce dispositif mécanique oscillant de chez TA, DMA Q800, une vitesse de chauffage de 2 K/min est retenue et l'amplitude d'oscillation est maintenue constante à 20 µm. Durant la mesure, les échantillons subissent des oscillations de 1 Hz alors que la température passe de 30°C à 120°C. Le montage correspond à une configuration de type double cantilever.

Résultats et discussion

I. Analyse spectroscopie infrarouge

Les analyses ont été effectuées de manière à confirmer l'effet des méthodes de modifications apportées aux fibres. Les spectres des fibres non traitées, prétraitées en milieu alcalin et acétylées sont superposés sur la figure 4.

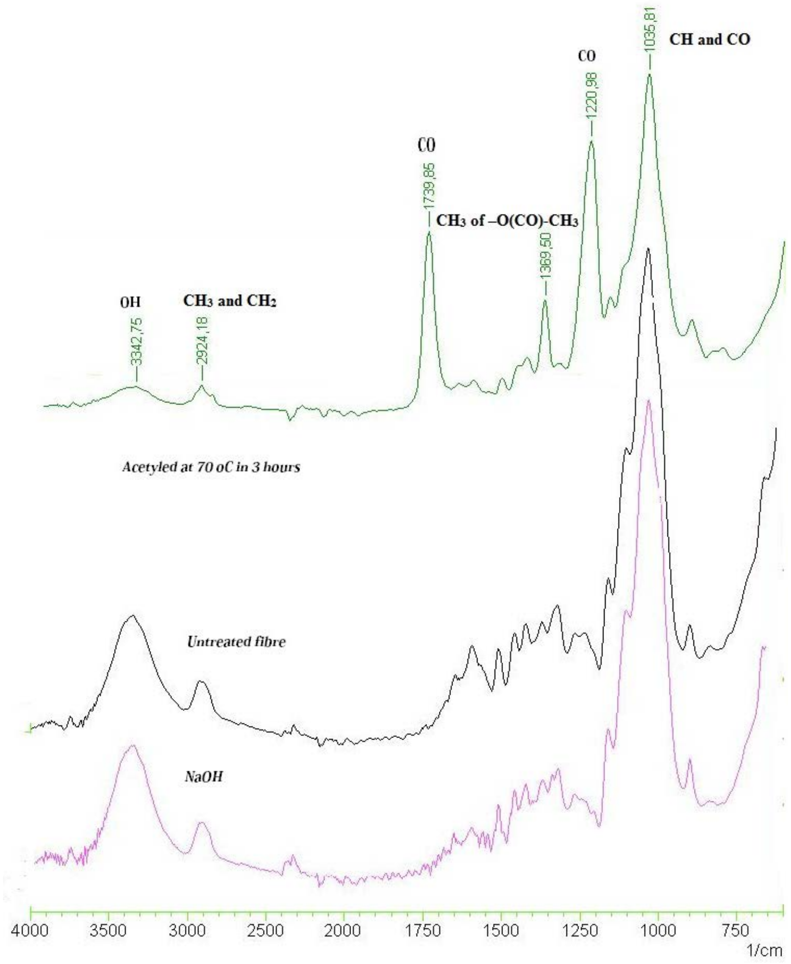


Figure 4 : Spectres infrarouge des fibres de bambou. Le traitement est précisé sur le graphique

Une bande large et forte à environ 3342 cm^{-1} est observée pour les 3 spectres est affectée à la vibration d'élongation de la liaison O-H de la fonction hydroxyle [19, 20]. La bande d'absorption à 2924 cm^{-1} peut être attribuée à l'élongation C-H des groupes méthyle et méthylène. Les bandes à 1739 cm^{-1} sont identifiées comme des vibrations d'élongation du groupe C=O. Après le traitement alcalin suivi de l'acétylation, le pic d'absorption à 1220 cm^{-1} correspondant à l'élongation de la liaison C-O et celui à 1739 cm^{-1} de la liaison C=O du groupe ester sont clairement visibles.

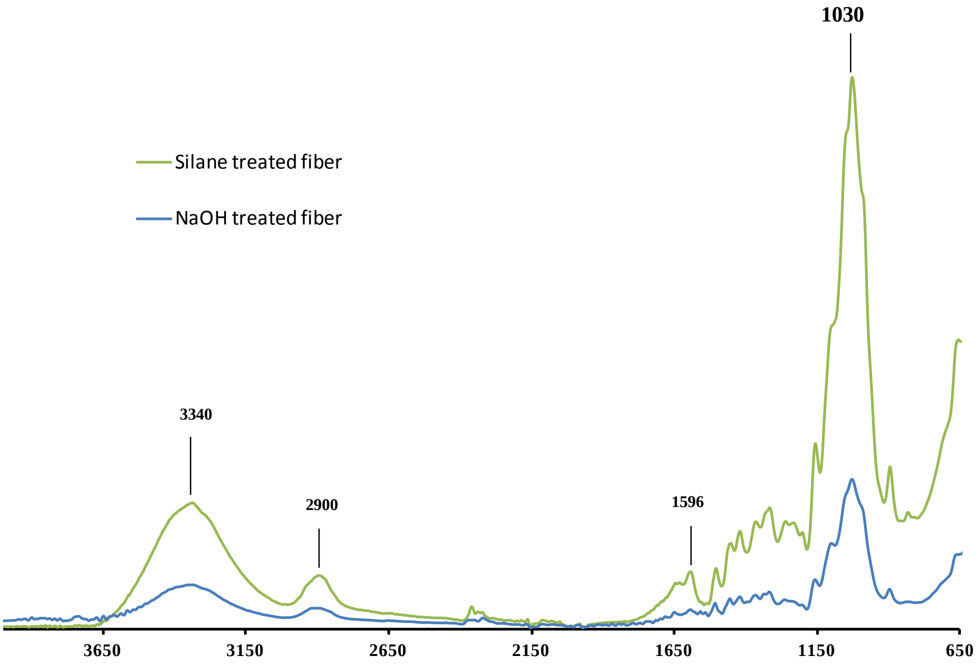


Figure 5 : Spectres FTIR des fibres de bambou traitées par silanisation et en milieu alcalin

Pour les fibres traitées par silanisation, l'observation de la modification est rendue difficile car les fréquences de vibration du groupe siloxane O-Si-O sont similaires à celles des vibrations de la fibre de bambou. Ainsi, le groupe amine montre des pics vers 1596 cm^{-1} très faibles dont l'attribution doit être prise avec précaution car ils sont recouverts par des groupes C-H des fibres. Les pics vers 750-850 cm^{-1} est l'un des modes de vibration du groupe O-Si-O. Ces pics se chevauchent avec les groupes C-H et C-O des fibres.

II. Degré d'acétylation et de substitution

Les degrés d'acétylation (% Acétyl) et de substitution calculés sont respectivement de 18,68% et 0,86. Cela signifie que les fibres sont bien modifiées. En outre, après le processus d'acétylation, la masse des fibres est augmenté de 11,5% et confirme la réussite de l'acétylation.

III. Analyse ATG

Les analyses thermogravimétriques ont été réalisées pour les fibres, le polymère et les composites. Les composites se dégradent plus lentement que le polymère. Les courbes de dégradation des composites (matrices PBS ou P34HB) sont toujours situées entre celle des matrices et celle des fibres de bambou.

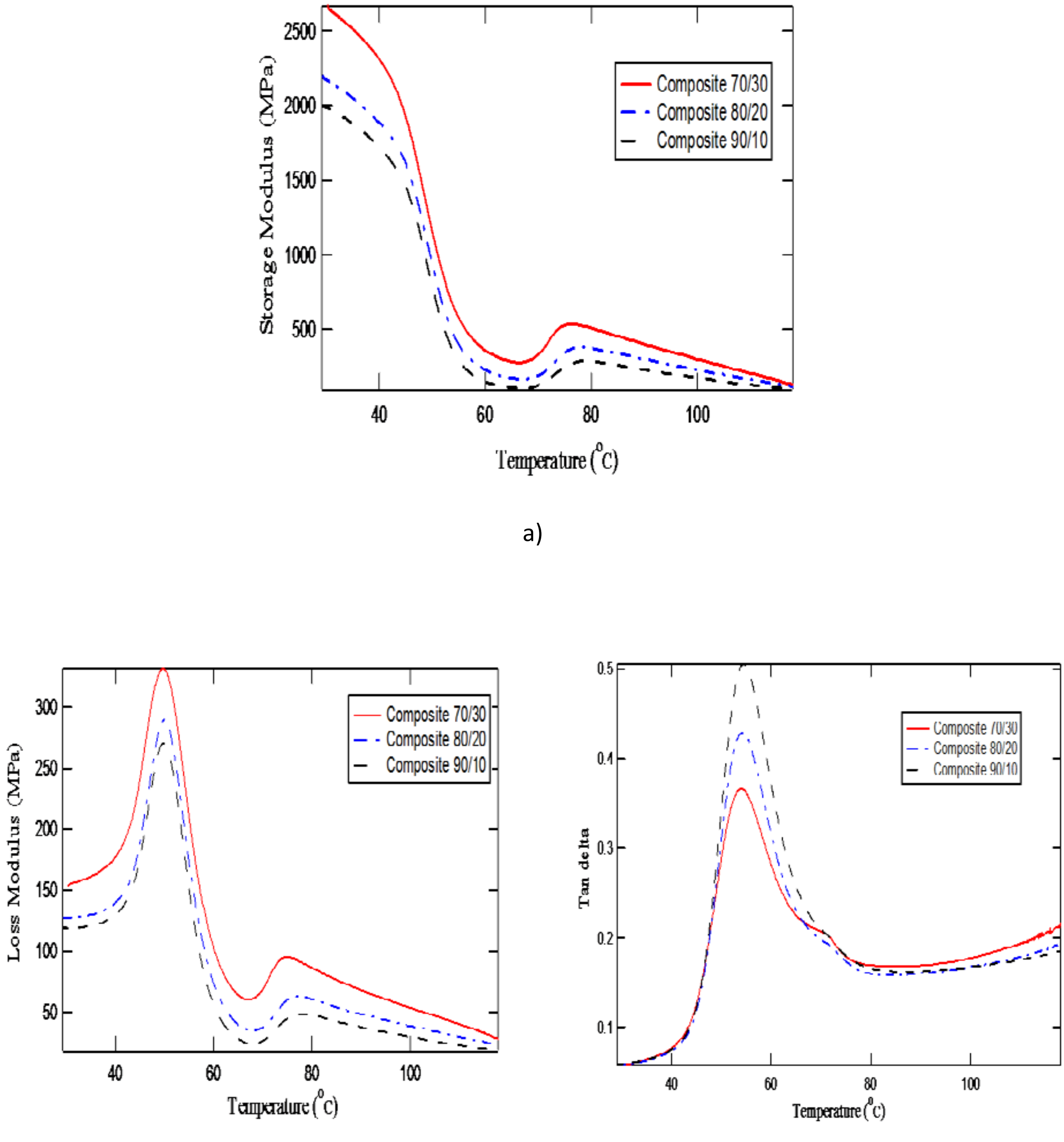
IV. Analyse DSC

La DSC a été utilisée pour déterminer la température de fusion et celles de cristallisations froide et principale (lors du refroidissement) des polymères et des composites. En outre, par DSC, il est possible de calculer et d'évaluer l'évolution du degré de cristallinité. Les analyses des composites à base de P34HB montrent l'augmentation de cristallinité lors de l'ajout des fibres traitées avec la méthode combinée d'acétylation et de silanisation. Il s'agit d'un effet de nucléation provoqué par les fibres modifiées. Contrairement, la cristallinité des composites de matrice PBS diminue avec l'augmentation du pourcentage de fibres de bambou. Dans ce cas, les fibres jouent le rôle de charge.

V. Analyse DMA

L'analyse montre que le module de conservation augmente avec l'augmentation du taux de fibres sur toute la plage de température. C'est une indication de l'action du renfort. En outre, le module de perte augmente également avec l'addition des fibres mais dans une moindre mesure. Les pics plus larges ont été obtenus avec l'augmentation du taux de fibre. La courbe de tanδ se définie comme étant le rapport du module de perte sur le module de conservation. La hauteur de tanδ diminue avec l'augmentation de la quantité de fibres de bambou et rend compte d'une augmentation plus importante du module de conservation comparativement au module de perte. L'effet de l'augmentation de la quantité de fibres qui influe le module de conservation est plus important que celui lié à la qualité de l'interface entre la fibre et la matrice.

Les essais de DMA pour des échantillons de P34HB / fibres traitées par la méthode combinée d'acétylation et de silanisation sont présentés dans les figures 6 ci-dessous :



a)

b)

c)

Figure 6 : a) module de conservation, b) module de perte, c) tanδ

VI. Essais de traction

Les essais de traction ont été menés afin de déterminer les propriétés mécaniques des composites. Comme mentionné ci-dessous, il y a des facteurs décisifs dans la détermination de ces propriétés, comprenant le pourcentage de fibres, la méthode de préparation, l'orientation des fibres et l'adhérence à l'interface des fibres et de la matrice. Dans cette étude, nous nous concentrons sur la mise en évidence par les tests de traction de la modification des fibres en admettant l'hypothèse que ces modifications ont permis d'améliorer l'adhérence entre les fibres et la matrice [15, 23].

En comparaison avec les composites renforcés de fibres non traitées, ceux renforcés par des fibres traitées ont montré un meilleur module et une meilleure contrainte à la rupture. Ce constat est observé quel que soit la nature de la matrice des composites : P34HB ou PBS. Ces résultats prouvent que la modification des fibres joue un rôle dans l'amélioration de la résistance du composite. D'ailleurs, de toutes les méthodes qui ont été utilisées, c'est celle combinant l'acétylation et la silanisation qui présente les meilleurs résultats.

Toutefois, sauf pour le module et par rapport au polymère seul (P34HB ou PBS) la contrainte à la rupture n'a pas été améliorée par l'addition de fibres. La diminution de la contrainte à la rupture des composites suggère que l'adhérence doit être encore améliorée même s'il existe bien une interaction entre les fibres et la matrice. Le module augmente considérablement. L'effet est dû à la présence de fibres. Ces dernières ont un meilleur module que celui des matrices.

Toutefois, la région d'interface entre les fibres et la matrice reste limitée, ce qui correspond à un manque de cohésion à l'interface. Par conséquent, la résistance à la rupture diminue avec l'augmentation du pourcentage de fibres. La compatibilité entre la matrice et la fibre est un facteur décisif pour la résistance à la traction. Le pourcentage de fibres et le traitement subi par ces dernières sont des facteurs clé de l'augmentation du module. Il existe d'autres facteurs non pris en compte dans notre étude, tels que l'aspect dimensionnel de la fibre [23].

VII. Essais de flexion

Les tests de flexion ont également été réalisés afin de déterminer les propriétés mécaniques des composites P34HB / fibres de bambou. Contrairement à l'essai de traction où la contrainte se propage au travers de l'ensemble de l'échantillon, dans le test de flexion la contrainte reste localisée dans le domaine de la charge appliquée [22].

De même que pour l'essai de traction, le module des composites a été considérablement amélioré avec l'augmentation de la teneur en fibres. Le module double en utilisant 20% de fibres modifiées par la combinaison acétylation- silanisation, par rapport à la matrice P34HB seule ou au composite renforcé avec 20% de fibres non traitées. Ces résultats contribuent à conclure qu'il existe une adhérence entre la matrice et les fibres traitées qui permet la transmission de la contrainte de la matrice aux fibres conduisant à l'amélioration de la rigidité [22]. La résistance à la flexion, cependant, est à peu près la même pour un composite renforcé avec 10% de fibres qu’avec le P34HB seul et diminue légèrement lorsque la teneur en fibres est de 20% et 30%. Encore une fois, le composite renforcé par les fibres traitées avec la méthode combinée donne de meilleurs résultats que celui renforcé de fibres non traitées. Le module a même doublé lors du remplacement des fibres non traitées par celles traitées.

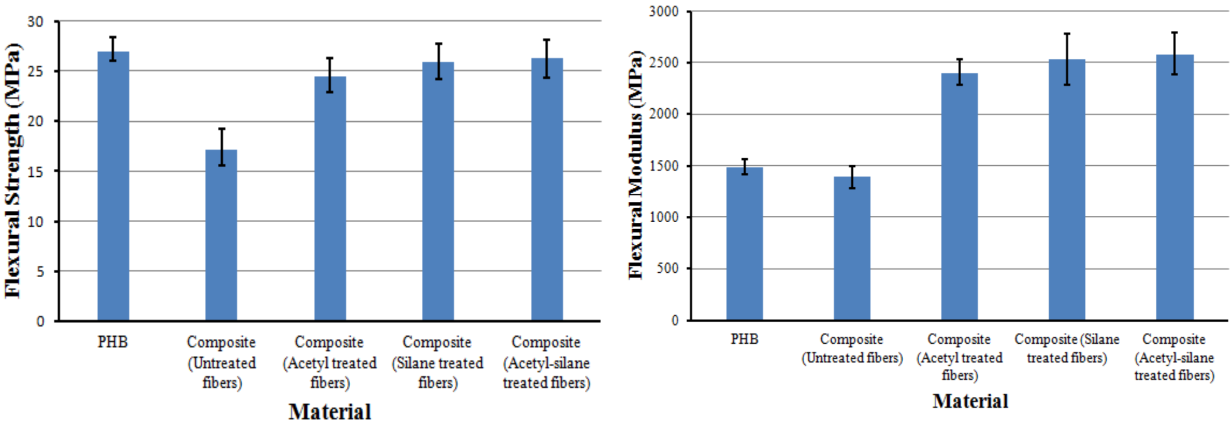


Figure 7: Influence des traitements de fibres à résistance à la flexion des composites (P34HB / 20% fibres de bambou).

VIII. Absorption d'eau

L'absorption d'eau est une propriété importante du composite renforcé de fibres végétales. Dans cette étude, tous les spécimens des composites P34HB / fibres de bambou ont été maintenus dans l'eau à 40°C et tous les échantillons composites contenant 20% de fibres de bambou. Le résultat a révélé que le polymère P34HB est le plus hydrophobe. Son absorption d'eau est très faible, tandis que le composite renforcé de fibres de bambou non traitées montre la valeur d’absorption la plus élevée à environ 13% après 30 jours. Le test a également prouvé le bon effet des traitements. Les composites renforcés par des fibres traitées par acétylation ou silanisation ont montré des valeurs stables de l'ordre de 8%. La combinaison des deux traitements montre une absorption plus faible. Ceci tend à montrer que l’association de la matrice hydrophobe et du traitement des fibres diminue la reprise d'humidité du composite. Cette reprise est d'autant limitée que si l'interface est de bonne qualité.

De plus, les fibres traitées seules absorbent moins d'humidité que les fibres non traitées. D'une manière générale, le P34HB (comme d'autres polymères classiques) sont plus hydrophobes que les fibres de bambou. Ce qui signifie que le P34HB empêche l'eau de pénétrer dans le matériau composite et il augmente l'imperméabilité et, en d'autres termes, rend les fibres de bambou plus difficiles à gonfler à l'intérieur du composite [21].

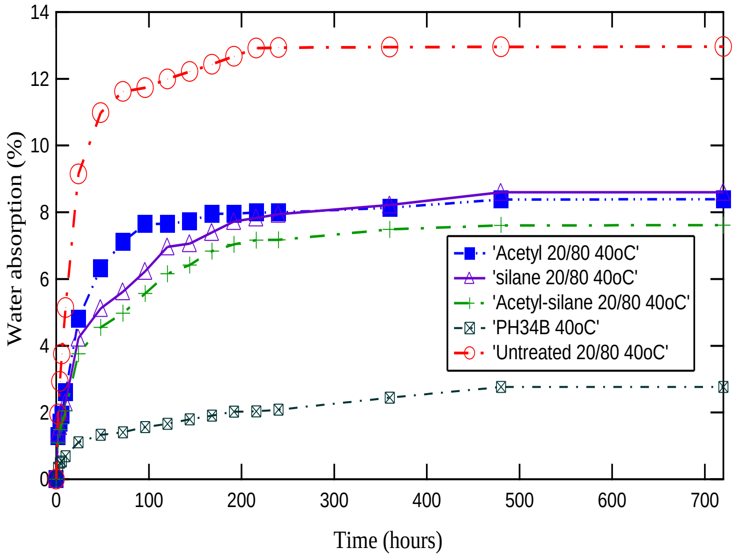
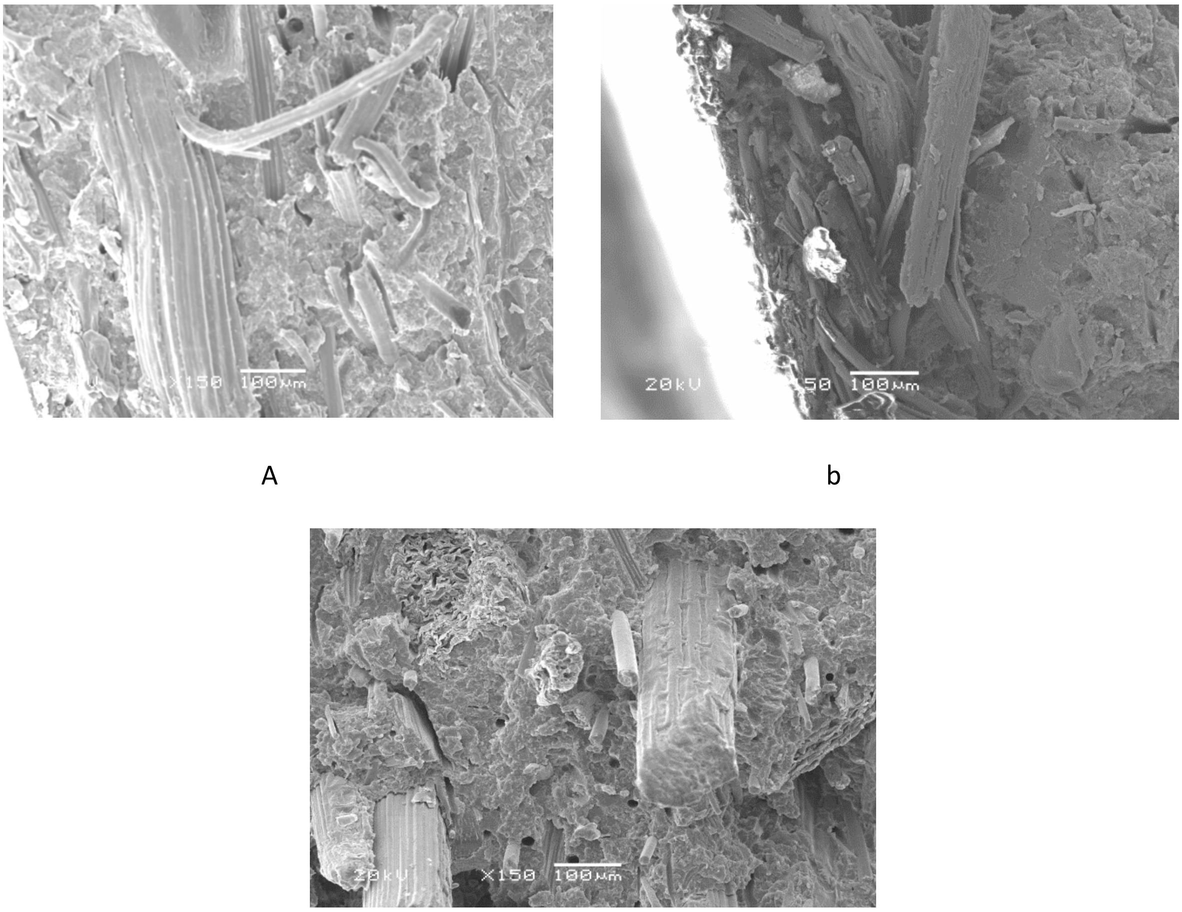


Figure 8: Courbe d'absorption d'eau des composites P34HB/20% fibres, selon traitement des fibres au cours du temps

IX. Morphologie des interfaces fibres/matrice des composites

La figure 9 montre les micrographies MEB de la surface des composites fracturés dans l'azote liquide. Les deux échantillons de composites contiennent la même quantité de fibres de bambou (20% en masse), les images reflètent les propriétés mécaniques des matériaux composites.



A

b

c

Figure 9: Micrographies MEB de surfaces de rupture des composites P34HB / fibres non traitées (UT) (a, b) et du composite P34HB / fibres traitées acétylation-silanisation (AS) (c)

Il existe encore des vides à l'intérieur. Ces vides proviennent peut-être de la rupture de l’interface fibres/matrice lorsque la cryofracture a été réalisée. La micrographie du composite renforcé avec des fibres traitées (c) montre que le polymère est plus présent à la surface des fibres et recouvre ces dernières, signifiant une meilleure adhésion.

En outre, les composites renforcés avec des fibres AS montre une meilleure compatibilité avec la matrice, le vide entre les fibres et la matrice est plus petit et étroit. Les fibres semblent être bien recouvertes par le polymère. Par conséquent, les propriétés mécaniques du composite AS sont les meilleures.

Conclusion

Dans cette étude, les matériaux composites poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P34HB) / fibres de bambou et poly(butylène succinate) (PBS) / fibres de bambou ont été préparés en utilisant le mélangeur interne et le moulage par compression. Les propriétés thermomécaniques de P34HB et de PBS ont été caractérisées. Les fibres de bambou ont été modifiées par différents traitements chimiques. Les propriétés mécaniques telles que la résistance à la traction, la résistance à la flexion, le module d'élasticité et les propriétés thermiques ont été étudiées. Pour les deux types de composites (P34HB et PBS), le module est significativement amélioré, cependant, la résistance du composite est légèrement diminuée. L'allongement à la rupture est plus faible que celui des polymères purs, ce qui indiquerait une bonne adhérence entre la matrice et les fibres. L'étude révèle que l'adhésion est améliorée avec les fibres modifiées avec le silane et l'acide acétique, ce qui entraîne une augmentation des propriétés mécaniques du matériau, par rapport à celles des composites renforcés avec des fibres non traitées. En outre, le taux de 20% de fibres est considéré comme la bonne composition de fibres pour garantir de bonnes propriétés thermomécaniques et une absorption d'eau faible.

En étudiant ces matériaux composites, nous visons à produire des matériaux respectueux de l'environnement. De plus, l'abondance des fibres de bambou permettra de réduire le coût de la matière première. Ce travail porte principalement sur la modification des fibres de bambou afin d'améliorer les propriétés globales des composites et sur la comparaison de ces propriétés par rapport à celles des fibres non modifiées. Pour atteindre une meilleure adhérence matrice-fibre, un agent de couplage et/ou compatibilisant peuvent être étudiés et utilisés dans une future étude.

Conclusion générale et perspectives

Dans cette étude, l'addition de fibres de bambou dans un matériau polymère agro-sourcé révèle une voie prometteuse pour créer un matériau composite qui respecte l'environnement. Trois procédés de modification chimique des fibres ont été utilisés pour améliorer l'adhérence entre les fibres de bambou et les matrices thermoplastiques. Dans cette étude, deux types de polymères, le P34HB (poly(3-hydroxybutyrate-co-4-hydroxybutyrate)) et le PBS (poly(butylène succinate)) ont été utilisés.

Les fibres sont préalablement traitées en milieu alcalin pour éliminer les cires, les pectines et les autres substances. Ces produits sont censés diminuer l'adhésion avec la matrice. Les succès de la réalisation des traitements ont été vérifiés par FTIR, ATG, essai d'absorption d'eau, MEB ...

Les influences des traitements chimiques des fibres dans les composites ont également été étudiées. Nous nous efforçons de mettre l'accent sur la modification des fibres susceptible d’améliorer la compatibilité entre la matrice et les fibres. Les résultats de microscopie électronique à balayage sont en accord avec ceux des propriétés mécaniques.

Dans tous composites produits avec l'addition de fibres de bambou modifiées ou non, la résistance à la traction et la résistance à la flexion ont diminué, tandis que le module a été considérablement amélioré. Dans le cas du PBS, les différences de résistance à la traction entre le polymère pur et les composites sont insignifiantes. Le PBS a une température de fusion plus basse, mais il est beaucoup plus difficile à utiliser. Par exemple, dans notre étude, il est difficile de contrôler la fabrication des échantillons employant le PBS car ce dernier est très fluide aux températures supérieures à celle de sa fusion. Par conséquent, il est difficile de contrôler la dispersion des fibres dans la matrice du PBS. En outre, lorsque la température refroidit, la viscosité devient très élevée et il est difficile d'obtenir des plaques de composites.

Les résultats ont également prouvé que les méthodes de modification des fibres ont des effets bénéfiques sur les propriétés globales des composites, par rapport aux composites renforcés par des fibres non traitées. Ainsi, toutes les propriétés thermiques et mécaniques sont améliorées, l’absorption d'eau est diminuée. Parmi toutes les méthodes de traitement, celle qui combine l'acétylation et la silanisation se révèle optimale. Cette étude fournit une solution simple et efficace de traitement des fibres.

Nous pouvons tirer profit de la quantité abondante de bambou, en employant ses fibres comme renfort dans les composites à matrice thermoplastique. C’est un matériau respectueux de l'environnement qui convient à l'utilisation de matériaux présentant des propriétés mécaniques acceptables.

Par ailleurs, il est possible d'améliorer la résistance mécanique à l'aide d'un agent de couplage. L’utilisation des agents de couplage est probablement une bonne solution pour améliorer l'adhérence et la compatibilité entre les fibres et la matrice. D’autres méthodes de préparation des échantillons peuvent également être étudiées. En outre, l'effet de la taille des fibres, de la dispersion des fibres dans le composite et de la quantité de silane utilisée pour le traitement doivent également faire l’objet d’études.

Enfin, d'autres propriétés peuvent être étudiées afin d’approfondir les connaissances sur l'adhérence et la compatibilité entre les fibres et la matrice de polymère. L’efficacité de nouvelles méthodes de traitement et de conditions expérimentales pourraient révéler de nouvelles caractéristiques dans la modification de l’interface entre les fibres et la matrice.

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List of abbreviations

PHB : Polyhydroxybutyrate
P34HB(PH34B) : Poly(3-hydroxybutyrate – co – 4-hydroxybutyrate)
PBS : Polybutylene succinate
BF : Bamboo fiber
FTIR : Fourier Transform Infrared Spectroscopy
DSC : Differential Scanning Calorimetry
TGA : Thermogravimetric Analysis
DMA : Dynamic Mechanical Analysis
SEC : Size Exclusion Chromatography
SEM : Scanning Electron Microscopy
DS : Degree of Substitution
Tg : Glass transition temperature
Tm : Melting temperature
ΔH_f : Heat of fusion
Tc : Crystallization temperature
FTIR : Fourier Transform Infrared spectroscopy
RH : Relative humidity
NFRT : Natural fiber reinforced thermoplastics
HDPE : High density polyethylene
LDPE : Low density polyethylene
APS : 3-aminopropyltrimethoxysilane
PP : Polypropylene
NDS : Natural digestion system
MAH : Maleic anhydride
MAH-PP : Polypropylene – maleic anhydride
APTES : 3-aminopropyltriethoxysilane
PLA : Polylactic acid
Tcc : Cold crystallization temperature
MCP : Multicomponent polymerization
LDI : Lysine based diisocyanate
AS fiber : Acetyl – silane treated fiber
UT fiber : Untreated fiber

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GENERAL INTRODUCTION

Elaboration of polymer composite from renewable resources reinforced with bamboo fibers.

General introduction

Annually, with the development of science and technology, a lot of products of polymer are produced. However, most of polymers are synthesized from fossil fuel. These kinds of polymers are also non-biodegradable materials and if there is no treatment method, they will become waste and harmful to the environment.

Indeed, the shortage of oil and fossil fuel are the problems for many years which raise the concern worldwide. It also affects dramatically to the chemical industry. For example, one statistic in 2012 showed that plastic had an annual production of 200 million tons [1] and at present, it is predominately derived from petroleum. Therefore, with the exhaustion of crude oil resource, the manufacture of conventional plastics becomes more and more expensive. As a result, it is necessary to find the alternative, sustainable raw materials to replace fossil resources. In order to make a new material that is non fossil fuel based, we think of natural resources, especially the one that is friendly environment. A good approach is to produce biopolymers using starch, sugars, or cellulose to substitute conventional plastics. Besides derived from sustainable biomaterials, these biopolymers are generally bio-degradable, making it an environmental beginning process [1]. Moreover, we think of taking advantage of the abundant and available natural fibers. With the abundant resources of fibers and the new biopolymer coming, we expect to produce new composite with lower cost and environmental friendly.

The advantage of natural fibers over inorganic materials such as glass fiber is that they involve with reduced cost. Their attributions also include low density, high specific strength to density ratio, low abrasiveness, biodegradability and the fact that they are produced from a renewable resource [3]. Besides, their flexibility during processing, and highly specific stiffness make them attractive to manufacturers [6]. Moreover, natural fibers can be processed with thermoplastic. In recent years, the mechanical properties of high grade thermoplastics have reached a level as good as, or better than, thermosetting plastics, resulting in thermoplastic composites being increasingly used [4]. The high performance composites by polymeric material reinforced with natural fibers can be mixed and molded using already available production machinery such as extrusion and injection molding with minimal strength degradation [2, 5]. Natural fibers reinforced plastics by using biodegradable polymers as matrix are the most environmental friendly materials which can be composted at the end of their life cycle.

However, composites reinforced with natural fibers exhibit some drawbacks. For example, the overall physical properties are worse than that of glass-fiber reinforced thermoplastics. The processing temperature is low due to the possibility of lignocellulosic degradation and/or the possibility of volatile emissions that could affect composite properties. The processing temperatures are thus limited to about 200^{o}C, although it is possible to use higher temperatures for short periods [64]. The most popular thermoplastic to be used as the matrix in natural fiber reinforced thermoplastics (NFRT) are PE, PP, PVC, PHA ... During the production of natural fiber reinforced thermoplastics (NFRT) the processing temperature is typically kept below 200^{o}C [2].

One of the drawbacks to consider is the high moisture absorption of the natural fibers. This relatively high moisture absorption can result in swelling of the fibers, and significantly affect to the dimensional stability of the natural fiber composites. These problems cannot be ignored. The absorption of moisture by the fibers is minimized in the composite due to encapsulation by the polymer. If necessary, the moisture absorption of the fibers can be significantly reduced through the acetylation of some of the hydroxyl groups present in the fiber or compatibilizer can be used to improve the adhesion between the fibers and matrix, but it will lead to the increase in the cost of the fiber.

The major problem associated with integrating natural fibers into commodity thermoplastics is the chemical incompatibility between the hydrophilic fibers and the hydrophobic polymer. This incompatibility results to poor adhesion and a reduction in the ability of the matrix to transfer stress to the fibers. In general, to improve this compatibility, it is possible to make the fibers less hydrophilic or make the polymer less hydrophobic. One of the most popular methods to improve the adhesion is using the coupling agents, which are chemicals that contain polar and non-polar groups in their structure to form a bridge between fibers and matrix. We can also modify the fibers to improve the adhesion.

In this study, we try to find the optimum conditions for producing a new material. The research of this optimum must take account the best mechanical properties on one side, and the lower cost of production on the other side. Besides, we also concern about life performance and biodegradation [7].

CHAPTER 1: Bibliographic Study

Chapter 1: Bibliographic study

I.Plant fibers /Bamboo fibers

I.1.Plant fibers

There is now a growing trend to take advantage of natural fibers as fillers and/or reinforcers in plastic composites. Natural fibers have flexibility during processing, highly specific stiffness, and low cost (on a volumetric basis) which make them attractive to manufacturers even though they bare some properties which are not good for the material [6]. When natural reinforced plastics were subjected, at the end of their life cycle, to a combustion process or landfill, the released amount of CO_2 of the fibers is neutral with respect to the assimilated amount during their growth.

Natural fibers reinforced plastics by using biodegradable polymers as matrix are the most environmental friendly materials which can be composted at the end of their life cycle. Although the overall physical properties of those composites are not as good as those of glass-fiber reinforced thermoplastics, the natural fibers attract a lot of researchers based on their advantages. Moreover, a balance between life performance and biodegradation has to be developed [7].

I.1.1.Classification

The plants, which produce natural fibers, are classified as primary and secondary depending on their utilization as shown in table 1. Primary plants are those grown for their fiber content, while secondary plants are plants in which the fibers are produced as a by-product. Jute, hemp, kenaf, and sisal are examples of primary plants. Pineapple, oil palm and coir are examples of secondary plants [6].

Table 1: Classification of plant fibers, origin, world annual production and cost (interview in 2006) [14].

Fibre type	**Botanical name**	**Plant origin**	**Production (10^3 Tonnes)**	**Cost ($/ kg)**
Abaca	*Musa textilis*	Leaf	91	
Bagasse		Stem	102,000	
Banana		Leaf	200	0.1
Bamboo	*Gigantochloa scortechinii* *Dendrocalamus apus*	Stem	10000	
Coir	*Cocos nucifera L.*	Fruit	650	0.84
Cotton	*Gossypium spp.*	Seed	19010	2
Flax	*Linum usitatissimum*	Stem	830	0.6 - 0.8
Hemp	*Cannabis sativa L.*	Stem	214	0.7 – 0.8
Jute	*Corchorus capsularis* *Corchorus olitorius*	Stem	2850	0.8 – 0.9
Kapok	*Ceiba pentandra*	Seed	123	0.2
Kenaf	*Hibiscus cannabinus*	Stem	970	0.7 – 0.8
Phormium	*Phomium tenax*	Leaf	-	
Pineapple	*Ananas cosmosus Merr.*	Leaf	-	
Ramie	*Boehmeria nivea Gaud*	Stem	100	
Sisal	*Agave sisilana*	Leaf	318.8	0.74

I.1.2.Properties of plant fibers

I.1.2.1.Components and structure

Although the different kinds of plants have different conditions to grow up (weather, minerals …), they still have the same general features. The main components of natural fibers are cellulose, hemi-cellulose, lignin, pectin, waxes and water soluble substances, with cellulose, hemi-cellulose and lignin as the basic components with regard to the physical properties of the fibers.

Natural fiber cell is divided into 2 layers: the primary and secondary layer. A single fiber of all plant based natural fibers consists of several cells. These cells are formed of crystalline microfibrils based on cellulose, which are linked to a complete layer, by amorphous lignin and hemicellulose. Multiples of such cellulose – lignin/hemicellulose layers in one primary and three secondary cell walls stick and gather together to form a multi-layer composite.

These cell walls differ and vary in their composition (ratio between cellulose and lignin/hemicellulose, Table 2) and in the orientation of the cellulose microfibrils [6].

Table 2: Chemical composition of some plant fibers [6]

	Cotton	*Jute*	*Flax*	*Ramie*	*Sisal*
Cellulose	82.7	64.4	64.1	68.6	65.8
Hemi-cellulose	5.7	12.0	16.7	13.1	12.0
Pectin	5.7	0.2	1.8	1.9	0.8
Lignin	_	11.8	2.0	0.6	9.9
Water soluble	1.0	1.1	3.9	5.5	1.2
Wax	0.6	0.5	1.5	0.3	0.3
Water	10.0	10.0	10.0	10.0	10.0

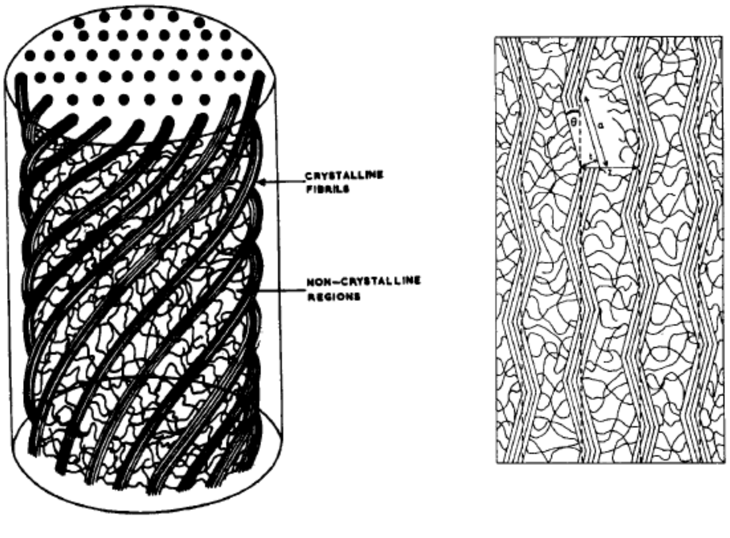
I.1.2.2.Composition of different cellulose based natural fibers

Till date, many authors tried to describe the mechanical characteristic values of natural fibers in term of their structure. The basic idea of the model which was described by Hearle and applied by Mukherjee et al. on various natural fibers is given in Fig 2 [7].

The data on chemical composition of some plant fibers are also presented in another research as shown in Table 3 [7]. This chemical composition obviously depends on the species of bamboo.

Table 3: Chemical composition of some common natural fibers [7]

Fiber	Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)	Waxes (wt%)
Bagasse	55.2	16.8	25.3	-
Bamboo	26-43	30	21 – 31	-
Flax	71	18.6 – 20.6	2.2	1.5
Kenaf	72	20.3	9	-
Jute	61 – 71	14 – 20	12 – 13	0.5
Hemp	68	15	10	0.8
Ramie	68.6 – 76.2	13 – 16	0.6 – 0.7	0.3
Abaca	56 – 63	20 – 25	7 – 9	3
Sisal	65	12	9.9	2
Coir	32 – 43	0.15 – 0.25	40 – 45	-
Oil palm	65	-	29	-
Pineapple	81	-	12.7	-
Curaua	73.6	9.9	7.5	-
Wheat straw	38 – 45	15 – 31	12 – 20	-
Rice husk	35 – 45	19 – 25	20	14 – 17
Rice straw	41 – 57	33	8 – 19	8 – 38



(a) (b)

Figure 1: Model for the description of the stiffness of the fibre : (a) *S*2—layers in a 3D view; (b) *S*2—layers projected into a 2D view [6].

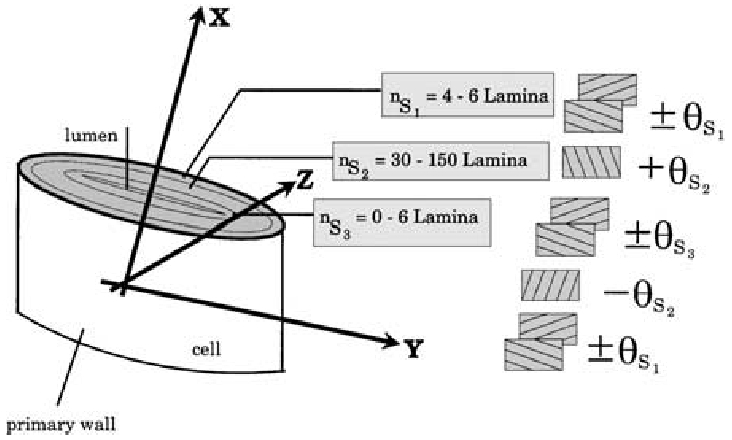


Figure 2: Single fiber cell [7]

To investigate more about the fiber, an illustration of one single fiber cell as general model for modeling in Figure 1 was shown [15]. Natural fiber is a composite of the three polymers (cellulose, hemicelluloses and lignin), in which the unidirectional cellulose microfibrils constitute the reinforcing elements in the matrix blend of hemicellulose and lignin. The structure of such a fiber was built as multiply construction with layers P, S1, S2 and S3 of cellulose microfibrils (where P is the primary layer and S is the secondary layer) at different angles to the fiber axis (Figure 2). Depending on the single fiber cell layer, the different spiral angle of those layers will have a pronounced influence on the properties of the fiber. The relative thickness of the different layers were estimated to be P = 8%, S1 = 8%, S2 = 76%, and S3 = 8% [7].

Besides, there is another thing that should be noted: crystallinity values of natural fibers vary in different parts of the plant. The crystallinity tends to decrease as the plant matures, but the difference between libe and core fibers is inconclusive [7]. Therefore, when choosing the fibers for experiment, the fibers should be selected carefully to make sure that all the fibers have the same conditions (same kind of fibers, plants were grown at same area and climate, fibers are cut and extracted from the same part of the plants …) and same properties.

I.1.2.3.Physical and mechanical properties

Table 4: The fiber sizes of some plant fibers [14]

Fiber type	*Diameter (µm)*	*Length (mm)*	*Aspect ratio (l/d)*	*Micro – fibril angle (θ)*	*Bulk density (Kg/m³)*
Abaca	17.0 -21.4	4.6 – 5.2	257	-	1500
Bagasse	20	1.7	-	-	550 – 1250
Banana	-	2 – 3.8	-	11 – 12	1300 – 1350
Bamboo	10 – 40	2.7	-	-	1500
Coir	16.2 – 19.5	0.9 – 1.2	64	39 – 49	1250
Cotton	11.5 – 17	20 – 64	2752	20 – 30	1550
Flax	17.8 – 21.6	27.4 – 36.1	1258	5	1400 – 1500
Hemp	17.0 – 22.8	8.3 – 14.1	549	6.2	1400 – 1500
Jute	15.9 – 20.7	1.9 – 3.2	157	8.1	1300 – 1500
Kapok	15 – 35	-	724	-	384
Kenaf	17.7 – 21.9	2.0 2.7	119	-	1220 – 1400
Phormium	15.4 - 16.4	5.0 -5.7	337	-	-
Pineapple	20 – 80	-	-	6 – 14	1520 – 1560
Ramie	28.1 – 35.0	60 – 250	4639		1550
Sisal	18.3 – 23.7	1.8 – 3.1	115	10 - 22	1300 – 1500

Fruit fibers, leaf fibers and bast fibers are usually separated as bundles of fibers. The exact number of ultimate fibers in one bundle is not understood since it is not possible to model the separation processes to produce a specific bundle diameter. The authors have tried to quantify the number of ultimate fibers per bundle they did not describe the methods. However, the length of fiber ultimates of leaf fibers is between 2 - 60 mm [14].

Table 4 illustrates some physical properties of the plant fibers. Of all the natural fibers, the physical characteristics of cotton fiber seem the most interesting. Cotton fiber has the layer arrangements like other plant fibers, but its unique helical fibril winding formation distinguishes it from other fibers. The winding formation of the fibril along the major axis tends to have an alternate reversal direction as it winds along the fiber axis [14].

Natural fibers are in general suitable to reinforce plastics (thermosets as well as thermoplastics) due to their relative high strength and stiffness and low density. The range of the characteristic values, however is so large and significantly higher than those of glass fibers. This drawback can be explained by differences in fiber structure due to the overall environmental conditions during growth. Natural fibers can be processed in different ways to yield reinforcing elements having different mechanical properties. The elastic modulus of bulk natural fibers such as wood is about 10 GPa. Cellulose fiber with moduli up to 40 GPa can be separated from wood, for instance, by chemical pulping processes [6, 7]. In general, currently the fibers which are popular used are produced commercially by the pulp and paper industry and relate to the second level of value of elastic modulus. Discussion and future potential relate to the third and fourth levels of modulus [6].

The fiber properties and fiber structure are influenced by several conditions and varies by area of growth, its climate and the age of the plant. Furthermore, the technical digestion of the fiber is another important factor which determines the structure as well as the characteristic values of the fibers. As in the case with glass-fibers, the tensile strength of natural fibers also depends on the test length of the specimens which is of main importance regarding reinforcing efficiency. The actual tensile strength of a single fiber is typically given for a test length of zero as in the case for glass-fibers (This fact can be one further reason for the differences in strength of one natural fiber type). For example, examinations dealing with that were made by Koher et al. [18], Mieck et al. [17] on different types of flax and pineapple-fibers. Their results illustrate that the tensile strength of flax-fibers is significantly more dependent on the length of the fiber than for the case of glass fibers. Tensile strength is also decided by the refinement of the fiber [19]. A decrease in fiber fineness leads to higher fiber strength. As referred above, hydrophilic nature is a major problem for all cellulose-fibers if used as reinforcement in plastics, thus, a number of treatments were developed to improve this property.

The moisture content of the fibers depends on content of non-crystalline parts and void content of the fiber, amounts up to 10 wt % under standard conditions [20]. The hydrophilic nature of natural fibers influences the overall mechanical as well as other physical properties of the fiber itself [21]. Among the well-known natural fibers, bamboo has one of the most favorable combinations of low density and high mechanical strength, that is, it has high specific stiffness and strength, as shown in Table 6 [22].

Table 5: Physico - mechanical properties of natural fibers [6]

Fiber	*Tensile strength (MPa)*	*Young's modulus (GPa)*	*Elongation at break (%)*	*Volumic mass [g/cm^3]*
Abaca	400	12	3 – 10	1.5
Bagasse	290	17	-	1.25
Bamboo	140 – 230	11 – 17	-	0.6 – 1.1
Flax	345 – 1035	27.6	2.7 – 3.2	1.5
Hemp	690	70	1.6	1.48
Jute	393 – 773	26.5	1.5 – 1.8	1.3
Kenaf	930	53	1.6	-
Sisal	511 – 635	9.4 – 22	2.0 – 2.5	1.5
Ramie	560	24.5	2.5	1.5
Oil palm	248	3.2	25	0.7 – 1.55
Pineapple	400 – 627	1.44	14.5	0.8 – 1.6
Coir	175	4 – 6	30	1.2
Curaua	500 - 1150	11.8	3.7 – 4.3	1.4

Table 6: Physico-mechanical properties of natural fibers (2) [22].

Fiber	*Volumic mass [g/cm^3]*	*Diameter [µm]*	*Elongation at failure [%]*	*Tensile strength [MPa]*	*E-modulus [GPa]*
Bagasse	-	490	-	70	-
Coir	1.2	-	30	175	4 - 6
Cotton	1.5-1.6	20	7.0 – 8.0	287 – 597	5 – 13
Curaua	1.38	66	3.9	913	30
Flax	1.5	50 – 100	2.7 – 3.2	345 – 1035	50 – 70
Hemp	1.10	120	1.6	389 – 900	35
Henequen	-	180	3.7 – 5.9	430 – 570	10 – 16
Jute	1.3	260	1.5 – 1.8	393 – 773	26
Kenaf	1.31	106	1.8	427 – 519	23 – 27
Pineapple	1.32	-	2.4	608 – 700	25 – 29
Ramie	1.50	34	3.6 – 3.8	400 – 938	24 – 32
Sisal	1.5	50 – 80	2.0 – 2.5	337 – 413	8 -10
Bamboo	0.88 – 1.1	100 – 200	-	391 – 713	18 – 55
E-glass	25	9 -15	2.5	1200 – 1500	70
Carbon (PAN)	1.4	5-9	1.4 – 1.8	4000	230 - 240

I.2.Bamboo fibers

The bamboo is grown in various continents of the world, it has been divided accordingly; Asia–Pacific bamboo region, American bamboo region, African bamboo region and European and North American region (Table 7).

Table 7: Bamboo export and import trade flow (data collected in 2012) [23]

Top exporters		**Top importers**	
Country	*US $ million*	*Country*	*US $ million*
Canada	3	Turkey	7
South Africa	3	Norway	8
Mexico	3	India	9
Nigeria	8	Mexico	9
Hongkong, China	9	South Africa	12
Malaysia	14	Hong Kong, China	13
Myanmar	15	Russia	19
Singapore	18	Switzerland	20
Thailand	18	Rep. of Korea	25
Philippines	30	Australia	26
USA	30	Singapore	31
EU- 27	54	China	40
Vietnam	84	Canada	54
Indonesia	269	Japan	194
China	1034	USA	254
		EU - 27	230

The Asia–Pacific bamboo region is the largest bamboo growing area in the world. In Asian countries, bamboo is known by different names. For instance, in China it is known as ‘‘friend of people’’, ‘‘wood of the poor’’ in India, ‘‘the brother’’ in Vietnam. FAO (Food and Agriculture Foundation) provided the data of bamboo production at global level as shown in Fig.3.

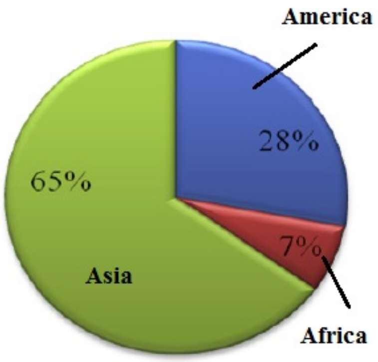


Figure 3: World percentage of bamboo from different continents (2012) [23]

In Asia, large area of bamboo is occupied by six countries: India, China, Indonesia, Philippines, Myanmar, Vietnam and others. Globally among sympodial and monopodial, sympodial type of bamboo dominates major part [23].

I.2.1.Chemical compositions and structure of bamboo fibers

There are various types of bamboos and depending on the type of bamboo as well as the condition of weather, climate, places of growth, the age of bamboo, the bamboo components vary. Similar to other natural fibers, the chemical composition of bamboo fiber constitutes mainly cellulose, hemicellulose and lignin. These components are actually same high-glycans, and occupy about 90% of total weight of bamboo fiber. The other constituents are protein, fat, pectin, tannins, pigments and ash. These constituents play important role in physiological activity of bamboo and they are found in cell cavity or special organelles. The chemical composition of the bamboo fiber is given in Figure 4. Usually, the chemical composition of bamboo changes with age of the bamboo, particularly cellulose content keeps on decreasing while age of bamboo is increased. Therefore, age of bamboo directly affects the chemical composition of bamboo fiber. The lignin is considered to provide stiffness and yellow color to bamboo fibers. Different treatments cannot remove all the lignin content of the bamboo fibers, because lignin has been found quite resistant to various alkalis. Non cellulosic components have enough contribution to fiber properties such as strength, flexibility, moisture, and even density [23].

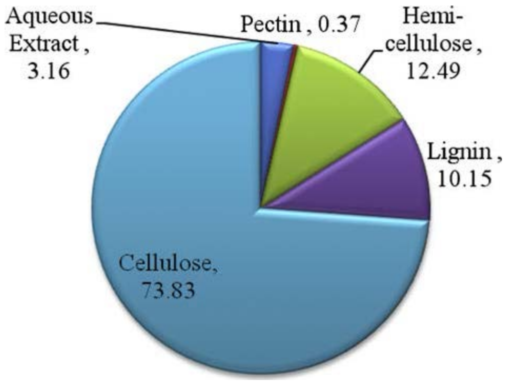


Figure 4: Chemical constituents of bamboo fiber [23]

A study on bamboo species Guadua angustifolia revealed the presence of irregular form and more precisely beam shaped pattern of bamboo fibers (Figure 5).

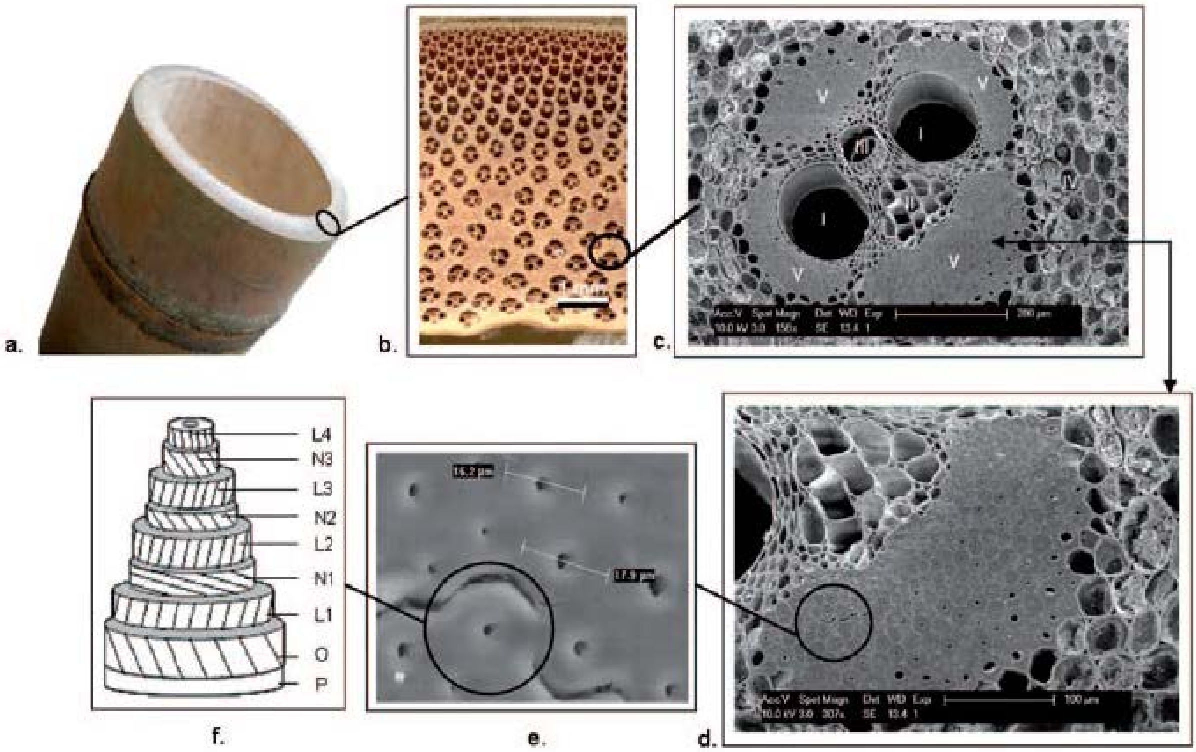


Figure 5: Bamboo microstructure [22]

Bamboo G. angustifolia microstructure: (a) bamboo G. angustifolia culm, (b) cross-section of the culm showing the fiber distribution through the wall thickness, (c) vascular bundle, the main anatomical constituent of the plant, composed of vessels I, floem II, protoxilem III, parenchyma tissue IV, and fiber bundles V, (d) bamboo fiber bundle composed by several elementary fibers, (e) elementary fibers with pentagonal or hexagonal shape, and (f) model of polylamellae structure of a thick-walled elementary fiber proposed by Liese where, in the thick lamellae (L1–L4), the cellulose fibrils are oriented at a small angle to the fiber axis, whereas the thin ones (N1–N3) show mostly a more transverse orientation, P, primary wall, O, external sheet of secondary wall [22].

I.2.1.1.Cellulose

Cellulose is the main, important and especial constituent of plant structures, bacteria (e.g., Acetobacter) and tunicates [5]. In general, cellulose is considered as a linear condensation polymer consisting of D-anhydroglucopyranose units joined together by β -1,4-glycosidic bonds. Haworth projection suggested a formula of cellulose as follow [6]:

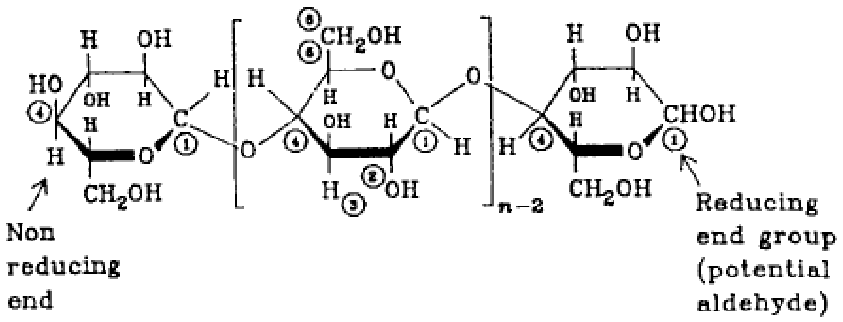


Figure 6: Cellulose structure [6]

In the fully extended molecule, adjacent chain units are orientated by their mean planes. The repeating unit in cellulose is the anhydro-cellulobiose unit and the number of repeating units per molecule is half the Degree of Polymerization. This may be as high as 14000 in native cellulose, but purification procedures usually reduce it to something in the order of 2500 [1]. Each repeating unit contains three hydroxyl groups. Two of these hydroxyl groups form intermolecular bonds, while the third one forms intramolecular hydrogen bonds [2].

The mechanical properties of natural fibers depend on its cellulose type, because each type of cellulose has its own cell geometry and the geometrical conditions determine the mechanical properties [1].

Cellulose is supposed to be resistant to strong alkali, however it is easily hydrolyzed by acid to water-soluble sugars. Cellulose is relatively resistant to oxidizing agents.

I.2.1.2. Hemicellulose

Hemicellulose is not a form of cellulose. They include a group of polysaccharides (excluding pectin) and this group remains associated with the cellulose after lignin has been removed. There are 3 different things between hemicellulose differs from cellulose in three important aspects. Firstly, hemicelluloses contain several different sugar units while cellulose contains only 1,4-β-D-glucopyranose units. Secondly they exhibit a considerable degree of chain branching, whereas cellulose is a strictly linear polymer. And thirdly, the degree of polymerization of native cellulose is ten to one hundred times higher than that of hemicellulose [1]. Degree of polymerization of hemicellulose is around 50–300, whereas that of native cellulose is 10–100 times higher than that [5]. Hence, molecular weight of hemicellulose is significantly lower than cellulose [5]. Hemicelluloses form the supportive matrix for cellulose microfibrils, presumably by hydrogen bonding. Because of its open structure containing many hydroxyl and acetyl groups, hemicellulose is hygroscopic, partly soluble in water, soluble in alkali and easily hydrolyzed in acids [2].

I.2.1.3.Lignin

Lignin is defined as a complex hydrocarbon polymer three-dimensional copolymer of aliphatic and aromatic constituents with very high molecular weight [5]. Their main monomer units are various ring- substituted phenyl propanes connected together. The mechanical properties are worse than those of cellulose. Besides, lignin is totally amorphous and hydrophobic in nature. And this compound gives rigidity to the plants. Lignin has a glass transition temperature of around 90°C and melting temperature of around 170°C. It is not hydrolyzed by acids, but soluble in hot alkali, readily oxidized and easily condensable with phenol. The structure is presented in Figure 7 [6]. The main difficulty in lignin chemistry is that no method has been established by which it is possible to isolate lignin in its native state from the fiber [5].

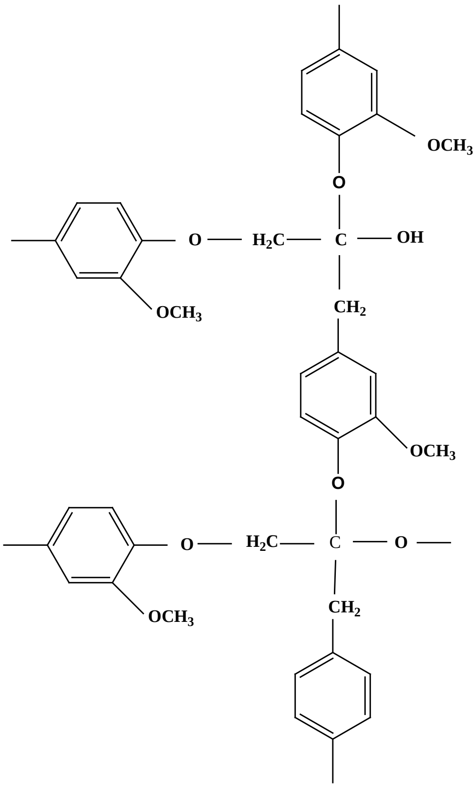


Figure 7: Lignin structure [6]

I.2.1.4.Pectin

Pectin consists essentially of polygalacturon acid. It is soluble in water only after a partial neutralization with alkali or ammonium hydroxide [1]. It provides flexibility to plants [5].

I.2.1.5.Waxes

Waxes make up the part of the fibers, which can be extracted with organic solutions. These waxy materials consist of different types of alcohols, which are insoluble in water as well as in several acids (palmitic acid, oleaginous acid, stearic acid) [1].

Figure.8 describes the certain position of bamboo fiber across the cell wall. A surface of fiber was captured. As can be seen, the morphology of bamboo fibers showed the clean surface with no apparent damage, the roughness found at surface will help in fiber matrix bonding, the main utilization of bamboo fibers.

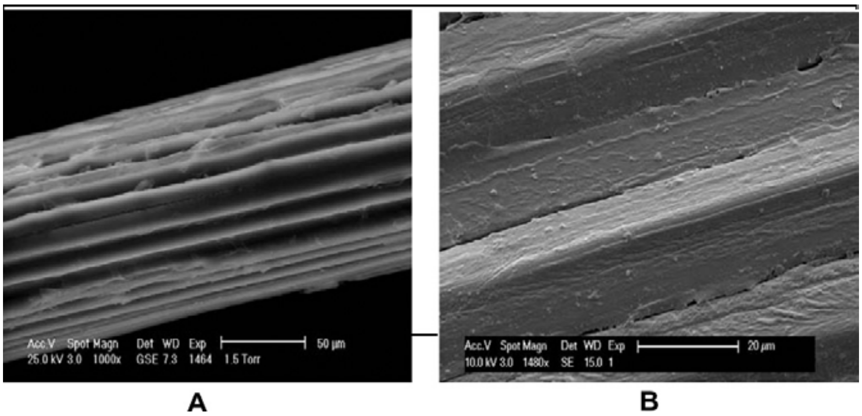
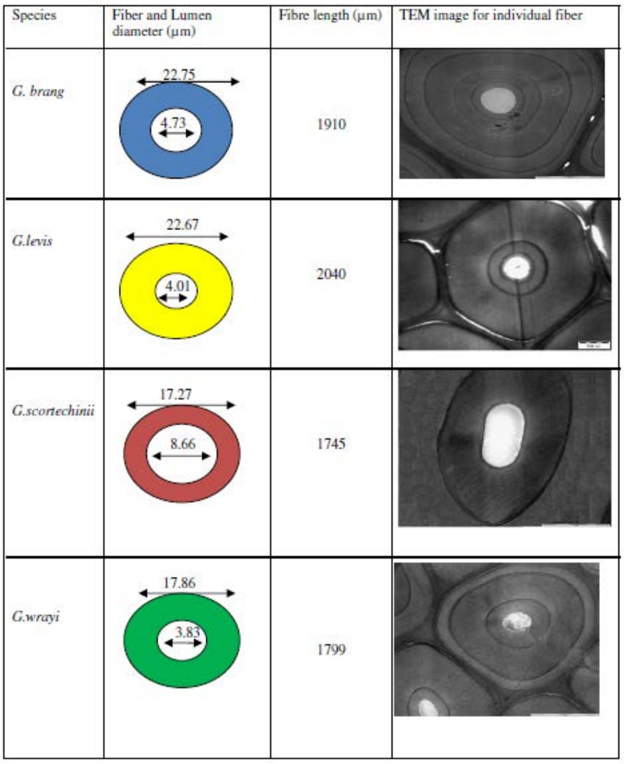


Figure 8: Images of bamboo

(A) SEM images of bamboo (G. angustifolia) fiber bundle after mechanical extraction. Note: The fiber bundle is composed of several elementary fibers, and (B) SEM images of bamboo (G. angustifolia) showing the roughness of the fiber bundle after mechanical extraction [23]

It is reported that the fiber dimensions of different species of bamboo fiber obtained from different position of respective bamboo culms (Figure 9). The polylamellate structures do not exist in the cell wall of the fibers of the normal wood. Based on its anatomical properties, ultrastructure and plant fracture mechanism bamboo establishes itself as a superior natural fiber [23]. As shown in Fig.10 and 11, the fiber in cross-section of the bamboo culm is distributed densely in the outer layer and sparsely in the inner layer.



Species	Fiber and Lumen diameter (µm)	Fibre length (µm)	TEM image for individual fiber
G. brang	22.75 4.73	1910	
G.levis	22.67 4.01	2040	
G.scortechinii	17.27 8.66	1745	
G.wrayi	17.86 3.83	1799	

Figure 9 : Fiber dimensions and TEM images of different species of bamboo [23]

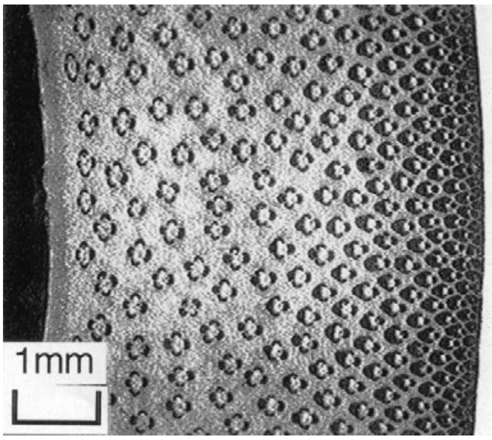


Figure 10: Cross-section of bamboo culm [24]

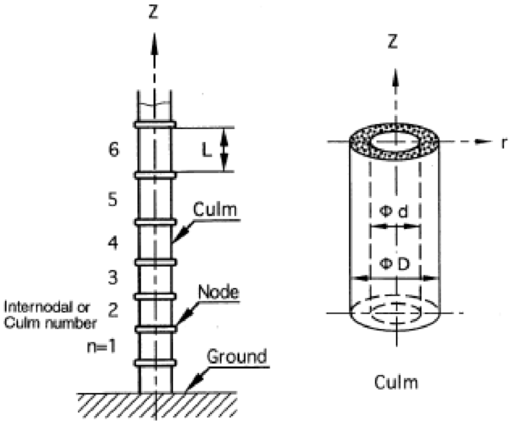


Figure 11: Coordinate system [24]

I.2.2. Mechanical properties of bamboo

Table 8: Some typical mechanical properties of plant fibers

Woods	*Strength σ_f (MPa)*	*Young's Modulus E (GPa)*	*Specific mass ρ (g/cm^3)*
Cedar	29.3 – 48.5	4.4 – 9.8	0.29 – 0.46
Fir	30.7 – 33.8	5.9 – 6.7	0.31 – 0.34
Pine	34.0 – 41.6	6.5 – 8.8	0.35 – 0.42
Spruce	31 -40	7.3 – 8.5	0.38
Hickory	62.5 – 81.0	8.9 – 11.4	0.56 – 0.67
Oak	47.7 – 74.9	7.9 – 12.4	0.53 – 0.61
Bamboo (fiber)	610	46	1.16
Bamboo (matrix)	50	2	0.67
Bamboo (composite)	140 - 230	11 – 17	0.6 – 1.1

Table 8 summaries some typical mechanical properties of plant fibers. As can be seen from this table, bamboo fiber exhibits its better strength in comparison with other plant fibers. Bamboo is obviously a typical natural composite material which is undirectionally reinforced by fibers. The fracture property of this kind of material depends on the fracture origin where a fracture initiates. There are two places where a fracture initiates: the matrix region and fiber region [24]. Bamboo fibers can probably a good candidate of plant fibers to be used as the reinforcement for polymer composite.

I.2.3. Modification of fiber

The properties of the fiber–matrix interface are of great importance for the macroscopic mechanical properties of composite. Therefore, it is necessary to apply some treatments for fibers. Both physical and chemical treatments can be used to optimize this interface and the efficiency of fibers varies with the materials and the methods used [12]. Because of poor and weak interface compatibility, and since the interfacial adhesion determines the final product mechanical properties, it is necessary to compatibilize fibers and polymer [13]. The treatment has been shown to improve the adhesion characteristics, due to improved work of adhesion because it increases the surface tension and surface roughness. Fiber modification can also be used to improve properties in composites made of both natural and synthetic resources used for geotextiles, filters, sorbents, packaging, and non-structural composites [64]. The resulting composites showed improvements in the compressive strength and water resistance [16]. In order to improve the mechanical properties of the final composite, a number of methods have been used to treat the fibers; this induces physical or chemical bonds between the matrix and the fibers as it is presented below [12].

I.2.4.Physical treatments

Reinforcing fibers can be modified by physical and chemical methods. Physical methods, such as stretching, calendering or thermo-treatment do not change the chemical composition of the fibers. However, physical treatments can change structural and surface properties of the fiber and hence influence the mechanical bonding to polymers [7].

I.2.4.1. Plasma treatment

Electric discharge (corona, cold plasma) is one of the most popular physical treatments. For plasma method, a variety of surface modification could be achieved, depends on nature and type of the employed gases. Following that, surface crosslinking can be induced, surface energy can be increased or decreased, reactive free radicals and groups could be produced [7]. Due to those modifications on the surface, plasma treatment helps to improve the compatibility between the fibers and matrix. This results to better properties of the composite. For example, the water absorption of the composite of flax fibers/ polyester decreases while the mechanical properties are improved by using the cold plasma in Helium [26]. Plasma treatment also brings to the clear modification on the surface morphology, water absorption and also the microstructure of the fibers. By plasma treatment, the surface gradually becomes hydrophobic and more compatible with the hydrophobic polymer [27].

Electric discharge methods are supposed to be very effective for ‘‘non-active’’ polymer substrates as polystyrene, polyethylene, polypropylene, etc. They are successfully used for cellulose-fiber modification, to decrease the melt viscosity of cellulose–polyethylene composites and improve mechanical properties of cellulose–polypropylene composites [7].

I.2.4.2.Modification by corona discharge

Corona discharge treatment (CDT) is one of the most interesting and popular techniques for surface oxidation activation. By using this method, it is possible to change the surface energy of the cellulose fibers and in case of wood surface activation, leading to the increase of the amount of aldehyde groups [7]. Also, CDT is an interesting technique of activation and surface modification of cellulosic fibers to achieve a good compatibilization between natural fibers and a non-polar matrix.

Corona discharge treatment exhibits as a valuable technique for the surface modification of cellulosic fibers used for manufacturing composite materials. It is an efficient and eco-friendly treatment that enhances the fiber/matrix interaction in composites. Moreover, it can be applied as a continuous processing, which is a common route that is widely applied in textile or paper industry. It has been shown to exert varying effects (surface roughness and morphology). For example, that rough surface contributes to the improvement of the mechanical properties of hemp-PP composites. The addition of cellulosic fibers firstly allows reaching good mechanical properties and moreover, the treatment of these reinforcements by means of corona discharge leads to greater characteristics (Young modulus, stiffness, elastic density energy) because it can improve the adhesion between matrix and fibers. These composites properties were found to be highly sensitive to interfacial phenomena. A striking result is that modification of cellulosic reinforcements rather than matrix allows a greater improvement in composite properties. This mechanical enhancement was exclusively dependent on the puzzle effect (etching effect) confirmed by SEM (Scanning Electron Microscope) analysis [13].

I.2.5. Chemical treatments

The high moisture sensitivity of lignocellulosic fiber can result in swelling of the fiber and it causes the dimensional instability and limits the use of fiber as reinforcement in composite materials. Low interfacial properties between fiber and polymer matrix often reduce their potential as reinforcing agents due to the hydrophilic nature of natural fibers; chemical modifications are considered to optimize the interface of fibers [28]. Cellulose fibers, which are strongly polar with the hydrophilic nature, are inherently incompatible with hydrophobic polymers. In many cases, it is possible to induce compatibility in two incompatible materials by introducing a third material that has properties intermediate between those of the two others, and this material plays a role of the bridge to connect these two materials. There are several coupling mechanisms in materials (e.g., weak boundary layers, deformable layers, restrained layers, wettability, chemical bonding, and acid–base effect) [7]. Generally, chemical coupling agents are molecules possessing two functions. The first function is to react with hydroxyl groups of cellulose and the second is to react with functional groups of the matrix. The moisture absorbed by the fibers can also be reduced by chemical modifications of fibers such as acetylation, methylation, cyanoethylation, benzoylation, permanganate treatment, acrylation etc [28]. In this study, we aim to modify the fibers using chemical modifications.

I.2.5.1.Alkali treatment

Alkali treatment is one of the most popular methods to modify the fiber surface. Firstly, the alkali treatment is simple and low cost and it is recommended to precede other sophisticated surface modification treatments on plant fibers. The mechanical properties of plant fiber-polymer matrix composites are controlled via the efficiency of bonding at the fiber-matrix interfacial boundary. The principal function of the interface is to facilitate transfer of stress from fiber to fiber, across the matrix. On the other hand, by this alkali treatment method, it is possible to get rid of some organic and inorganic substances on the fiber surface, which prevent direct contact between the molecules of the resin and the fiber, and the hydrophilic nature of cellulose. These substances themselves are responsible to mainly contribute to the poor bonding characteristics with synthetic resins.

The treatment of fiber with NaOH improves its wetting ability, therefore reduces porosity and gives rise to composites with improved strength and water resistance. Alkali treatment is therefore recommended to precede any surface modification procedure on plant fibers [29]. For example, a study on the effect of alkali treatment on the wetting ability and coherence of sisal-epoxy composites has been examined. Treatment of sisal fiber in a 0.5N solution of sodium hydroxide, resulted into more rigid composites with lower porosity and hence higher density. The treatment has exhibited the improvement of the adhesion characteristics, due to improved work of adhesion because it increases the surface tension and surface roughness [29].

Alkali treatment in 18% NaOH for 24 h showed considerable improvement in the strength of the composites [29]. Similar investigations in a sisal-polyester system were made. The fibers were immersed in 5% NaOH for various periods of time. The given result showed that the strength of the composite increased by nearly 100% when fibers were treated for periods of 80–90 hours, and dropped for longer periods [111]. Similarly, cotton fibers have showed the positive results when they were immersed in the reagent. It can be observed the increase in adsorption constants and diffusion coefficients, which defines its dyeability implying increased wetting ability. Joseph et al. [112] improved the tensile properties of the sisal fiber – reinforced LDPE (low density polyethylene) composites significantly by using chemicals such as sodium hydroxide, isocyanate, permanganate and peroxide for the fiber treatment. The effectiveness of mercerization was also demonstrated on the viscoelastic behavior of isoprene rubber composites filled with cellulose fibers. The treatment substantially increased the storage modulus.

Also, the study on cotton fibers proved that mercerization process caused profound changes in the structure of fibers at both molecular and macromolecular levels. The considerable changes on the molecular orientation, crystal structure, degree of crystallinity, and morphology of cotton fibers are clearly observed. And these changes are attributed to the increase in the sorption, tensile strength, extensibility, and roundness of the fibers [29].

Besides some positive features mentioned above, alkali treatment has however, some drawbacks when used on composite fiber bundles. For example, using SEM to investigate the surface morphology of sisal fibers subjected to alkali and acid treatments it was observed that alkali treatment caused the sisal fiber to fibrillate into the ultimate while acid treatment showed fibrillation due to intracrystallite swelling [29].

It is a common practice in the textile industry to use sodium hydroxide solution for the mercerization process. However, other alkali solutions are also potentially viable for mercerization, although they vary in their effectiveness. Chen et al [16], reported the ranking of three alkali, they are, LiOH, NaOH and KOH, and showed that the mercerization was most effective with LiOH followed by NaOH.

Besides the conventional mercerization technique, load application technique during mercerization has been employed in order to improve mechanical properties of the fiber. A chemical treatment apparatus with tensile loading portion for applying monofilaments was recently developed. The ramie fiber was alkali-treated by 15% NaOH solution with applied loads of 0.049 and 0.098 N. The results showed that tensile strength of the treated ramie fiber was improved, 4–18% higher than that of the untreated ramie fiber, while Young's modulus of the treated fibers decreased. It should be noted that fracture strains of the treated ramie fiber drastically increased to 0.045–0.072, that is, twice to three times higher than those of the untreated ramie fiber. It was considered that such property improvements upon mercerization were correlated with change of morphological and chemical structures in microfibrils of the fiber [25].

I.2.5.2.Acetylation treatment

Acetylation of natural fibers is a well-known esterification method which triggers plasticization of cellulosic fibers. There exist the polymer hydroxyl groups of the cell wall of natural fibers. These hydroxyl groups can react with acetyl groups and this reaction can modify the properties of those polymers so that they become hydrophobic which could stabilize the cell wall against moisture, improving dimensional stability and environmental degradation. The principle of the method is to transform the hydroxyl groups (–OH) of the fiber constituents in acetyl groups (CH_3CO–). By replacing some of the hydroxyl groups on the cell wall polymers with bonded chemical groups, the hygroscopicity of the lignocellulosic material is reduced [64].

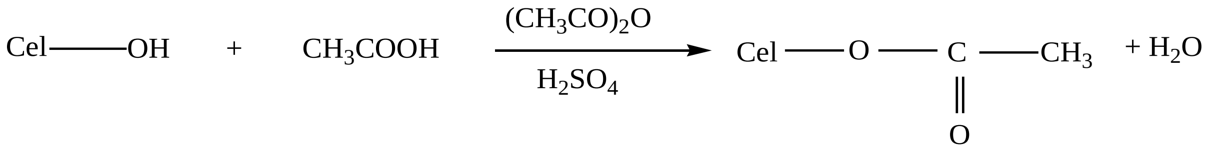
Moreover, the reaction is known to proceed to full esterification of all the three hydroxyls of anhydro-D-glucose when it is carried out in a homogeneous phase (i.e. when cellulose is dissolved). In the case of fibers and wood, the reaction is heterogeneous. Therefore, the esterification process is thought to occur on the fiber surface, leading to a highly non-uniform product. In these cases, it is necessary to use catalyst speeding up acetylation process. There are large number of catalysts that have been used in the past, including sulfuric acid, pyridine, potassium and sodium acetate, gamma-rays, etc [28].

In general, acetylation is a method known for years and was originally applied to wood cellulose in order to stabilize the cell wall against moisture so that it improves dimensional stability and environmental degradation. Also, it was applied for such long time on textile goods, and recently there have been research work that regards to its usefulness in natural fibers for reinforcement of polymer composites.

The method is based on the reaction of lignocellulosic material with acetic anhydride at elevated temperatures, usually without catalyst. Acetic anhydride reacts with reactive hydroxyl groups. The simplest form of the process involves with the immersion of plant fiber in acetic anhydride. As acetic acid does not completely react with cellulose, anhydride acetic was used. Acetic anhydride is not a good agent to swell cellulose. Hence, firstly the fibers should be mercerized in acetic acid and subsequently modified with acetic anhydride. It will help accelerate the reaction. Acetyl treatment also helps decrease water absorption significantly, results in a stable composite [7, 68]. Besides, acetyl method can help improve the tensile strength of composites, and the thermal stability [28].

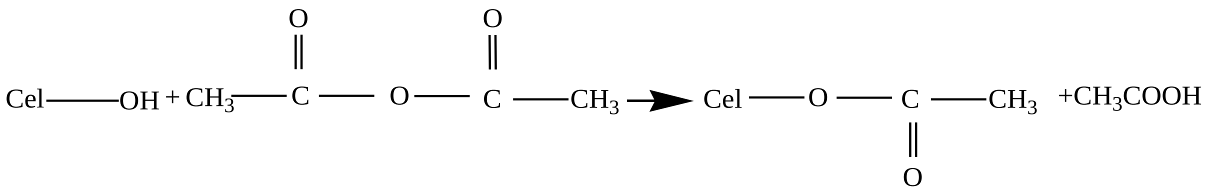
Acetylation is widely applied to modify the cellulose fibers to stabilize the cell walls and improve the stable size. There are 2 methods of using acetylation:

Acetylation with the acid catalyst:



$$\mathrm{Cel{-}OH} + \mathrm{CH_3COOH} \xrightarrow[\mathrm{H_2SO_4}]{\mathrm{(CH_3CO)_2O}} \mathrm{Cel{-}O{-}}\underset{\displaystyle \mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{{-}CH_3} + \mathrm{H_2O}$$

Acetylation without the presence of acid:



$$\mathrm{Cel{-}OH} + \mathrm{CH_3{-}}\overset{\displaystyle \mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{{-}O{-}}\overset{\displaystyle \mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{{-}CH_3} \longrightarrow \mathrm{Cel{-}O{-}}\underset{\displaystyle \mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{{-}CH_3} + \mathrm{CH_3COOH}$$

I.2.5.3.Enzyme treatment

The use of enzyme technology is becoming increasingly substantial for the processing of natural fibers. It is now widely applied since the fact that the application of enzymes is environmentally friendly. Currently, the use of enzymes in the field of textile and natural fiber modification is also rapidly increasing. The catalyzed reactions are very specific and have a focused performance. Bledzki et al. investigated PP (Polypropylene) composites which are reinforced with enzyme treated abaca fibers. The surface morphologies of enzyme treated and untreated abaca fibers are shown in Fig.12. In Fig. 12a, it was observed that the untreated fiber surface is rough, containing waxy and protruding parts. The surface morphology of treated fibers is observed in Fig.12b and c. If the waxy material and cuticle in the treated surface are removed, the surface becomes smoother. Fibrillation is also thought to occur when the binding materials are removed from the surface of the treated fibers. Fiber surface damage was also observed for naturally digested fibers which occur in natural digestion systems.

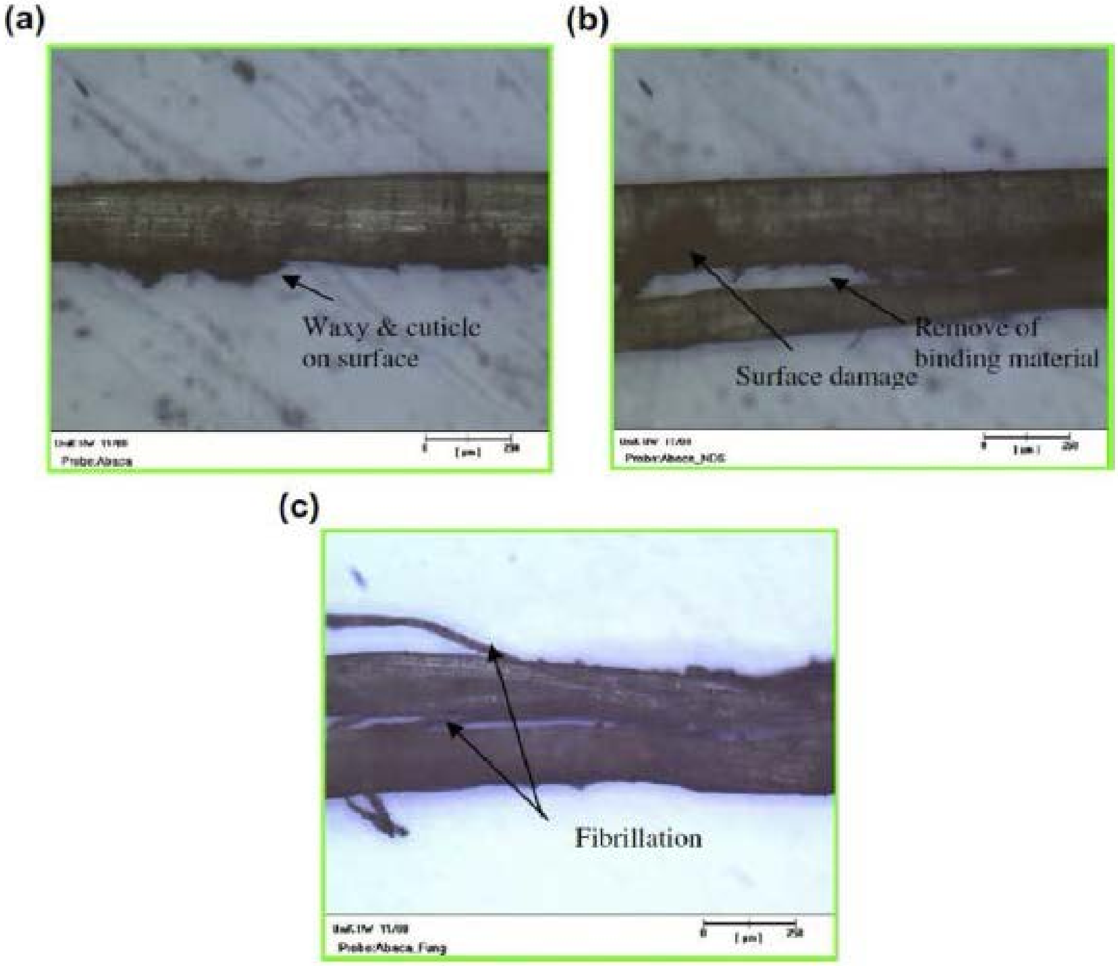


Figure 12: Micrograph of abaca fiber surface morphology

(a) unmodified (b) Natural digestion system (NDS) modified (c) fungamix modified [7].

In addition, enzyme treatment can improve some mechanical properties, for example, it helps to increase the tensile and flexural strength of abaca fiber (Figure 13) [7]. The tensile strength of enzyme treated abaca composites was found to have increased 5–45% because of modification. Natural digestion system (NDS) modified abaca fiber composites showed little improvement in comparison with unmodified abaca fiber composites.

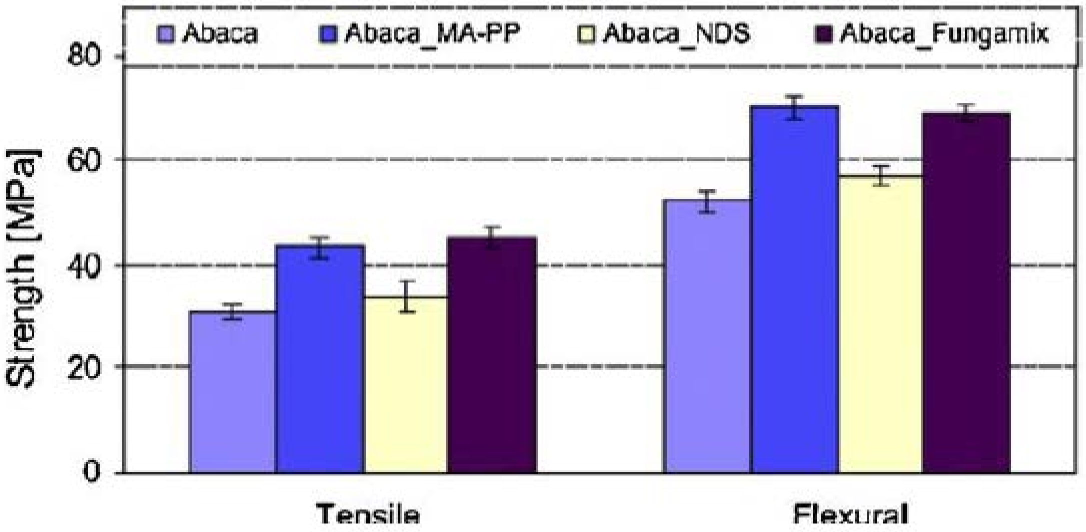


Figure 13: Tensile and flexural strength of enzyme treated and unmodified abaca–PP composites [7].

I.2.5.4. Maleated coupling treatment

Maleic anhydride (MAH) coupling is now widely used to strengthen natural fiber reinforced composites and demonstrates to be the very effective means of treatment. Compared with other chemical treatments, maleic anhydride is not only used to modify fiber surface, but also the polymeric matrix to achieve better interfacial bonding between fiber and matrix and to improve mechanical properties of composites. Moreover, using MAH can improve the compatibility between fibers and matrix. Many works have proved that the mechanical properties and the adhesion between matrix and fibers are significantly improved by using MAH.

Some mechanical properties like Young's modulus, flexural modulus, hardness and impact strength of plant fiber-reinforced composites increased after maleic anhydride treatment. The effects of MAH coupling agent on rice-husk flour reinforced PP composites were evaluated. The tensile strengths of the composites decreased as the filler loading increased, but the tensile properties were significantly improved with the addition of the coupling agent. Both the notched and unnotched Izod impact strengths remained almost the same with the addition of coupling agents. A morphological study revealed the positive effect of a compatibilizing agent on interfacial bonding [7].

The treatment of cellulose fibers with polypropylene–maleic anhydride (MAH–PP) co-polymers, provides covalent bonds across the interface. The mechanism of reaction can be divided into two steps: activation of the copolymer by heating (170°C) (before fiber treatment) and esterification of cellulose.

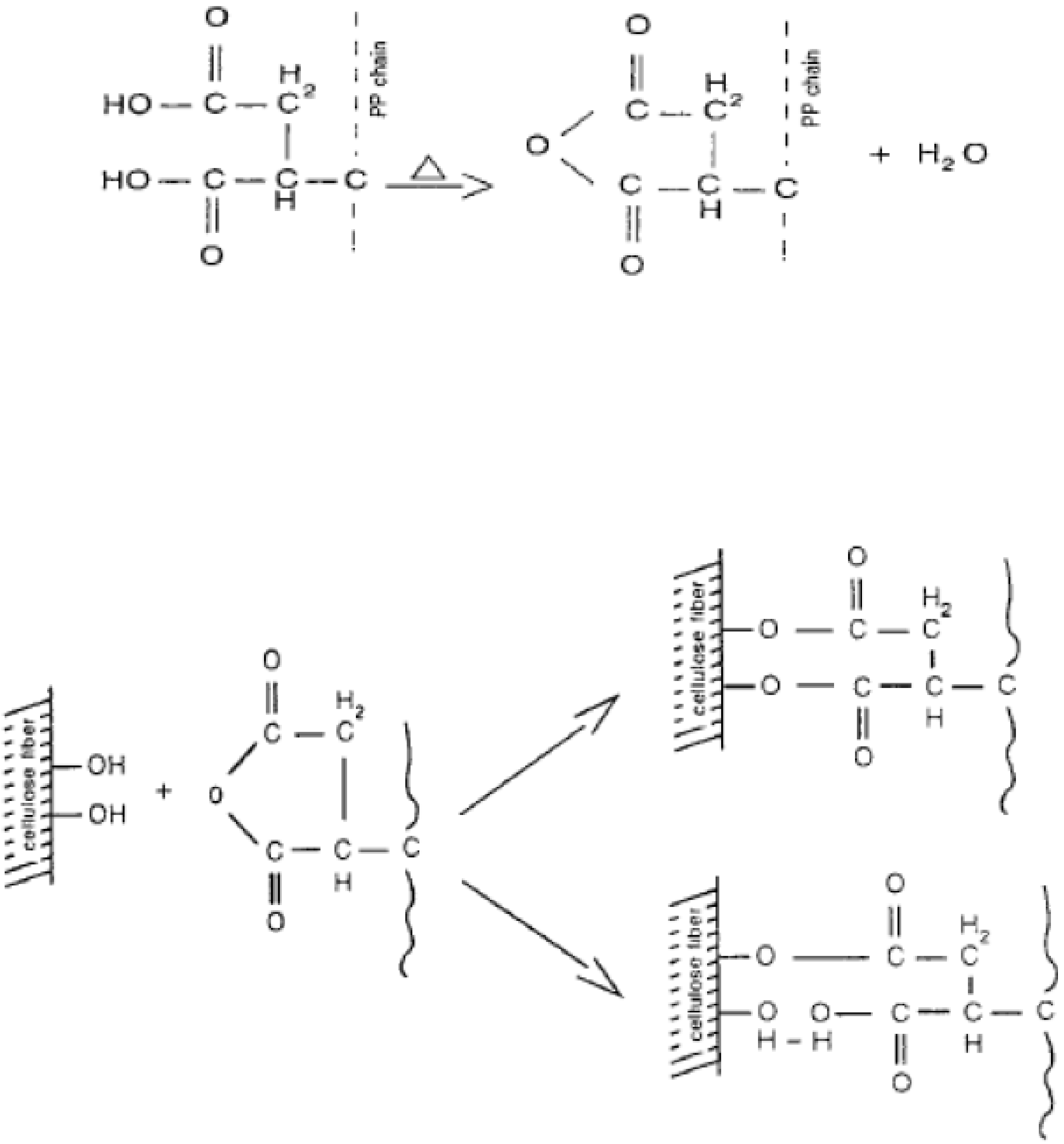


Figure 14: Mechanism of maleate coupling reaction [6]

At the end of this treatment, the surface energy of the fibers is increased to a level much closer to the surface energy of the matrix and therefore a better wettability and a higher interfacial adhesion were obtained. The polypropylene (PP) chain permits segmental crystallization and cohesive coupling between the modified fiber and the PP matrix.

The effectiveness of MAH as coupling agent has been investigated on thermal and crystallization properties of sisal fiber/PP composites, tensile properties of fiber/PP composites, surface properties and water uptake behavior of flax, hemp fiber reinforced PP composites, and dynamic mechanical properties of flax and hemp fiber/PP composites… [6].

I.2.5.5. Silane treatment

In order to improve the compatibility, it is necessary to modify the fibers or matrix by making fibers less hydrophilic or matrix less hydrophobic. Indeed, the surface energy of fibers is closely related to the hydrophilic nature of the fiber. There are many works concerning with methods to decrease hydrophilicity. Silane coupling agents are supposed that they can contribute hydrophilic properties to the interface, for example epoxies and urethanes silanes, are used as primers for reactive polymers. The primer may supply much more amine functionality than that can possibly react with the resin in the interphase. Those amines could not react, however, they are hydrophilic, hence causing the poor water resistance of bonds. With hydrophilic silanes, they can be effectively blended with hydrophobic silanes such as phenyltrimethoxysilane. Mixed siloxane primers also have an improved thermal stability, which is typical for aromatic silicones.

One investigation indicated that silane treatment improved the storage modulus of abaca fiber reinforced polyester composites. There are plenty types of silane used for the treatment. Chemical modifications with silane amino-methacryl oxypropyl trimethoxy-silane and also with NaOH leaded to the maximum increase of the modulus. After the pre-treatment with 0.5% NaOH, fibers were treated with silane and the hydrogen-bond donating acidity is found to be the lowest for fibers. On the contrary, the highest value was noted for fibers treated with silane vinyl triethoxysilane. On the other hand, silane vinyl triethoxysilane exhibits the maximum overall polarity [113].

Another coupling agent that is widely used is (3-Aminopropyl) triethoxysilane (APTES). APTES has ethoxy groups that can hydrolyze in water producing a silanol which reacts with the –OH group of the cellulose fibers. The reaction forms stable covalent bond to the cell wall that is chemisorbed onto the fiber surface and this treatment enhanced the mechanical properties of composites reinforced with natural fiber [65].

Yanan Song et al. used different quantities of coupling agent APTES (3 amino propyltriethoxysilane) (1, 3 and 5 wt% of the fiber weight) for the surface treatment. These amounts of APTES were dissolved in water for hydrolysis. The solution was adjusted to pH value of 4 with acetic acid and stirred continuously for 1.5 h. The mixed coupling agent solution was sprinkled on fibers using an atomizer when the fibers were turned over continuously. Next the fibers were kept in air for 24 h to make sure the coupling agent infiltrating into hemp fibers and react with the OH group on the cell wall. At last, the hemp fibers were dried at 100°C for further use [65].

Similarly, Masud S. Huda succeeded in improving the properties of biocomposites using surface treatment by silane. Firstly, the fibers were pre-treated by alkali. And then for the silane treatment, 5wt% APS (3 aminopropyltriethoxysilane) (weight percentage compared to the fiber) was dissolved for hydrolysis in a mixture of water–ethanol (40:60 w/w). The pH of the solution was adjusted to 4 with acetic acid and stirred continuously during 1 h. Next, the fibers were immersed in the solution for 3 h. Fibers were then washed and kept in air for 3 days. Lastly, the fibers were oven dried at 80°C for 12 h. In this study, they used kenaf fibers to reinforce the composite with PLA (Poly lactic acid) matrix. All surface-treated kenaf fibers also showed the tendency to significantly increase the flexural modulus compared to neat PLA [66].

In another work, T. Deák et al. [67] also used silane method to improve the interfaces in composites. It is thought that the most effective way is to establish the strong chemical bonds between the matrix and the fibers. In the study, they took advantage of silane compounds to enhance the polyamide –basalt fibers. The structure of silane molecules is denoted as following: $R\text{–}SiX_3$ or $R\text{–}(CH_2)n\text{–}SiX_3$. One side of the molecule establishes bond with the surface of the fiber while the other end of the molecule establishes bond with the matrix.

X is a hydrolyzable ethoxy ($\text{–}OCH_2CH_3$) or methoxy ($\text{–}OCH_3$) group, which transforms in water solution through hydrolysis. Trihydroxy-silane formed during hydrolysis, which develops covalent or hydrogen bonds with the hydroxyl groups on the surface of basalt or glass fibers. When the fibers are dried, a reversible condensation occurs between the silane molecules and fiber and another condensation occurs between the neighboring silane molecules, forming a polysiloxane layer. The R groups establish bonds with the reactive side groups of the polymer matrix. Silane and titanate coupling agents are applied on the surface of fibers during fiber manufacturing. In this treatment, the coupling agents were dissolved in distilled water. T. Deák et al. [67] used 1% wt silanes in the ratio of basalt fiber. The basalt fibers were immersed in the solution for 2 hours in order to effectuate the hydrolysis of silanes and their bonding with the hydroxyl groups on the surface of basalt fiber. The water was evaporated at 80°C in an air circulating oven [67].

Silane method is expected to improve the interfacial adhesion significantly since new covalent bonds between the fiber surface and matrix are created. Hence, better mechanical properties can be obtained. In this method, the hydrolysis and mechanism of grafting on the fibers is shown on the diagram below [73]:

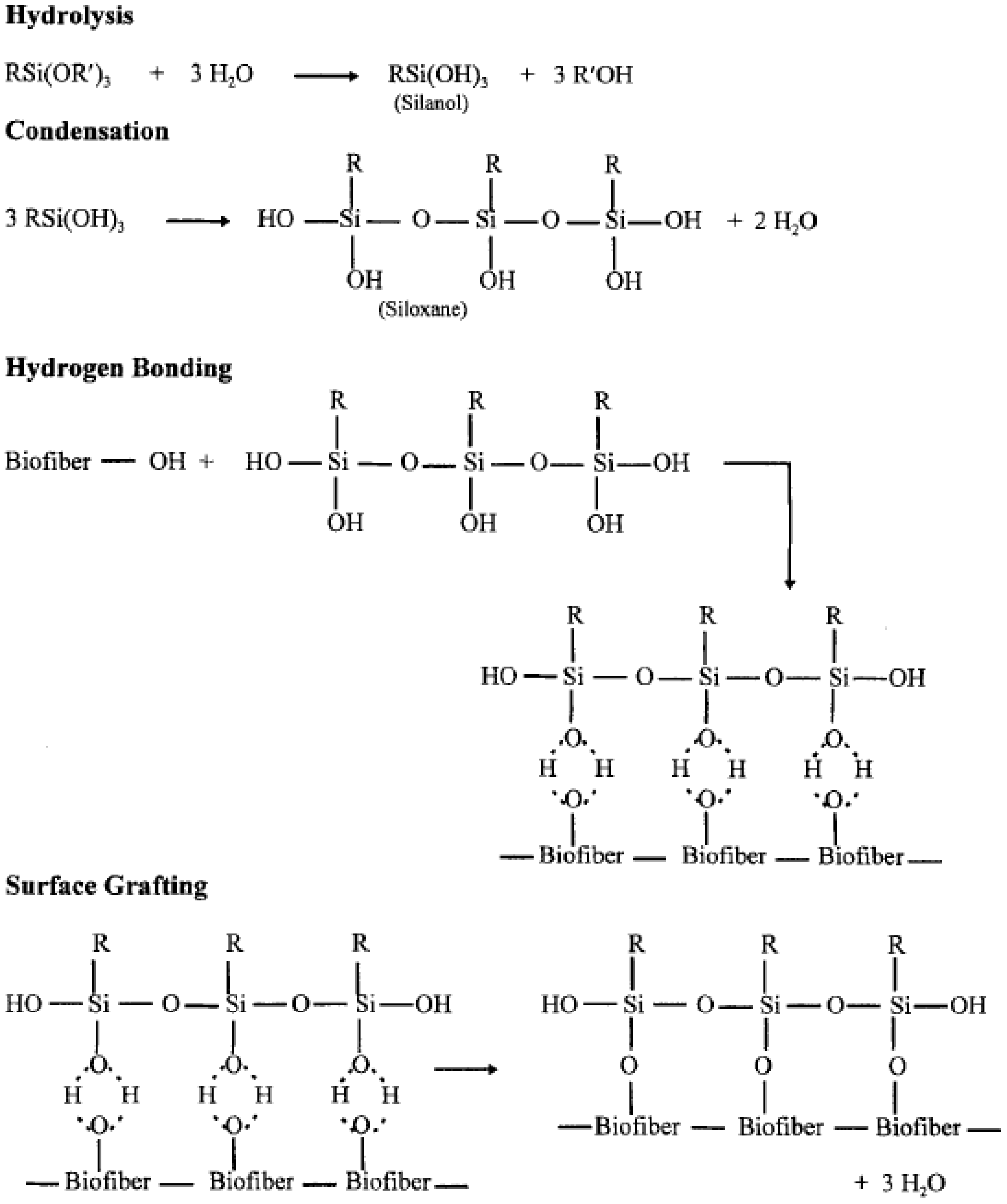


Figure 15: Reaction steps of silane grafting on biofiber [73]

II. Polymer matrix P34HB

II.1.Polyhydroxyalkanoate (PHA) family

PHAs are biodegradable, linear polyesters which are produced in nature by bacterial fermentation of sugar or lipids or synthesized by bacteria as energy and carbon storage material [8]. Their chemical composition can be controlled by the fermentation conditions. Indeed, by either direct bacterial synthesis or by the chemical modification of bacterially produced PHAs, polyesters with more than one hundred different types of repeating units have been identified and characterized [47]. Due to their good biodegradability and biocompatibility, PHAs have received considerable attentions as environmentally benign plastics to be used for a wide range of agricultural, marine and medical applications [45]. In addition, PHAs can also be produced from renewable resources, that is also a remarkable point. PHAs were really exploited since 1980s and are continued to be widely used, especially when the fossil fuel seems to be exhausted [48]. PHA productions are mostly based on pure cultures operated under sterile conditions, which increase the costs of these biopolymers. More than 150 different monomers can be combined within this family to give materials with greatly different properties. These plastics are biodegradable and are used in the production of bioplastics. They can be either thermoplastic or elastomeric materials, with melting points ranging from 40 to 180°C. PHA is defined as one of the most promising microbial polymers synthesized from renewable carbon sources [8]. Biodegradability and biocompatibility are important characteristics of PHAs. PHAs can be degraded to carbon dioxide and water by a large variety of micro-organisms in nature [9]. The physical and chemical properties of PHAs are greatly influenced by their monomer composition as well as chemical structure. For instance, the length of the pendant groups extends from the polymer backbone, the chemical nature of the pendant groups and the distance between the ester linkages in the polymer [57]. As materials made from PHAs inherit the similar properties to the thermoplastics and the good biodegradability, they are expected to replace the traditional petroleum based plastics. The development of copolymer production or blending PHAs with other monomers has widened their applications [9].

Among the PHA family, poly(3-hydroxybutyrate) is an saturated aliphatic polyester which is synthesized and accumulated by a variety of bacteria as a reserve energy source . It was attracted a lot by its characteristics. Similarly to many kinds of polymer in PHA family, PHB isolated from the bacteria is a partially crystalline polymer. PHB has many remarkable characteristics such as biodegradability, biocompatibility, and optical activity. Besides, PHB is a truly biodegradable material suitable for two promising applications: one is as a viable candidate for relieving environment concerns caused by disposal of non-degradable plastic;

the other is to provide new-type biomedical materials [11]. However, PHB has not been widely utilized due to its inherent physical properties such as high stiffness and brittleness, thermal unstability [49]. The brittleness of PHB is attributed to the high crystalline degree [57]. PHB also shows poor thermal stability at temperature above the melting point [49]. To improve those properties, several solutions were performed, including the use of rotors with different processing conditions for mixing, use of different strains and sources, blending with other biodegradable polymers, and incorporation of different types of fibers [48]. Among them, it might be a good solution to create the copolymer from this PHB polymer. Compared with pure PHB, the copolymers are thermally more stable and exhibit progressively larger processing window. The brittleness of PHB also could be greatly improved by the copolymerization [11]. A copolymer P3HB-P4HB (P34HB) exhibits its favorable biodegradability and also its mechanical properties can be tailored from highly crystalline plastic to elastic rubber by varying the ratio of P4HB and P3HB. This kind of polymer can be used in the medical field or other fields like agricultural plastic film or building wallpaper due to its biodegradable feature [10]. In this study, we take advantage of this P(3HB -4HB) which plays the role of matrix in composite.

II.2.Poly (3 -hydroxy butyrate)

Poly (3-hydroxy butyrate) is a well-known microbial and biodegradable polymer and it was found that prokaryotic microorganisms accumulate PHB up to 90% of their cellular dry weight, but this class contains many other polymers that are produced by a variety of organisms. Recently, PHB has attracted much interest from researchers because it is an environmentally compatible thermoplastic and its physical properties are remarkably similar to those of polypropylene (PP), even though the two polymers have quite different chemical structures. Also it is a polymeric material from renewable resources with a high melting temperature of around 180^{o}C [46].

Date back to 1920, when the discovery and chemical identification of poly(3-hydroxybutyrate) was made , as a granular component in bacterial cells proceeded without any of the controversies which marked the recognition of macromolecules by Staudinger. About thirty years after its discovery, PHB was recognized as the prototypical biodegradable thermoplastic to solve the waste disposal challenge [47]. Not until 1926 when Lemoigne truly discovered PHB using B. megaterium [48], he isolated and characterized poly-3-hydroxybutyrate, PHB, shown in Figure 16.

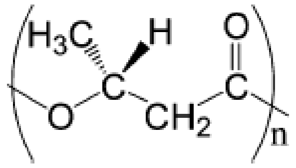


Figure 16: Poly 3 hydroxybutyrate (P3HB)

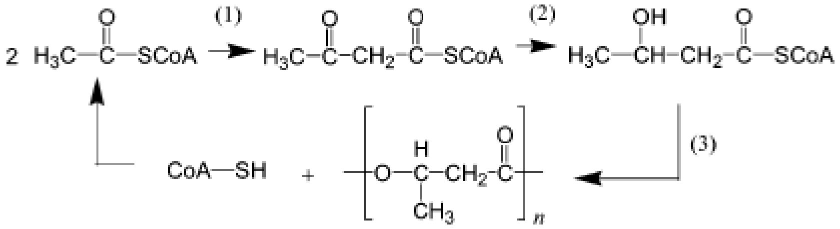
PHB is the reserve polymer found in many types of bacteria, which can grow in a wide variety of natural environments and who have the ability to produce and polymerize the monomer, [*R*]-3- hydroxybutyric acid. Lemoigne reported that the polymer is optically active. In fact, PHB is only the member of a family of natural polyesters having the same three-carbon backbone structure but differing in the type of alkyl group at the β or 3- position [47].

The homopolymer poly (3-hydroxybutyrate) (PHB or PH3B) can be considered as the most extensively studied PHA. PHB has a high degree of crystallinity because of its highly stereoregular structure. The high degree of crystallinity leads to a rather stiff and brittle material which limits its wide applications [45]. Furthermore, for processing, PHB has a very narrow processing window, and undergoes extensive thermal degradation above its melting temperature (Tm around 170°C) during extrusion or injection molding. In order to overcome these drawbacks, PHB should be copolymerized with another polymer that confers less stiffness and tougher properties and to reduce the melting point [55, 57].

There are some methods to synthesize PHB.

Biosynthesis of P3HB (or PH3B)

In 1973, Schlegel and Dawes announced their discoveries on the identification of the two enzymes involved in the reactions for converting acetic acid to 3-hydroxybutyric acid in the two different bacteria. For both bacteria, the enzymes were a ketothiolase which catalyzes the dimerization of the Coenzyme A derivative of acetic acid, acetyl-CoA, to acetoacetyl-CoA, and a reductase which catalyzes the hydrogenation of the latter to [R]-3-hydroxybutyryl- CoA, the monomer that is polymerized to PHB by a synthase, as shown in the following reaction scheme:



A detailed mechanism for the polymerization reaction was presented as follow:

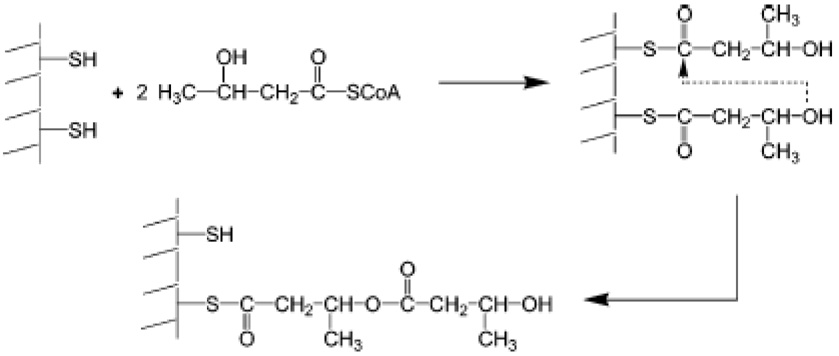


Figure 17: P3HB synthesis by polymerization reaction

In this mechanism, two thiol groups are involved in the active site for both the initiation and propagation reactions of the polymerization process. For initiation period, the two thiol groups form thioesters with two molecules of monomer, which then undergo a thioester-oxyester interchange reaction at the active site to form a dimer and release one of the thiol groups for the propagation reaction [47].

PHB has many interesting properties, such as low viscosity and biocompatibility, which makes it suitable for using in industrial applications. However, the price of PHB is still high which is a lot higher than plastics produced from petrochemicals. Thus, the research in this area is accelerating to develop new methods to obtain PHB as a viable thermoplastic, because if large quantities are produced, its price can decrease significantly and allow more extensive use. There are also some concerns about the environment with large quantities of PHB produced. Some of the properties of PHB reported include tensile strength: 43 MPa, Young’s modulus: 3.5 GPa (which are close to those of isotatic polypropylene), and % elongation of 5.5 (lower by 400% than polypropylene) [48].

Poly 3-hydroxybutyric acid is released by B. megaterium in an aqueous environment. In 1967, Williamson and co-workers identified a specific dehydrogenase that converted Poly-3-hydroxybutyric acid to acetoacetic acid, and in 1973, Dawes and co-workers found an enzyme for the conversion of acetoacetic acid to acetic acid so the entire intracellular pathway for the reconversion of PHB to acetic acid was established to include the following steps:

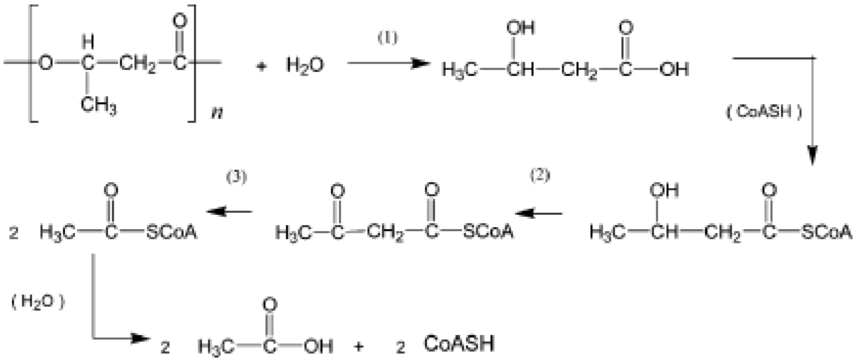


Figure 18: The process of P3HB biodegradability [47]

It is now known that microorganisms exist in all natural environments that are capable of degrading PHB and metabolizing Poly-3-hydroxybutyric acid by enzyme-catalyzed reactions, so by definition, PHB is a biodegradable polymer.

Given the wide interest into polyhydroxyalkanoates, research on PHB has been quite extensive both in academic and industrial centers. The focus is now on producing PHB from plants instead of bacteria.

II.3.Poly (4 -hydroxy butyrate)

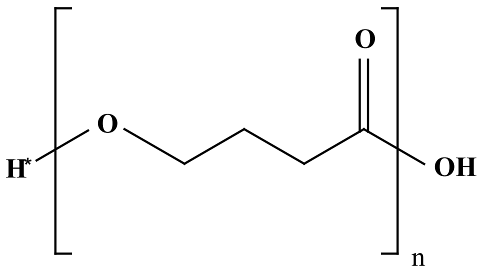


Figure 19: Structure of Poly 4 hydroxybutyrate (P4HB)

Similar to Poly (3-hydroxybutyrate), Poly(4-hydroxybutyrate) (P4HB) belongs to the family of bacterial polyhydroxyalkanoates (PHAs). Poly-4-hydroxybutyrate is a thermoplastic, linear polyester, produced by recombinant fermentation, that can be converted into a wide range of resorbable medical devices [121]. P4HB is a strong, flexible and absorbable material which has a large variety of medical applications like tissue engineering, drug delivery. For efficient production of P4HB recombinant Escherichia coli has been employed. It was previously found that the P4HB synthesis is co-related with the cell growth

[50]. In nature, this polyester is produced inside cell as storage granules and regulate energy metabolism [52].

P4HB biosynthesis has been studied for a few decades and it was still the first and only PHA-based product approved by the FDA (Food and Drug Administration) as an absorbable suture for clinical application. It is a strong, flexible thermoplastic material that can be processed easily to scaffolds, heart valves or cardiovascular tissue supports. The most important property of P4HB is its very high elasticity and molecular weight, as both benchmark closely to ultra-high molecular weight polyethylene. It can even be stretched 10-times its original length before breaking. In addition, P4HB is biocompatible and extremely well tolerated in vivo because biological hydrolysis of P4HB yields 4HB. It is highly desired to obtain P4HB in large scale at a competitive cost. It was reported that up to 50% of the total cost of poly(3-hydroxybutyrate) (P3HB) arises from the carbon source. Therefore, to reduce the cost of the carbon source used for large scale P4HB production, agricultural derived feedstock such as processed hemicelluloses may be employed as a co-substrate to produce the bacterial biomass [50].

Le Meur et al. [50] insisted that Wild-type E. coli strains could not synthesize any type of PHA, including P4HB. However, by introducing the P4HB synthesizing genes, recombinant E. coli strains are able to produce P4HB through the newly acquired biosynthetic Pathway.

Generally, P4HB is produced by microbial fermentation process, rather than a chemical synthesis [52].The high crystallinity and molecular weight of P4HB made it good thermoplastics. However, functionalization is difficult by this method. Chemical synthesis of P4HB via ring-opening polymerization (ROP) of γ-BL (Butyro lactone) has been tried for a long time and demonstrated to be difficult due to the small ring-strain of γ-BL [51]. Also, chemical synthesis by ring-opening polymerization of γ-BL, it can produces only low molecular weight oligomers that are viscous fluids rather than the much higher molecular weight, strong and flexible plastic that is derived from the fermentation process [52].

Li-jing Zhang et al. [51] developed a method to synthesize P4HB with controlled degradation behaviors and nonacidic degradation products. In this method, the polyesters were prepared by Passerini multicomponent polymerization (MCP) and the subsequent hydrogenation.

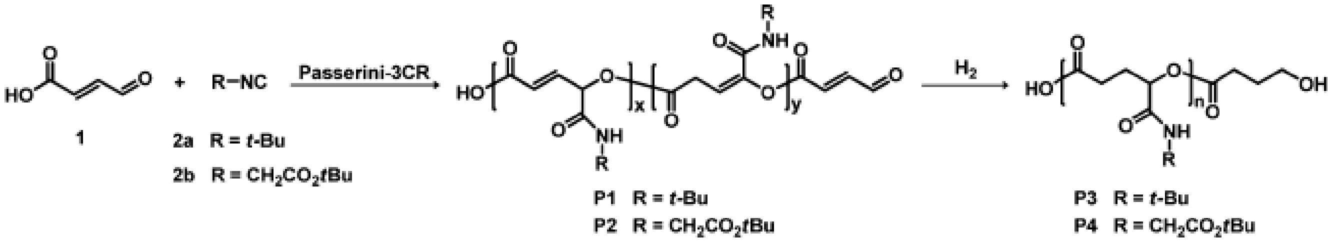


Figure 20: Synthesis of Functional P4HB by Passzerini MCP and Subsequen Hydrogenation

Despite the method of preparation, the structure of P4HB strongly resembles that of chemically derived polyesters. By chemical synthesis, it is considered impossible to produce the polyester with sufficiently high molecular weight necessary for most applications. The approach is reported to give some additional advantages. For example, it opens up additional options for tailoring properties by incorporating other co-monomers, and for varying molecular weight. Polymerization of PHB with other hydroxyl acid such as 3-hydroxybutyrate (3HB), for example, can yield elastomeric compositions at moderate 4HB contents (%), and relatively hard rigid polyesters at lower 4HB contents. Moreover, since molecular weight depends upon the activity of specific pathway enzymes within the cells, and these activities can be varied, there is a mean to control molecular weight [52]. P4HB molecular weights up to about 1 million have been produced with a polydispersity of 2-3.

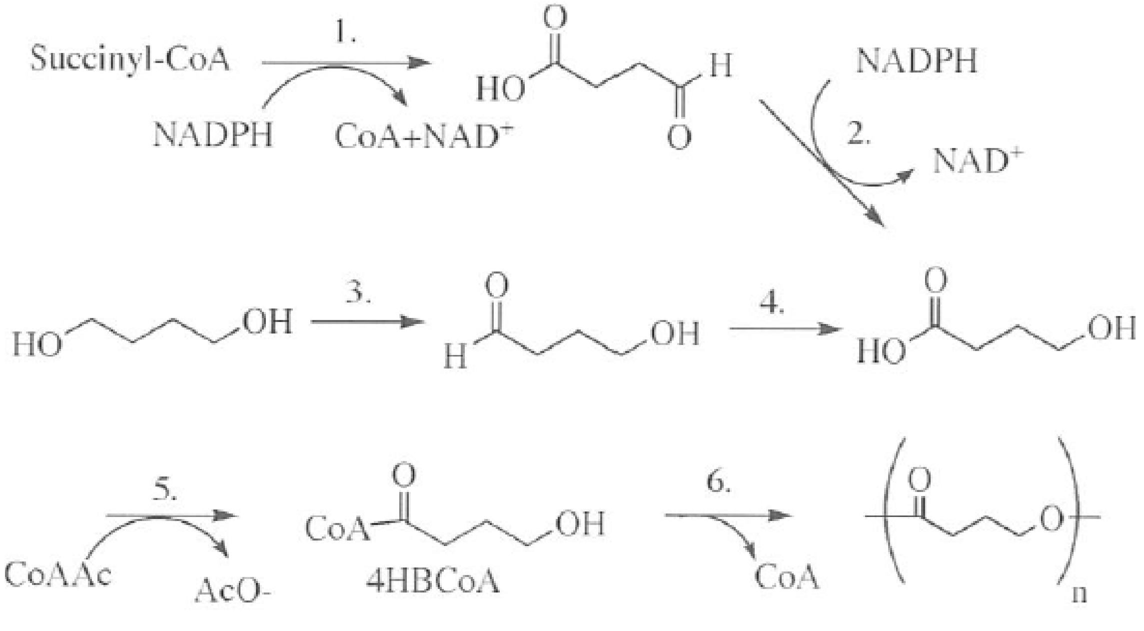


Figure 21: Biosynthetic pathways for production of P4HB.

Biosynthetic pathways for production of P4HB with different enzymes are: (1) succinic semialdehyde dehyrogenase (2) 4-hydroxy butyrate dehydrogenase (3) diol oxidoreductase (4) aldehyde dehyrogenase; (5) coenzyme A transerase and (6) PHA synthetase [52].

As mentioned above, P4HB is described as a strong pliable thermoplastic material, and in this aspect it is significantly more flexible (by up to two orders of magnitude) than synthetic absorbable polymers such as PGA (polyglycolide) and poly –L- lactide (PLLA). Relative to other thermoplastics, P4HB has a tensile strength that benchmarks closely to ultrahigh molecular weight polyethylene.

As P. Martin et al. [52], P4HB has a melting temperature (T*m*) of 60°C, and glass transition temperature (Tg) of -51°C. Besides, the tensile strength was recorded at 50 MPa; the tensile modus were 70 MPa. The absorption is fairly stable in the melt up to about 200°C, showing only modest molecular mass loss. High molecular weight P4HB (>800 000) may require higher temperatures for processing due to its high melt viscosity. Lower molecular mass P4HB can be melt processed fairly easily. Besides, P4HB is fairly soluble in solvents such as acetone and other similar polar alternatives. This is particularly useful in solution coating, phase separation techniques to make porous devices and preparation of microspheres, and could facilitate solution- spinning methods. Also, P4HB appears to be much less sensitive to hydrolysis by atmospheric or residual moisture than synthetic absorbable polyester derived from α-hydroxyl acids [52].

II.4.Poly(3-hydroxybutyrate-co-4-hydroxybutyrate)

The purpose of producing P34HB is to improve the properties of poly(3-hydroxy butyrate). The copolymer P(3HB-co-4HB) (or P34HB) has emerged as an excellent candidate of biomaterial since the presence of 4-hydroxybutyrate lowers the crystallinity of the copolymer. P(3HB-co-4HB) has been found to exhibit useful properties in relative to other PHAs as it can be altered to a variety of polymeric materials, from hard crystalline plastic to a very elastic rubber by varying the 4HB monomer composition. Besides, the properties of P(3HB-co-4HB) can be tailored in many ways to minimize or overcome the drawbacks such as absence of hydrophilicity and bioactivity, so that a new low-cost product can be obtained [56].

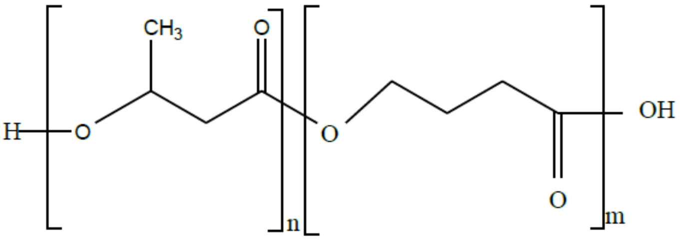


Figure 22: Structure of Poly 3/4 hydroxybutyrate

Poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P34HB) is generally fermented successfully from 4-hydrobutyric and butyric acid. The physical property of P34HB from semi-crystallization plastics to amorphous elastomers depends on the 4-hydroxybutyrate (4HB) content. As plastics, P34HB possesses fairly good processing property. However, the thermal stability of P34HB is less than 250^{o}C and needs to be improved. In addition, when P34HB was used as elastomers, it had very low tensile strength and limited elongation at break. P3/4HB has been produced in large industrial scale with the hope of becoming novel, resources renewable, and non-fossil based commodity polymers [53].

The present of P4HB helps reducing polymer crystallinity and typically provides flexible/elastic properties. It has been reported that the strength of P(4HB) fibers prepared by melt extrusion typically compare well with those of traditional suturing materials. P(4HB) and P(3HB-co-4HB) may be useful in a wide variety of medical fields, such as cardiovascular, wound healing, orthopedic, drug delivery and tissue engineering [54].

Up to now, several wild-type bacterial strains have been reported to be able to produce P(3HB-co-4HB) copolymer, they are: Ralstonia eutropha, Alcaligenes latus, Comamonas acidovorans, Comamonas testosteroni and Hydrogenophaga pseudoflava. Saito et al. reported the production of P(3HB-co-4HB) copolymers by R. eutropha using different carbon sources with or without 4HB as precursor, however, only very low cellular polymer contents were obtained . It was also reported that a maximum of 21% w/w of P4HB can be achieved by C. acidovorans when using 4HB or 1,4-butanediol as precursor . Kim et al. performed fed-batch experiments with R.eutropha supplying in the first step fructose and in the second step only 4HB. They obtained a cell concentration of 33.6 g/ L and a P(3HB-co-4HB) copolymer content of 41.7% w/w with 25 mol% 4HB [50]. In the copolymer, the mobility of both the 3HB and 4HB units is found to increase with increasing 4HB content of the copolymer. In both copolymers, the segmental motion of the 4HB unit was found to be 2-4 times faster than that of the 3HB unit. Moreover, one study stated that there was a decrease in crystallinity as the percentage of 4HB units in P34HB copolymers increase was accompanied by a decrease in Tg, which leads to increase elastomeric behavior at room temperature [58]. The study also revealed the change in the percentage of P3HB and P4HB caused a significant different in the properties of the copolymer. For example, they prepared 2 kinds of P34HB with 18 and 69% 4HB content and the result was shown below [58].

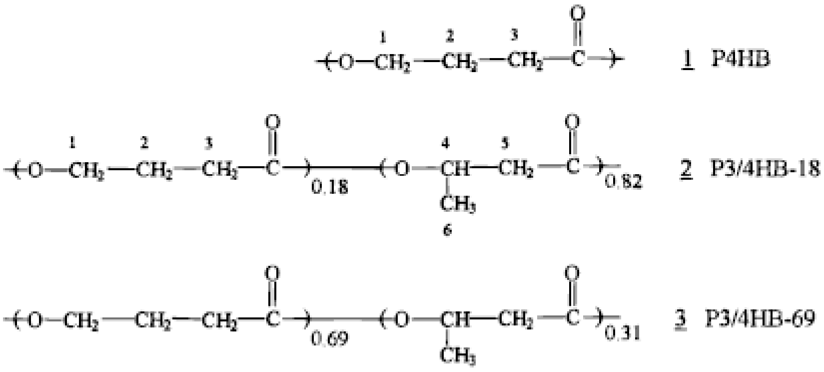


Figure 23: Structure of the 3 investigated polymers [58].

Table 9: Physical properties of P4HB and P3/4HB-18 and P3/4HB-69 [58]

	T_g (°C)	T_m (°C)	Crystallinity (%)	Tensile strength (MPa)	Elongation to break (%)
P4HB	-48	54	25 ±5	104	1000
P3/4HB – 69	-36	50		~17	~591
P3/4HB – 18	-4	165	30±5	~26	~444

Also, in another study, the incorporation of 4HB as a monomer into P3HB has resulted in the production of commercially attractive copolymers, copolymers of scl (Short chain length) and mcl (Medium chain length) monomers combine the strength of P3HB and the flexibility of mcl PHA. So far, random copolymers including poly(3-hydroxybutyrate-co-4-hydroxybutyrate) P(3HB-co-4HB), have been found to exhibit useful thermal and mechanical properties although they still suffer from property detrimental aging effects. Block copolymerization seems to be popular and is another approach to gain novel polymers with new properties. Block polymer chains contain two or more different regions (or "blocks") of polymer covalently bonded together. The structures of block copolymers include A-B diblock, A-B-A or A-B-C triblock, and (A-B)n repeating multiblocks. Block copolymerization can result to additional physical properties that cannot be obtained by random copolymerization, polymer blending, or filler-adding techniques, because this block structure captures the properties of each block. Die Hu et al. [59] also focused on the differences of thermal and mechanical properties between the block copolymer P34HB and the others. The block, random copolymers and blend polymer showed different thermal behaviors due to their different microstructures (Table 10). The random copolymer had a single Tg with small Tm and without Tc, demonstrating its amorphous nature as a result of the random assembly of its components in the chain segment instead of repeated chain segments. While, the block copolymer revealed two Tm of 54 and 161^{o}C, but only one Tg of -47^{o}C [59].

Table 10: Thermal Properties of P3/4HB Random Copolymer, P3HB-b-P4HB Block Copolymer and Blend Sample of P3HB and P4HB Homopolymers Compared with Their individual Homopolymers [59]:

Sample (PHA)	T_g (^{o}C)	T_m (^{o}C)	T_c (^{o}C)
P3HB	0.7	171.6	41.0
P4HB	-45.67	50.1	-0.69
Random copolymer	-22.4	50.1	
Blend sample	-48.6[b]	56.0 ; 171.2	-12.7
Block copolymer	-47.3[b]	54.2 ; 161.4	-6.7

[a] Random copolymer : P(3HB – co -70 mol % 4HB); Blend sample: P3HB (20%) + P4HB (80%); Block sample: P3HB (20%) - b – P4HB (80%).

[b] Cannot detect from the DSC thermograms since the cooling crystallization peak covered the second T_g.

Compared with other commercially available PHA, especially PHBHHx, the novel P3HB-b-P4HB block copolymer improved properties in tensile strength and elongation at break. Compared to other scl PHA, mechanical properties of the block copolymer appears to be significantly improved. The crystallization rate due to different size polymer domains may cause differences between random copolymer and block copolymer (Table 11) [59].

Table 11: Mechanical Properties of P3HB4HB Random Copolymer, P3HB-b-P4HB Block Copolymer, and Blend Sample of P3HB and P4HB Compared to Commercially Available PHBHHx (Poly 3hydroxy butyrate –co-3-hydroxyhexanoate) [59].

Sample	Yield strength (MPa)	Tensile strength (MPa)	Elongation at break (%)
PHBHH*x* copolymer	12.5	7.0	400
Random copolymer	7.3	9.9	729
Blend sample	10.9	16.5	357
Block copolymer	13.3	19.9	438

PHBHH*x* consists of 12 mol % 3HH*x* ; Random copolymer: P(3HB – co – 70 mol % 4HB); Blend sample: P3HB (20%) + P4HB (80%); Block sample: P3HB (20%) – b –P4HB (80%).

Moreover, it is might be suitable to take advantage of the copolymer P34HB as the matrix because when the copolymer combines with cellulose fibers (as the reinforcement), the presence of cellulose fibers can increase the rate of PHB crystallization due to a nucleating effect while thermal parameters, such as crystallinity content remained unchanged. Studies on the crystallization behavior of PHB/kenaf fiber biocomposites showed that the nucleation by kenaf fibers affected the crystallization kinetics of the PHB matrix. Differences in the effect of cellulose fibers on the crystallization process were attributed to the lignin content at the surface/interface of the cellulose fiber. The addition of cellulose fibers led to some improvement in tensile strength and stiffness, but the composites remained brittle. At low content, the incorporation of cellulose fibers lowered the stiffness, however, higher amounts of cellulose fibers greatly improved the mechanical properties of PHB. For biocomposites based on cellulose fibers and PHB, the effect of fiber length, surface modification on the tensile and flexural properties should be investigated [57].

Our Poly 3/4 hydroxy butyrate was provided by Tianjin GreenBio Materials (Tianjin, China) with the density of 1.25 g/cm^3 and melt index of 170°C.

III. Polymer matrix Polybutylene Succinate (PBS)

In order to make a comparison with composite based from PHB, we also tried to study with another conventional polymer. The employed polymer also has to meet the demand of solving the problems of waste management especially when the waste treatment and the accumulation of non-biodegradable polymers (i.e. Polyethylene) become serious problem of many countries (especially in South East Asia) so that the biodegradable polymer is the good choice [78, 80]. Moreover, biodegradable polymers reveal their excellent medical applications [79]. Among biodegradable polymers, polybutylene succinate (PBS) exhibits the desirable properties [76]. Firstly, PBS is considered as a promising biodegradable material that can be easily decomposed by the cleavage of ester bond link. This ester bond can also make it easily degrade in water [77].

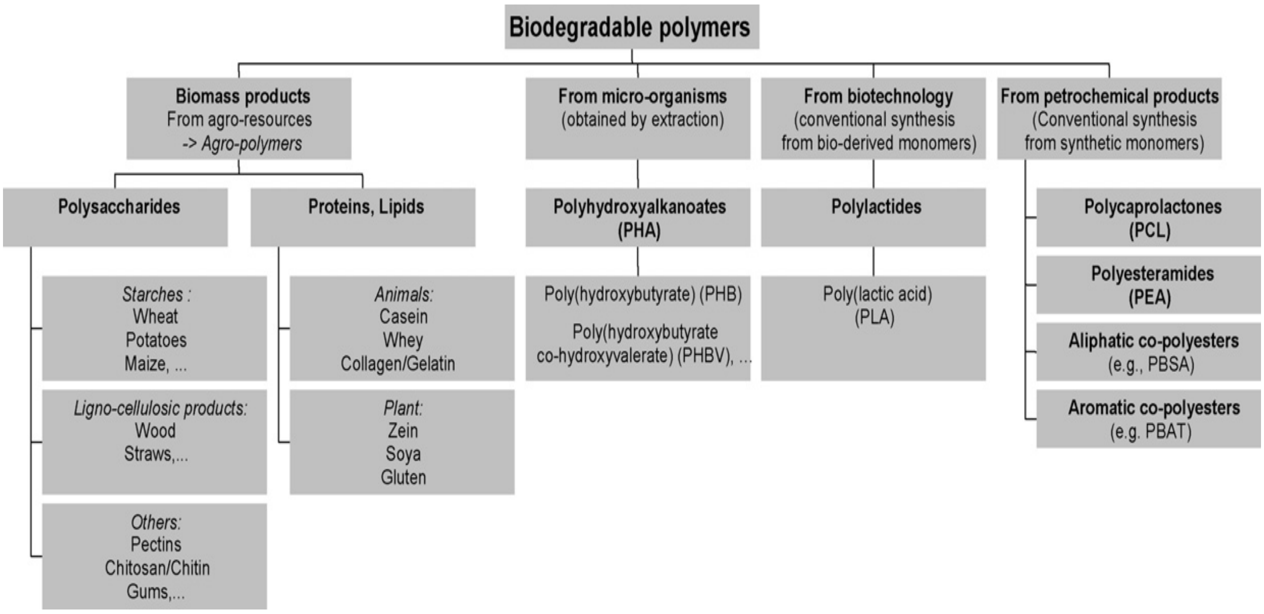


Figure 24: Classification of the biodegradable polymers [88].

PBS is a white semi-crystalline thermoplastic with melting point of about 90–120^{o}C (similar to LDPE), glass transition temperature between -45 to -10^{o}C. In addition, PBS has excellent processability and can be processed on polyolefin processing machines at temperatures of 160–200^{o}C, into various products, such as injected, extruded and blown ones. Also, it is reported that the raw materials, butanediol and succinic acid to synthesize PBS, are available from bio-based renewable resources [84].

As other polyesters, such as poly (ε caprolactone) (PCL), poly hydroxybutyrate (PHB) and poly lactic acid, PBS can be decomposed [79]. However, the rate of the decomposed process in water was recorded pretty slow [89].

Table 12: Weight-loss biodegradabilities and BOD (Biochemical oxygen Demand) biodegradabilities of aliphatic polyester films in different natural water for 28^{o}C at 25^{o}C [89].

Sample	**Freshwater (river)**		**Freshwater (lake)**		**Seawater (bay)**		**Seawater (ocean)**	
	WL Biodeg.^{a}	BOD Biodeg.^{b}	WL Biodeg.^{a}	BOD Biodeg.^{b}	WL Biodeg.^{a}	BOD Biodeg.^{b}	WL Biodeg.^{a}	BOD Biodeg.^{b}
P(3HB)	100±0	75±16	93±7	52±7	41±16	27±10	23±13	14±10
P(3HB-*co*-14%HV)	100±0	76±2	100±0	71±1	100±0	84±2	100±0	78±5
P(3HB-*co*-10%4HB)	100±0	90±1	74±26	55±17	70±30	51±27	59±15	43±14
Poly(ε-caprolactone)	100±0	75±8	100±0	77±1	100±0	79±2	67±21	56±9
Poly(ethylene succinate)	100±0	83±2	100±0	77±2	2±1	1±1	5±2	3±2
Poly(ethylene adipate)	100±0	70±3	95±5	68±8	100±0	65±13	57±14	46±13
Poly (butylene succinate)	2±1	3±1	22±14	12±8	2±2	1±1	2±3	2±0
Poly(butylene adipate)	24±	20±4	80±13	50±10	34±2	20±2	11±10	10±5

^{a}Weight-loss biodegradability

^{b}BOD biodegradability

Besides, PBS is considered to be easily processed and relatively low cost compared with those polymers [76]. In addition, thermoplastic PBS also reveals the good mechanical properties, closely comparable to those of widely-used polyethylene (PE) and polypropylene (PP) [76].

However, the intrinsic inflexible biodegradability of PBS and its high cost limit its practical use. Therefore, to control the biodegradability and reprocessability is of great importance that can widen the usage of this polymer [76, 80]. Also, to date, cellulose fibers like rice straw, abaca fiber, kenaf fiber , jute fiber , alkaline lignin , bamboo fiber , water bamboo, husk wood flour and starch have been used as natural fillers to enhance the properties of PBS and reduce the cost [80].

III.1.Synthesis of PBS

Poly (butylene succinate) is not a new polymer, however it was not until 1950s or 1960s that PBS was developed commercially as it was done with commodity polymers. PBS is one of the 'old' polyesters and regains interest because of the current preoccupation with the environment [89].

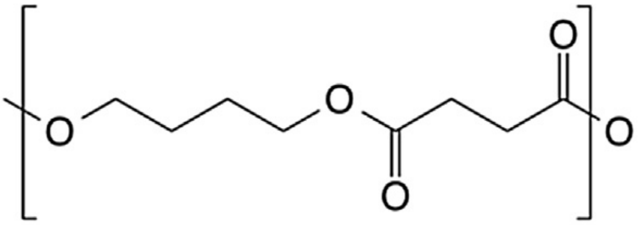


Figure 25: Formula structure of Polybutylene Succinate

PBS can be produced through direct esterification in open and closed systems, in the presence and absence of nitrogen, using two different monomers (succinic acid and anhydride). PBS was also produced through transesterification at different temperatures and using different metal catalysts. There are 2 main routes to synthesize PBS: the trans-esterification process (from succinate diesters) and the direct esterification process starting from the diacid .

In 1975, a patent published by Coquard et al. [90] reported the synthesis of PBS from diethyl succinate and butanediol in the presence of zinc acetate and antimony trioxide as catalysts. However, they did not give the information on the molecular weight of the final product.

Commonly, PBS is synthesized by the direct esterification of succinic acid with 1,4-butanediol in a two steps process [81, 82, 83]. First, an excess of the diol is esterified with the diacid to form PBS oligomers with elimination of water. More specifically, N. Jacquel et al carried out the experiment with the molar proportion of [COOH]/[OH] groups that was fixed at r = 0.95 corresponding to a molar excess of butanediol of 5 mol %. The reaction mixture was then heated to 225°C under a 2 bar nitrogen pressure and stirred at a constant speed (150 rpm). A mixture of water containing 1.5–2 mol % of tetrahydrofuran (THF) produced by the dehydration of butanediol was distilled off from the reactor.

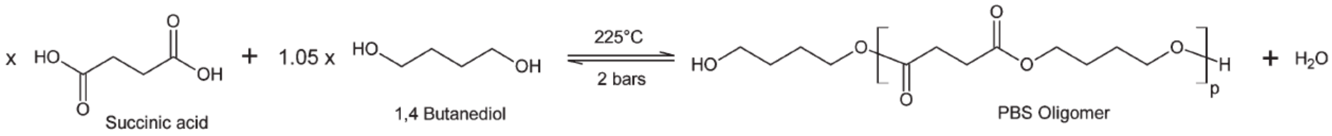


Figure 26: First step of PBS synthesis

In the second step, the obtained oligomers are trans-esterified under vacuum (the pressure was reduced to 0.7 mbar in 120 min) to form a high molar mass polymer, and the temperature was raised to 230^{o}C to initiate the transesterification. Low-pressure conditions were maintained until the desired torque. The polymer strand is then withdrawn and quenched in a water bath. Crystalline PBS pellets were obtained after granulation.

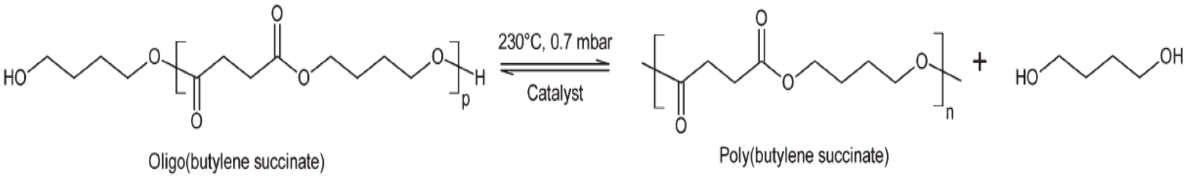


Figure 27: Second step of PBS synthesis

This step requires an appropriate catalyst such as organo-metal (Ti, Zr, Sn, Hf, and Bi) and metal oxide- (Ge and Sb). For these two types of catalysts, appropriate preparation procedures were set. Due to their sensitivity to water, organo-metals were added after esterification, whereas metal oxides were introduced with monomers at the beginning of the reaction [83]. These catalysts were used because they are, individually, the ones used most often for synthesis of PBS. It was proposed that the catalytic efficiency of the organometal catalysts was as follows: Ti>>Z ~Sn>Hf>Sb>Bi. [82, 83] In fact, PBS synthesis is mainly carried out with titanium (IV) isopropoxide, titanium (IV) isobutoxide14 or titanium (IV) n-butoxide [81, 83]. Recently, new catalysts have been developed that are based on rare-earth metals, such as scandium $Sc(OTf)_3$ or $Sc(NTf_2)_3$ [84].

Turki et al. [91] have synthesized a PBS by bulk polymerization between dimethyl succinate and a slight excess (10% mol.) of BDO (butanediol) in the presence of titanium tetrabutoxide (IV) as a catalyst. Montaudo et al. [92] performed the same kind of study with esters of sebacic and adipic acids.

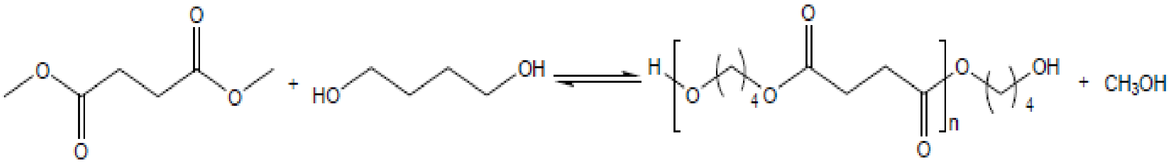


Figure 28: First step of transesterification between butanediol and a dimethyl ester of succinic acid

In both studies, the authors separated the two-step reaction: transesterification at 180°C under nitrogen flow where methanol is the by-product of reaction, followed by polycondensation vacuum between 200 and 240°C. By this method, Tserki et al. [91] obtained PBS with a mass Mn equal to 59,500 g/mol and a Mw equal to 104,100 g/mol.

PBS can also be prepared by the direct esterification of a carboxylic acid and alcohol catalyzed by $Sc(OTf)_3$ and it was reported that this breakthrough made it possible to synthesize aliphatic polyesters without transesterification under milder conditions compared to conventional methods. Owing to the polycondensation, it was revealed that $Sc(OTf)_3$ can also catalyzes etherification as a side reaction, which depends on the chain length (methylene number) of the diols. The catalyst make it possible to prepare biodegradable polyesters, the obtained PBS having a Mn of >10 000 even at 35°C and this is regarded as an environmentally friendly process. Moreover, the catalyst could be recycled for the polyester synthesis [84].

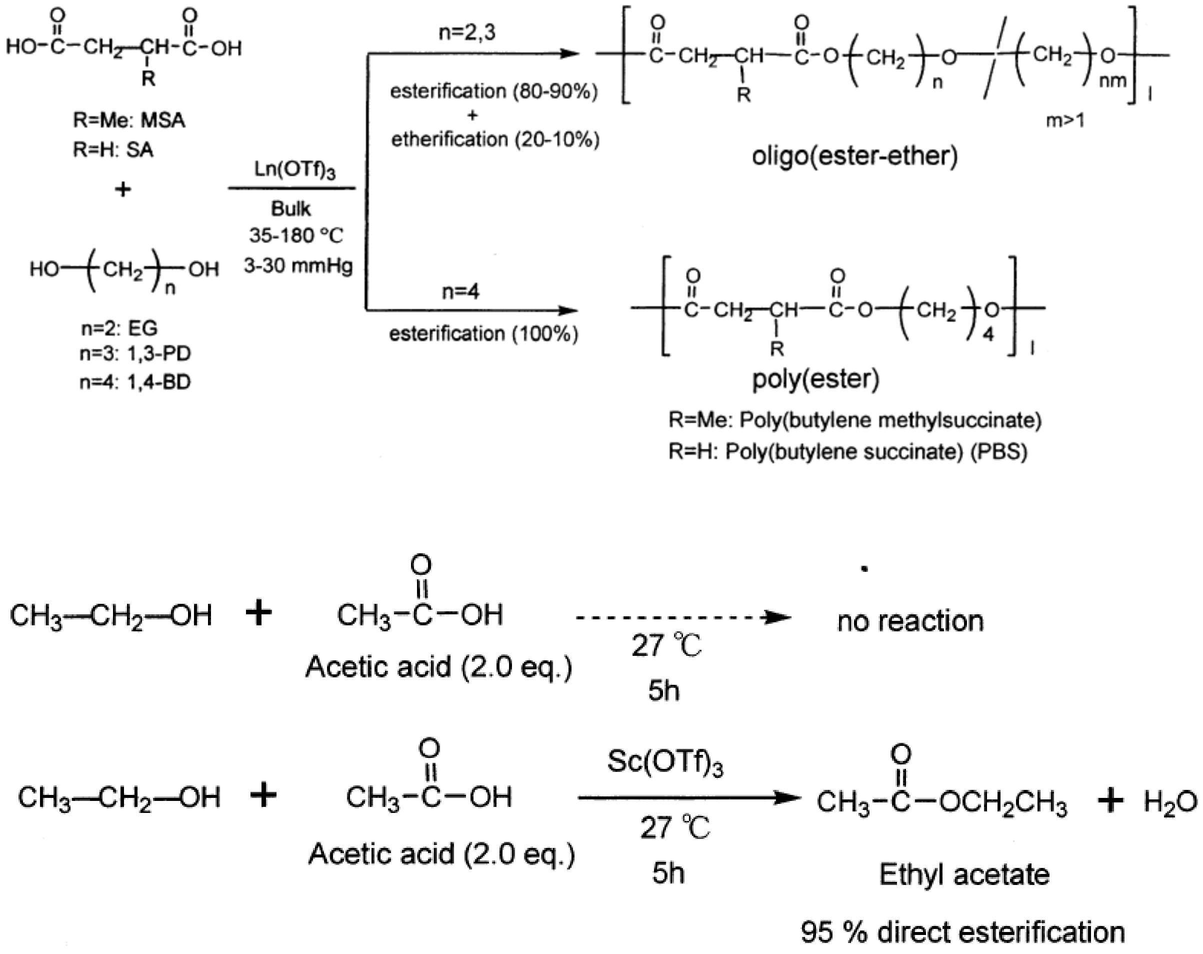


Figure 29: Direct esterification of carboxylic with alcohols [84]

The molar mass of polymer is also important. Depending on the reaction mechanism and the catalyst, the molar mass varies. For examples, PBS obtained by the method referred above (using butanediol) has Mn ranging from 20 000 to about 50 000 g/l [83]. In other study, it is indicated that direct polycondensation of succinic acid and 1,4-Butadiol using the recovered catalyst gave PBS with a Mn of 14300 (Mw/Mn = 1.49). In general, the synthesis is commercially produced by the polycondensation of aliphatic dicarboxylic acid and diol compounds at 200-250°C under highly reduced pressure. However, it was very difficult to prepare aliphatic polyesters with a high molecular weight by direct polycondensation because of the thermal degradation at high temperature and low hydrolytic stability in one step [84]. Polycondensation time at such temperatures remains very long (>50 h), and the final number average molar mass of Mn, ranging from 5000 to 12,000 g/mol, is relatively low. Using stannic components, such as distanoxannes or tin salts can bring about the much higher molar mass Mn of 117,000 g/mol. However, it is not a favorable process because of the use of solvent and the long reaction times (24–80 h) [83].

III.2.Properties of PBS

III.2.1.General properties

PBS can be decomposed due to the cleavage of ester bond linkage. The biodegradability of aromatic and aliphatic is supposed to be strongly affected by the composition sequence distribution, crystallinity, structure of the crystallites and melting temperatures [78] as well as other structures such as stereochemistry, hydrophilicity, flexibility of chains [79]. Generally, biodegradable polymers can be degraded to low molecular weight compounds due to water or the enzymes exerted by microorganisms. During the degradation process, the amorphous will gradually disappear, trigger the rapid increase of the crystallinity of the samples and the crystallinity will levels off to a much slower rate. The amorphous part will degrade prior to the degradation of the crystalline regions. Also, the chain mobility of the amorphous regions and the rate of degradation are affected by the size, number of crystallites [79].

PBS is a white semi-crystalline thermoplastic with a melting point of around 90–120°C and the glass transition (Tg) is ranging from -45 to -10^{o}C. Its mechanical properties are very similar to those of polyethylene or polypropylene. In addition PBS has good processability, better than that of poly lactic acid (PLA) and poly glycolic acid (PGA) [93].

Hydrolytic degradation of polymers is also an important factor of degradation. It is affected by the polymer morphology that controls the diffusion of water into the polymer matrix: water penetrates at a higher rate in the amorphous region than in the crystalline region, which results in a higher hydrolysis rate in the amorphous region [79]. Besides, the effect of the microstructure of crystalline morphology, such as the size, form, and internal structure of crystallites, on hydrolytic degradation is still not understood thoroughly.

In the case of PBS, it has a high crystallization rate. Hence, the crystalline microstructure can be well controlled by changing the crystallization conditions and subsequent thermal treatment, which maintains similar crystallinity [79].

Here below showed some tables from several publications about the fundamental properties of PBS:

Table 13: Structure and properties of different polyesters [92]

No.	Sample[a]	Synthesis method	ηsp/c[b]	Mn[c]	Mw[c]	Mw/Mn[c]	Tm[d] (°C)	Crystallinity[e] (%)
1	PBSu	I	0.56	28000	49700	1.77	114	34
2	PBSe	I	0.43	17800	31500	1.77	65	56
3	PBSe	II	0.74	33600	61400	1.83	65	34
4	PBAd	I	0.30	10500	23500	2.23	63	
5	PBAd	II	1.08	36150	101500	2.81	64	30

a PBAd=poly(butyleneadipate); PBSu=poly(butylenesuccinate);
PBSe=poly(butylenesebacate)

b Intrinsic viscosity determined in $CHCl_3$, 30°C.

c Number-average and weight-average molar masses determined using the calibration curve obtained with PS standards in $CHCl_3$.

d Determined by DSC.

e Determined using the Vonk's method

Homopolyesters and copolyesters were synthesized by melt polymerization starting from stoichiometric amounts (method I) of dimethyl esters and 1,4-butanediol, or using an excess of 10% (method II) of 1,4-butanediol, in the presence of titanium (IV) butoxide as esterification catalyst [92].

Table 14: Composition, intrinsic viscosity and molecular weight of different polyesters [91]

Polymer	**Feed composition (mol%) (Su/Ad)**	**^{1}H NMR composition (mol%) (Su/Ad)**	**Intrinsic viscosity [ɳ] (dl/g)**	**Mn**	**Mw**	**Mw/Mn**
PBSu	100/0	100/0	0.88	59500	104100	1.75
PBSA (80/20)	80/20	78.2/21.8	0.80	46700	86400	1.85
PBSA (60/40)	60/40	56.8/43.2	0.78	45200	83200	1.84
PBSA (50/50)	50/50	47.1/52.9	0.55	27100	66100	2.44
PBSA (40/60)	40/60	37.4/62.6	0.68	33600	79000	2.35
PBSA (20/80)	20/80	18.6/81.4	0.76	42500	82900	1.95
PBAd	0/100	0/100	0.56	31100	69700	2.24

Where: PBSu : Poly butylene succinate/ PBSA: poly butylene succinate co butylene adipate

Table 15: Physical data of some commercial biopolyesters [88].

	PLA Dow-Cargill (NatureWorks)	PHBV Monsanto (Biopol D400G – HV=7 mol%)	PCL Solvay (CAPA 680)	PEA Bayer (BAK 1095)	PBSA Showa (Bionolle 3000)	PBAT Eastman (Eastar bio 14766)
Density	1.25	1.25	1.11	1.07	1.23	1.21
Melting point (^{o}C)	152	153	65	112	114	110-115
Glass transition temperature (^{o}C)	58	5	-61	-29	-45	-30
Crystallinity(%)	0-1	51	67	33	41	20-35

In addition, it is reported that a polymer with a lower melting point is generally more susceptible to biodegradation than one having a higher melting temperatures because they have more flexible chains which can fit into the active sites of the enzymes than those with higher melting points [78]. PBS, however, is one of aliphatic polyesters having the highest melting temperatures. Poly (butylene adipate), PBA has the lower melting point, therefore it can be more rapidly degraded than PBS [78].

III.2.2.Mechanical properties

PBS is regarded as a thermoplastic whose mechanical and physical properties are good and desirable compared with other degradable polymers. Depends on the specific factors such as crystallinity, morphology, molecular weight, … the properties may vary. The bending test from Chiharu Kanemura’s study was recorded and the bending strength was about 42 MPa [77]. PBS has the tensile strength between those of PE and PP, and stiffness between those of LDPE (Low density polyethylene) and HDPE (High density polyethylene) [87].

Reprocessability

Reprocessability is one of the important properties of PBS. Many researchers have studied this property for years. C Kanemura et al. [77] examined this property by measuring the bending test. The specimens were immersed in water in certain time, these specimens were then measured the bending strength before and after the recycle process. The results showed that mechanical properties of PBS were enhanced after reprocessing, which could not be observed in other types of biodegradable materials such as PLA. However, the mechanical properties could not be as good as that of the original PBS.

III.3.Composite from PBS reinforced with cellulose fibers

Cellulose fibers have many advantageous features as fillers in polymer composites since they are low in cost, environment-friendly, renewable, biodegradable, and available in high quantities, those are good advantages compared with artificial fibers. However, their drawbacks lie on moisture absorption, quality variation, low thermal stability, and poor compatibility with hydrophobic polymer matrix, which lead to composites with undesirable properties. Nevertheless, these undesirable properties can be improved by physical and chemical treatments such as surface modification using coupling agents. And silane coupling agents are reported as an effective agent to improve interfacial strength [80]. Hence, in this study, we attempt to elaborate material from bamboo fiber as the reinforcement and PBS**.**

III.3.1.Preparation

Firstly, PBS can hydrolyze, therefore, to get rid of moisture absorption, PBS should be dried carefully (about 50°C for 24 hours in the oven (PBS)). The polymer sheet can be prepared under hot pressing machine at 30°C above the melting temperature [77,78]. In Kanemura's study, PBS was molded at 140°C for 30 min at a pressure of 0.34 MPa using a hydraulic compression molding machine since the glass transition temperature and the melting point of PBS were -32°C and 115°C, respectively [77]. S.H. Lee prepared the composite by introducing the mixture of PBS and bamboo fibers in the batch mixer, rotating at 30 rpm. And then the rotation speed was increased to 70 rpm. LDI (lysine-based diisocyanate) was also used as a coupling agent. The blended mixture was finally compression-molded into sheets under a pressure of 150 kgf/cm^2 at 140°C (PBS/BF composite) [87].

III.3.2.General properties

The tensile strength of the composite based from PBS and bamboo fiber decreased with the increase in bamboo fiber content due to the poor interfacial adhesion between the filler and the matrix. This is considered as a general phenomenon in incompatible composites with different characteristics, such as hydrophobicity of the polymer matrix and hydrophilicity of the filler. The Young modulus, on the other hand, saw a singnificant increase with the increase load of bamboo fibers [87].

In another study, jute was used as a reinforcement. It is proved that, the modification on the jute's surface helped improve the interfacial adhesion with PBS. Thus, they obtained the better mechanical properties on tensile strength, modulus and flexural strength with the increase of fiber loadings [85].

Bamboo fiber is hydrophilic because it contains an abundance of hydroxyl groups, but PBS is a hydrophobic polymer. The water absorption for the composite from these 2 components increased greatly during the first 20 h and then leveled-off according to the study of S. H. Lee. In that study, the present of LDI caused the specimens to achieve the plateau in the shorter time and at the lower water absorption. It is attributed to the improved interfacial adhesion between the polymer matrix and bamboo fiber filler.

PBS has a crystallization temperature Tc of about 68.1°C. In the composite of PBS, the Tc shifted to high temperature by adding either BF (bamboo fiber) or LDI (lysine-based diisocyanate), and further increases as LDI content increases. These higher Tc values of the composites than the pure polymers indicate that the crystallization rate of the composites becomes more rapid in non-isothermal processes. And it was also reported that the increase in Tc could be considered to be due to the nucleation effect of the BF and LDI [87].

Melting temperatures (Tm) of pure PBS is 112.1^{o}C, and this Tm was not significantly affected by the addition of either BF or LDI as it was indicated in the study. However, the heat of fusion (ΔH_f) in the composite was decreased by addition of BF and LDI. This may be also attributed to the strong interfacial interaction between polymer matrix and BF, confining polymer chain orientation [87].

The degradation of pure PBS in enzyme was slower than that of its composite, indicating that bamboo fiber improved the degradation of the polymer. Compared between the composites (with the different contents of fiber loading) with and without LDI, all composites with LDI were more difficult to be degraded than those without [87].

IV. Composites

On the basis of matrix phase, composites can be classified into metal matrix composites (MMCs), ceramic matrix composites (CMCs) and polymer matrix composites (PMCs). This classification is according to types of reinforcement such as particulate composites (composed of particles), fibrous composites (composed of fibers) and laminate composites (composed of laminates). Fibrous composites can be further sub-divided on the basis of natural / biofiber or synthetic fiber. Bio-fiber encompassing composites are referred to as biofiber composites. They can be again divided on the basis of matrix i.e. non-biodegradable matrix and biodegradable matrix.

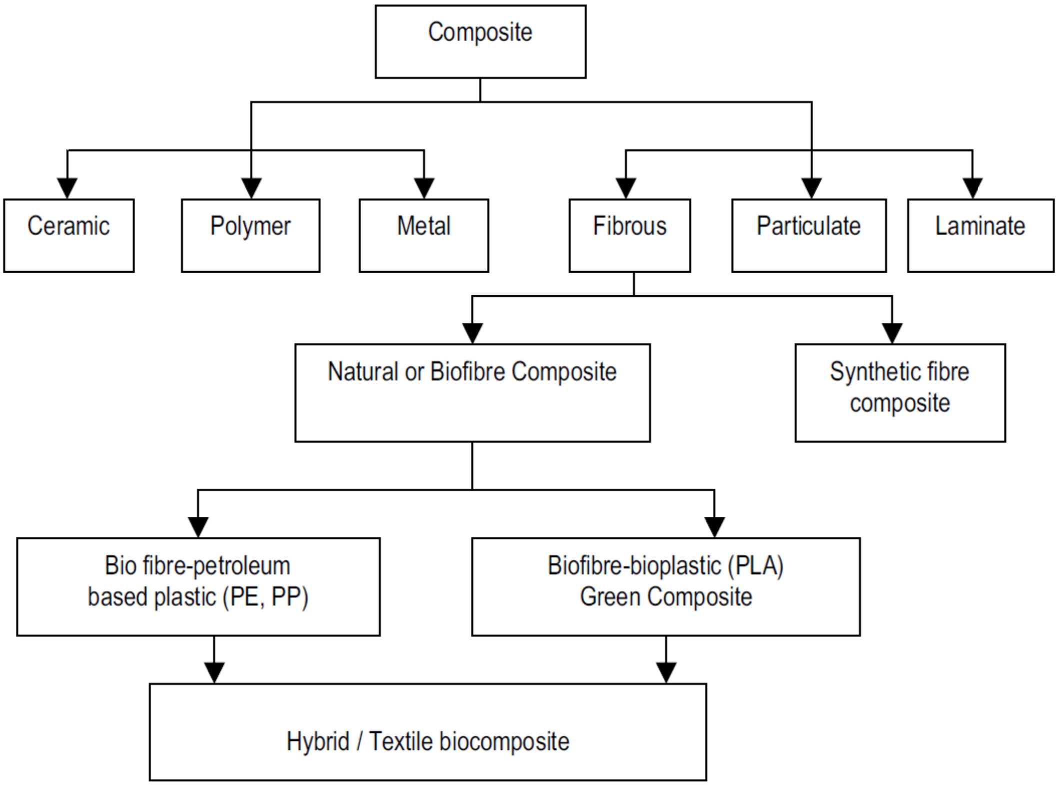


Figure 30: Scheme of classification of composites [62]

In this study, bamboo fibers is used as the reinforcement while polymer P34HB (P3HB-co-4HB) is employed as the matrix. After all, we also conducted the experiments with PBS as the matrix. Polymers are the most widely used matrix material for fiber composites and are used in more than 95% of the composite products in use today. Their chief advantages are low cost, easy processability, good chemical resistance and low specific gravity. On the other hand, low strength, low modulus and low operating temperatures limit their use [62]. This kind of composite is classified as Polymer matrix composites or more specifically, fiber reinforced composites.

V.Conclusions

In this chapter, the fiber and matrix were referred. Natural fibers are abundant and their cost is very low. Among natural fibers, bamboo fiber is one of the most popular. In this chapter, the compositions and structure of bamboo fiber were understood. Besides, it is important to modify the fiber to improve the adhesion with polymeric matrix. Therefore, the chemical and physical treatments were also referred. For the matrix, we took advantage of the bio-composites: P34HB (poly 3-hydroxybutyrate- co- 4 –hydroxybutyrate) and PBS (Polybutylene succinate). The general characteristics of these polymers were also described.

CHAPTER 2: Bamboo fiber

Chapter 2: Bamboo fiber

I.General information of bamboo fiber

Bamboo plants were cultivated in Hoa Binh, Vietnam and transferred to Hanoi University of Science and Technology, Ha Noi. There, the plants were cut and immersed in very dilute NaOH before the fibers were extracted by steam explosion. The ages of bamboo before being harvested are between 3 – 4 years.

Scientific name (Category of bamboo) : Dendrocalamus Membranaceus Munro

Place of growth: Hoa Binh – Vietnam

Composition:

The composition of bamboo fiber constitutes of cellulose (57.75%). Moreover, lignincompostion is nearly 26%, and lignin also contributes to antifungi, antibacterial properties.

Humidity: 8.5%

Cellulose: 57.75 %

Lignin 25.64 %

Compounds that dissolve in ethanol: 2.1 %

Ash 1.22 %

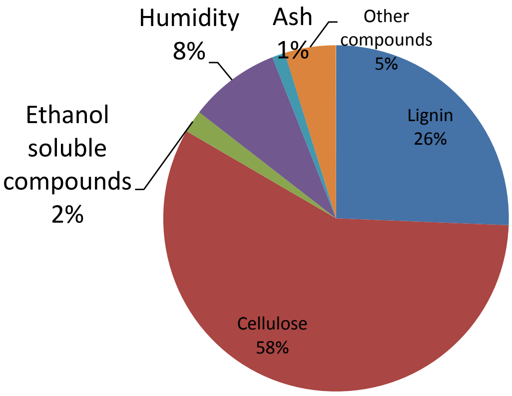


Figure 31: Composition of bamboo fiber

Figure 32: Bamboo fibers

Classify bamboo fibers by length

In this part, a number of bamboo fibers were taken in account to measure the length. Then the average fibers length will be understood. It is possible to use the sieve to classify the fibers in diameter.

The fibers' diameters (d) were classified into 4 sizes (the measurement was carried out over 300 fibers): The diameters were measured using a Zeiss Axio Scope.A1.

$d \leq 0.3$ mm : 70.83%

0.3 mm $< d \leq 0.5$ mm: 9.52%

0.5 mm $< d <$ 1 mm: 13.37%

$d \geq$ 1mm: 6.28%

The size of bamboo fibres in length (l):

$l < 5$ cm: 18.77%

5 cm $\leq l <$ 10 cm: 45.60 %

10 cm $\leq l \leq$ 15 cm: 19.92%

15 cm $< l \leq$ 20 cm: 8.24%

$l > 20$ cm: 7.47%

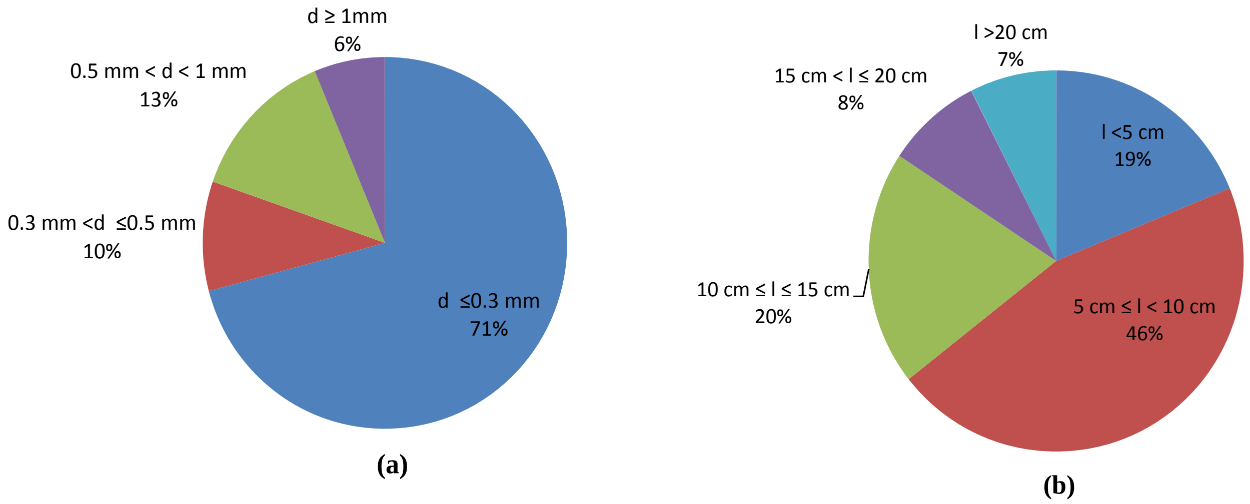


Figure 33: Diameter distribution (a) and length distribution (b) of bamboo fibers

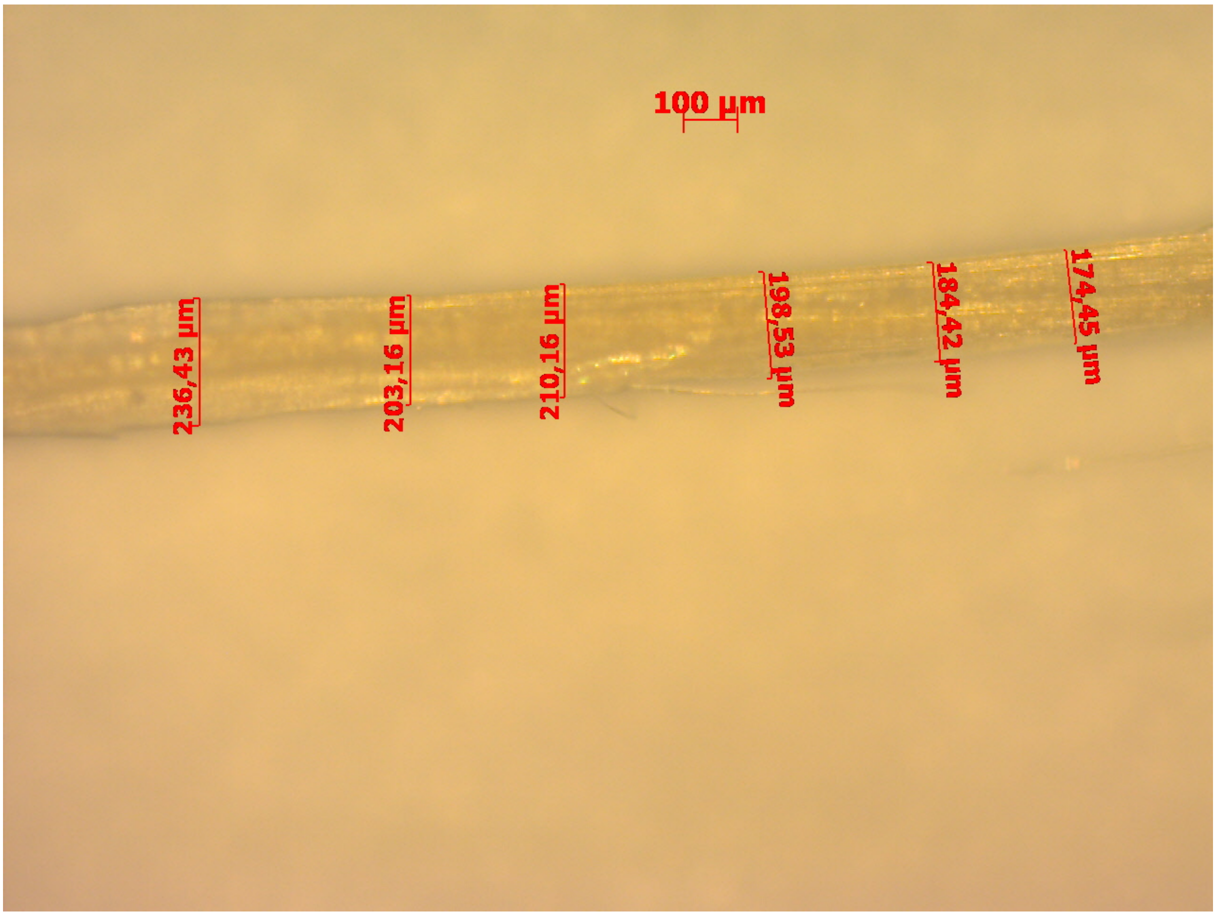


Figure 34: Bamboo fiber under optical microscope

II. Modification for bamboo fibers

II.1. Alkaline modification

The bamboo fibers were first modified with alkaline solution NaOH 0.1N for 3 days at room temperature. (Before this modification, the bamboo has already been soaked in NaOH 0.1N to extract the fibers). The bamboo fibers were then washed by distilled water until pH achieved 7.0. The treatment of fiber with NaOH improves its wetting ability, therefore reduces porosity and gives rise to composites with improved strength and water resistance. Alkali treatment is therefore recommended to precede any surface modification procedure on plant fibers. Alkali treatment leads to the increase in the amount of amorphous cellulose at the expense of crystalline cellulose. The important modification occurring here is the removal of hydrogen bonding in the network structure [63]. Alkali treatment also contributes greatly to the removal of lignin. With the same quantity of alkali treated fibers and untreated fibers are immersed in distilled water, the water used for the alkali treated fibers looks transparent while the other water shows the yellow colour because the untreated fibers contain lignin which provides yellow colour [23].

II.2. Acetylation modification

The modification process was conducted under different conditions: According to temperature (60, 70 and 80^{o}C) and according time (at 70^{o}C and duration time of 1, 2, 3 and 4 hours).

Pretreatment by alkali is needed since it helps to remove lignin, pectin, wax… which might prevent acetyl treatment. Moreover, partly of OH group is replaced by ONa which is easier to take part in acetyl reaction.

Acetyl group is expected to swell the fiber cells and make the fibers significantly decrease water absorption. Obviously, the acetylation process is affected by the experimental condition such as temperature, the ratio of two reagents (acid acetic and anhydride acetic) and the duration of the process. The below results reveals that the acetylation at 70°C in 3 hours is much better in comparison with the condition at 60^{o}C during 2 hours.

In this method, the fibers were immersed in the reagent of acetic acid and anhydride acetic (50/50 by volume). And before the immersion, the fibers were pretreated by alkali treatment and then they were dried at 70^{o}C for 12 hours until the constant mass was achieved. During the mercerization process in the reagent, the bamboo fibers were well stirred.

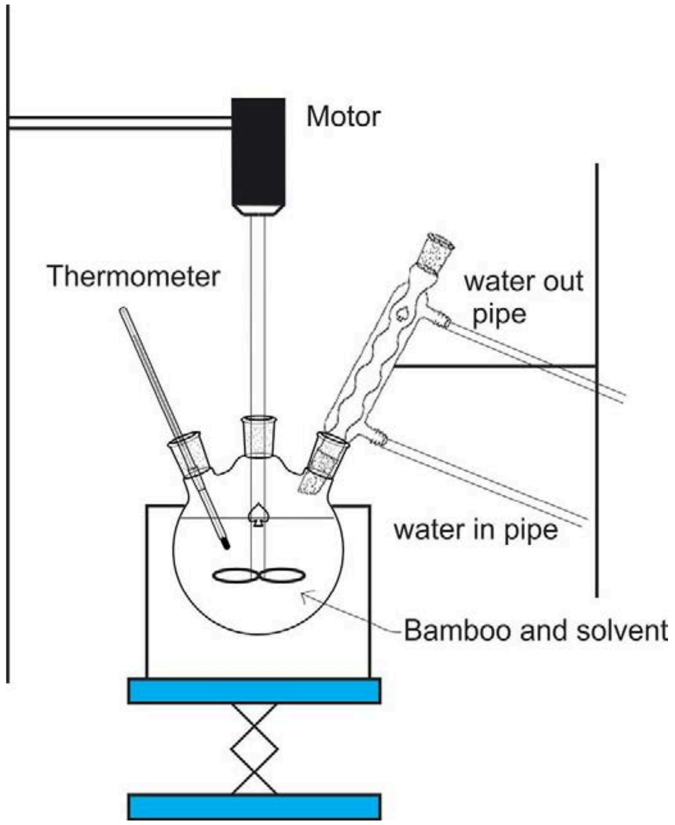


Figure 35: Acetylation process

Acetylation process: For acetylation process, a mixed reagent of anhydride acetic and acid acetic (50/50 by volume) were used. For example, 120ml acetic acid was firstly prepared in the 3 neck round flask and then 4.9 gram of bamboo fibers were placed in that 3 neck round flask until the bamboo fibers were completely soaked in the solution; and finally the same quantity of anhydride acetic was poured. It required 240 ml of mixture reagent with 3 droplets of acid sulfuric as a catalyst. This modification was carried out at 70^{o}C, the solution and bamboo was mixed using the anchor with the speed of 55 rpm in 3 hours. The fibers were finally washed by distilled water until the indicator agent showed the pH of 7.0

II.2.1. Changes in fiber mass

This parameter is important because it provides information about the conversion of the modification.

For example, in the first experiment at 60^{o}C in 2 hours, 4.7000 gram bamboo fiber (treated by NaOH 0,1N) was used for acetylation treatment. The obtained bamboo fibers showed the mass of 4.8062 gram. The weight gain was recorded: (4.8062-4.7)/4.7 x100% =2.26 %

Another experiment was conducted at 70°C in 2 hours. In the experiment, 4.8200 gram of bamboo fibers (treated by NaOH 0,1N) was used for acetylation treatment. The obtained bamboo fibers exhibited the mass of 5.3745 gram. The weight gain recorded was: (5.3745-4.8200)/4.82 x100% =11.50 %.

Here shows the result of percentage of weight gain for each experiment:

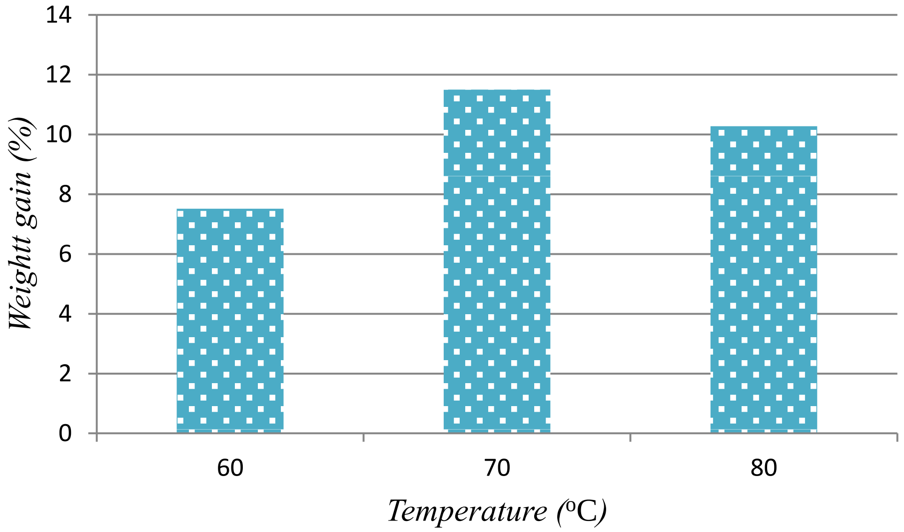


Figure 36: Depend of the weight gain on experimental temperature

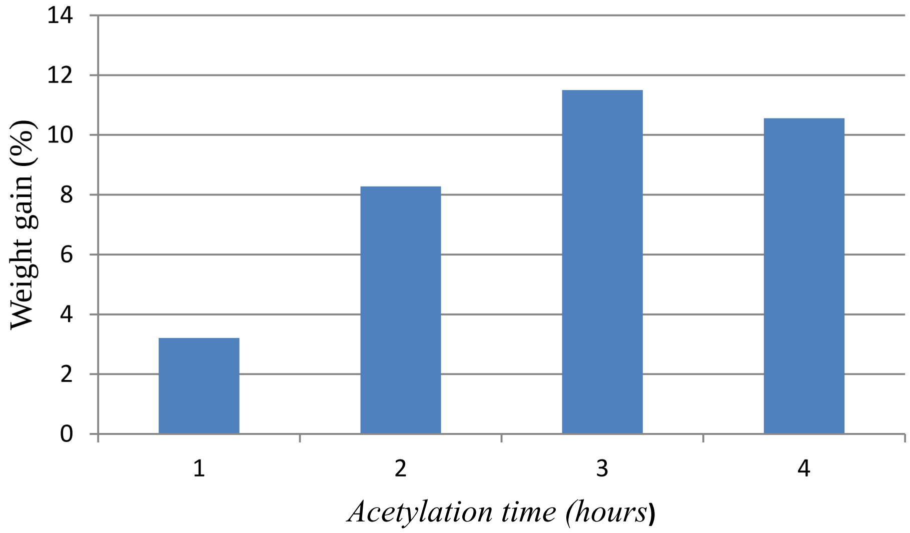


Figure 37: Depend of the weight gain on experimental duration time at 70°C

As it can be seen in Figure 36 and 37, acetylation at 70^{o}C during 3 hours showed the highest value of weight gain. Normally, when the temperature or time increases, it will activate the reaction and more acetyl groups are replaced. Here, the temperature at 80^{o}C may not show the difference in comparison with 70^{o}C since 70^{o}C is nearly optimum temperature and 3 hours is long enough to trigger the reaction. Moreover, the reaction also depends on the individual fibers and the contact between fibers and solvent. The fibers from different parts of the same plant (top of the tree, the middle and the bottom of the tree) or in the different layers (primary, secondary layer,…) may have different properties. It might be that at high temperature and long duration of reaction, more small particles of fibers will be separated, these particles can be dissolved in the reagent or they could not be kept after the filter of process, causing the decrease in weight.

Therefore, the condition at 70^{o}C in 3 hours is thought to be an appropriate condition for acetylation experiment.

II.2.2.FTIR results of fibers modified with acetylation method

FTIR (Fourier Transform Infrared Spectroscopy) experiments were performed on FTIR- 8400 S, Shimadzu, the wavenumber ranged from 600 cm^{-1} to 4000 cm^{-1}, and 150 scans were taken per measurement. FTIR analysis was conducted to confirm the effect of modification methods to the fibers.

Normally, the acetylated bamboo fibers must have those main groups: carbonyl C=O stretching vibration at 1755cm^{-1} (C=O), the methyl in-plane bending in –O(CO)–CH_3 at 1372cm^{-1} (C–H), and the C–O stretching of acetyl group at 1237cm^{-1} (C–O).

Table 16: FTIR results for plant fibers

Wavelengths (cm^{-1})	**Groups**	**References**
1022, 1050	C-H and C-O	[30,31,32,33]
1158	C-O-C	[31]
1237,1247	C-O	[30,31]
1322, 1372	C-H	[30,31]
1755,1750,1726	C=O	[30,31,32]
2887	C-H (methyl, methylene)	[31]
3324	OH	[31]

Claudia Merlini et al. investigated the IR spectra of banana fibers. And here shows their result [31]:

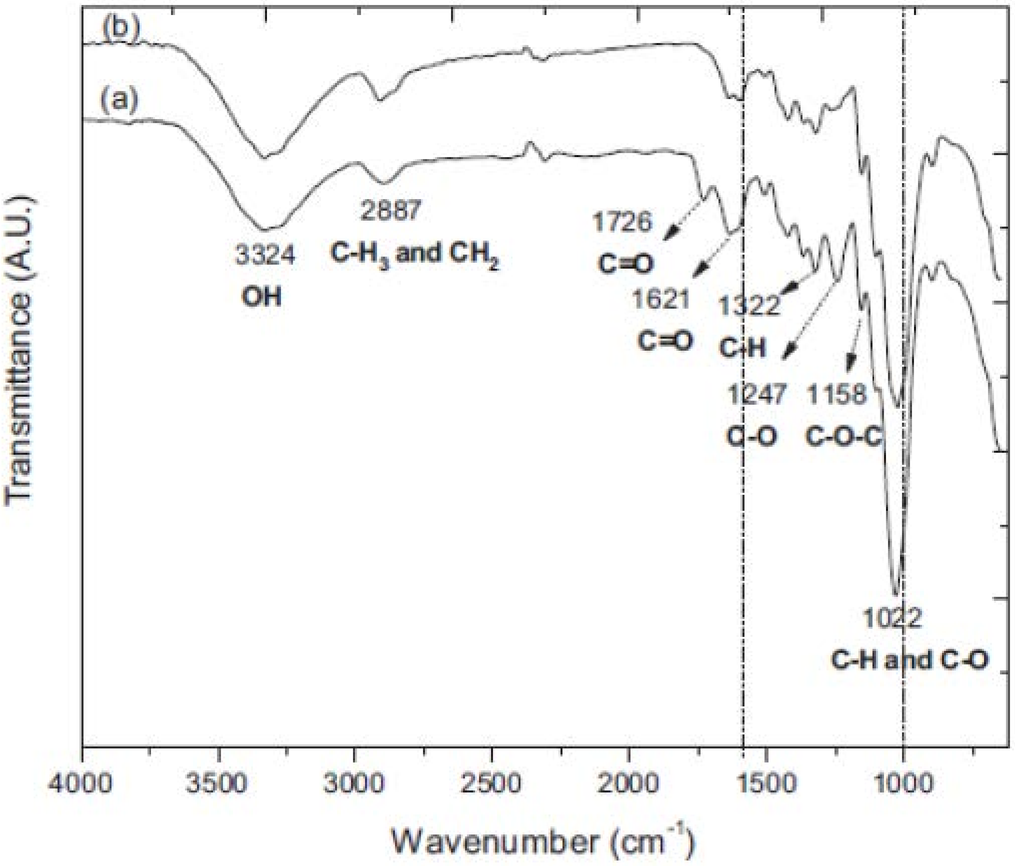


Figure 38: ATR-FTIR spectrum of banana fibers
(a) untreated and (b) treated for 1 h (by alkaline solution2.5 Mol/l) [31]

In Fig.38, a broad and strong band at 3324 cm^{-1} was assigned to the vibration stretching of the hydroxyl group. The absorption band at 2887 cm^{-1} can be attributed to C–H stretching of the methyl and methylene groups. The bands at 1726 and 1621 cm^{-1} which can be ascribed to vibrational stretching of unconjugated C=O groups, mainly due to hemicelluloses and to conjugated carbonyl present in the lignin, respectively. After alkaline treatment, the band at 1726 cm^{-1} was found to be almost absent in the treated fiber spectrum. In addition, the absorption intensity at 1247 cm^{-1} attributed to C–O stretching of acetyl groups in the hemicelluloses decreased with alkaline treatment. These results suggest a reduction in the hemicellulose and lignin content following alkaline treatment of the fibers [31].

In this study, firstly we investigated the influence of temperature on acetylated bamboo. The bamboo fibers were modified at 60, 70 and 80°C during 3 hours. The spectra show that at 70, 80^{o}C the –OH groups gradually disappear. This indicates that –OH was replaced more when the temperature grew. And the acetylated modification exhibited a good effect at 70^{o}C.

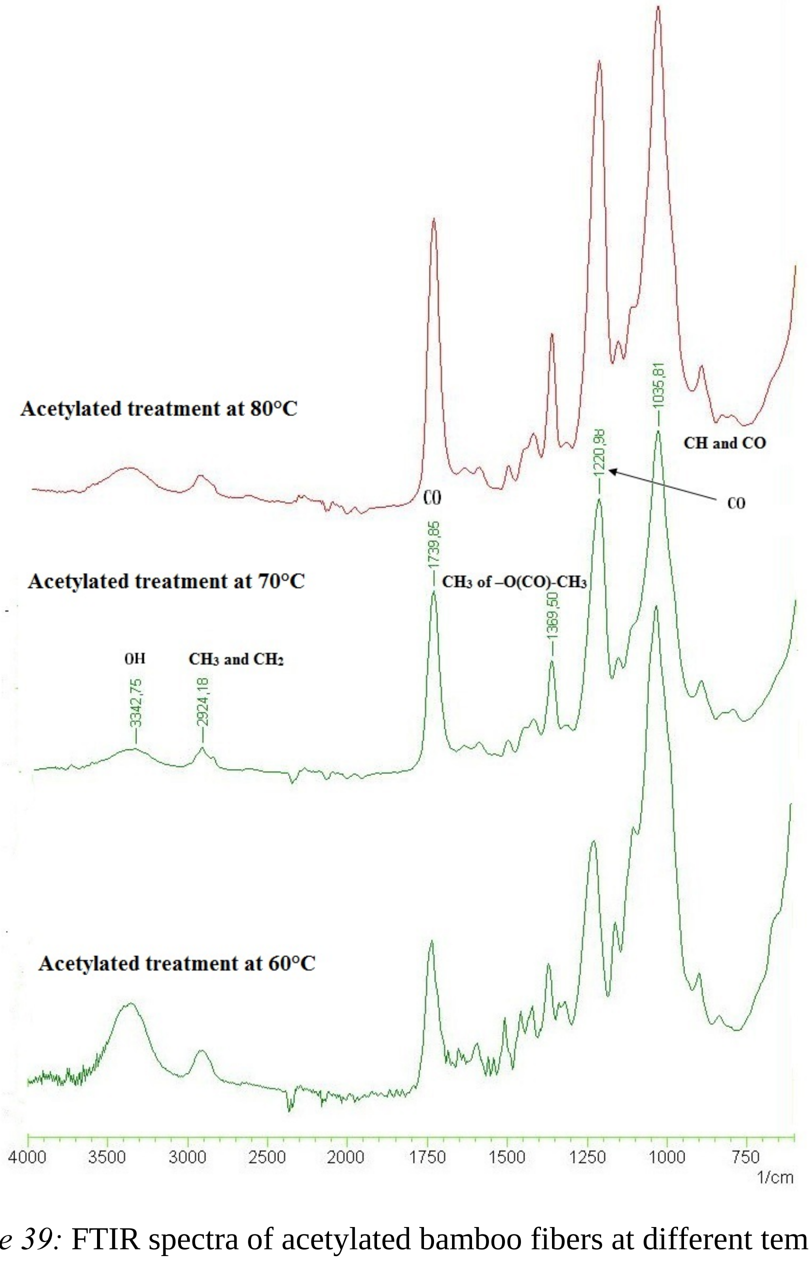


Figure 39: FTIR spectra of acetylated bamboo fibers at different temperatures

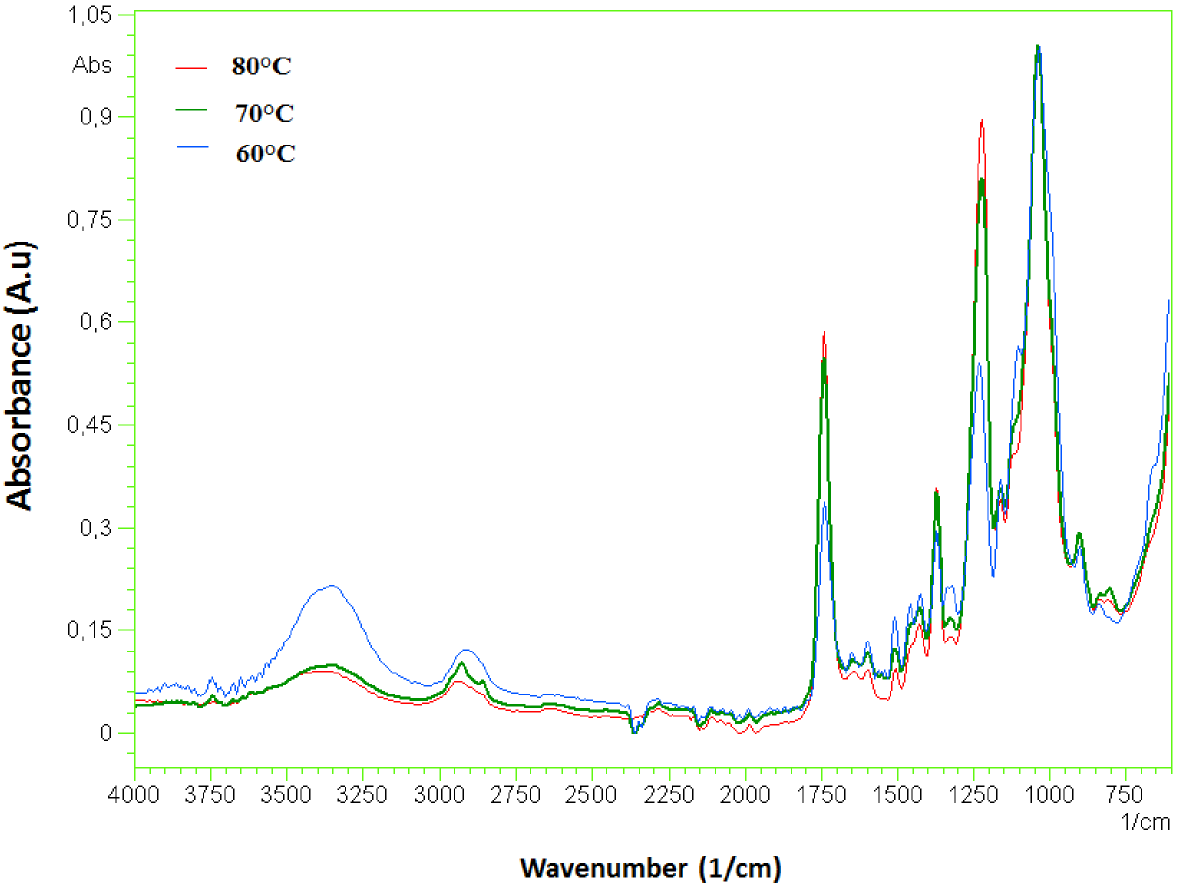


Figure 40: FTIR spectra (normalization) of acetylated bamboo fibers at different temperatures

The normalization is applied to understand the effect of acetylation treatment. The spectra obtained at 70°C and 80°C are quite similar while the lower peaks can be seen at 60°C. It suggests that the conversion is much better at 70°C and 80°C and 70°C is sufficient for the treatment. Based on this result, we chose 70^{o}C as the experimental temperature. The second step, we investigated the effect of experimental time on the modification.

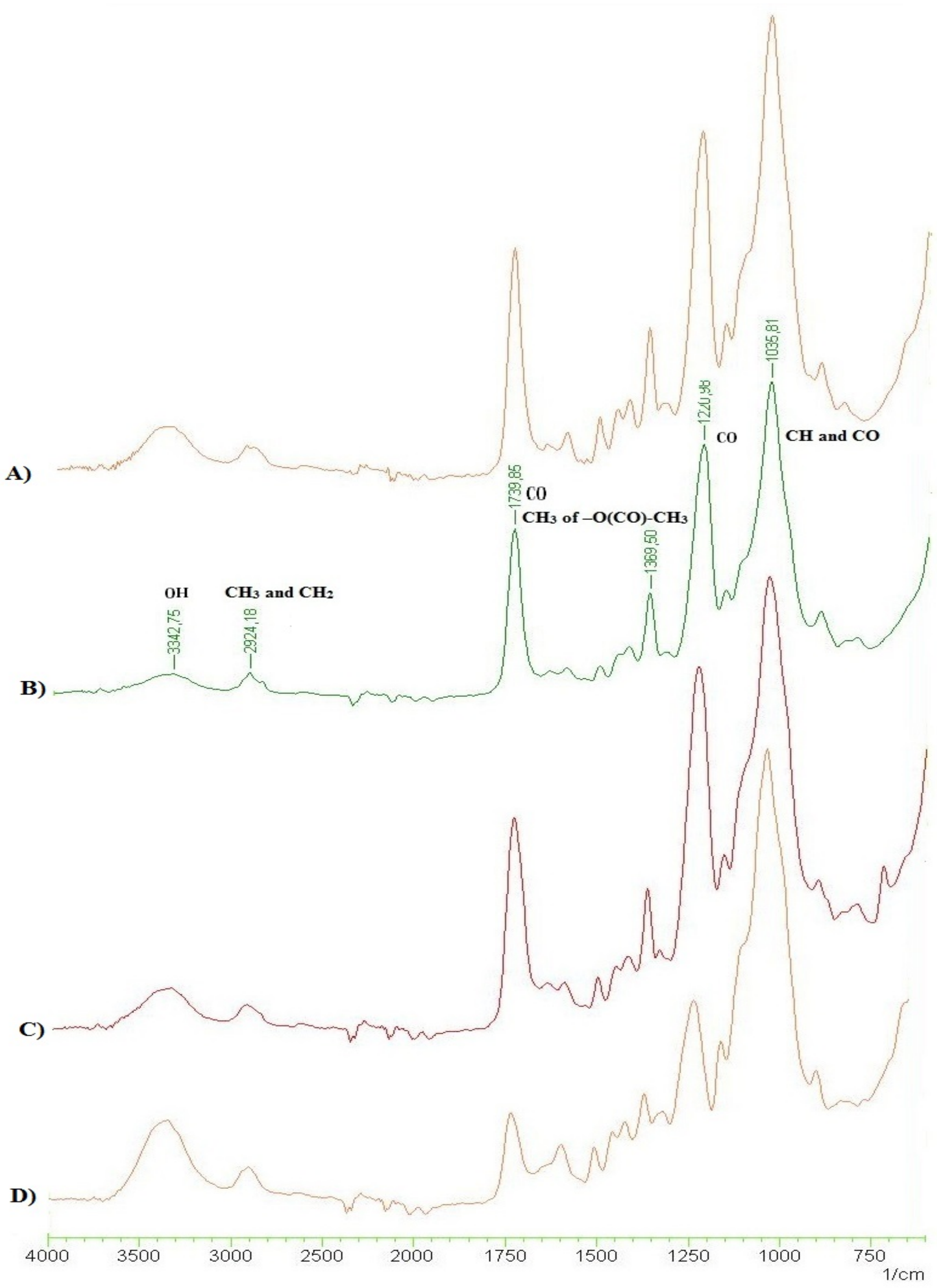


Figure 41: FTIR spectra of acetylated bamboo fibers at different duration times

A) Acetylated treatment in 4 hours; B) Acetylated treatment in 3hours;
C) Acetylated treatment in 2 hours; D) Acetylated treatment in 1 hour

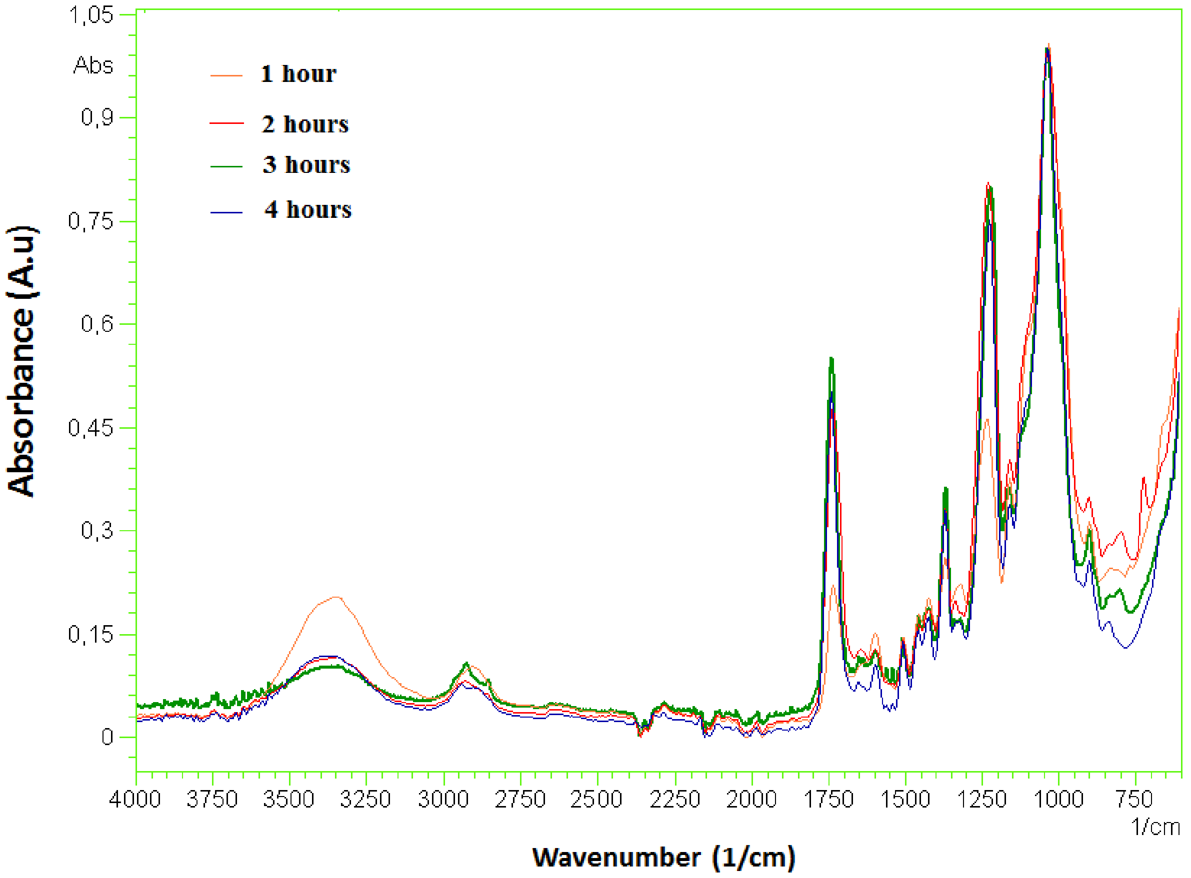


Figure 42: FTIR spectra (normalization) of acetylated bamboo fibers at different duration times

As can be seen, after 1 hour, the –OH still does not react as much as that of 2, 3 and 4 hours. After 3 hours, the acetylation shows the good effect. Hence, it is probably reasonable to carry out the acetylated experiment in 3 hours. We chose 3 hours since it is the sufficient time to keep the treatment stable.

Also, a comparison of the 3 spectra was made to demonstrate the effect of acetylated treatment:

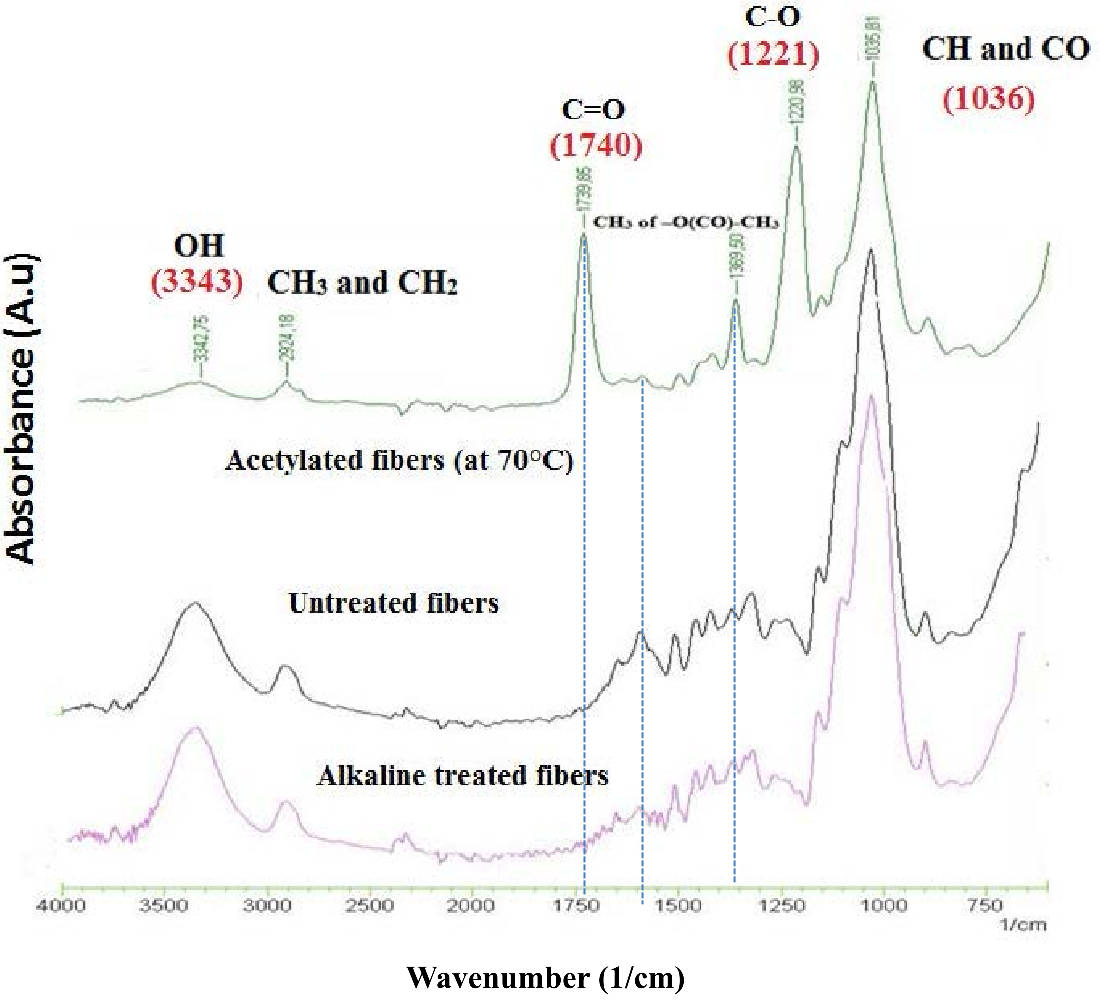


Figure 43: Effect of acetylated modification

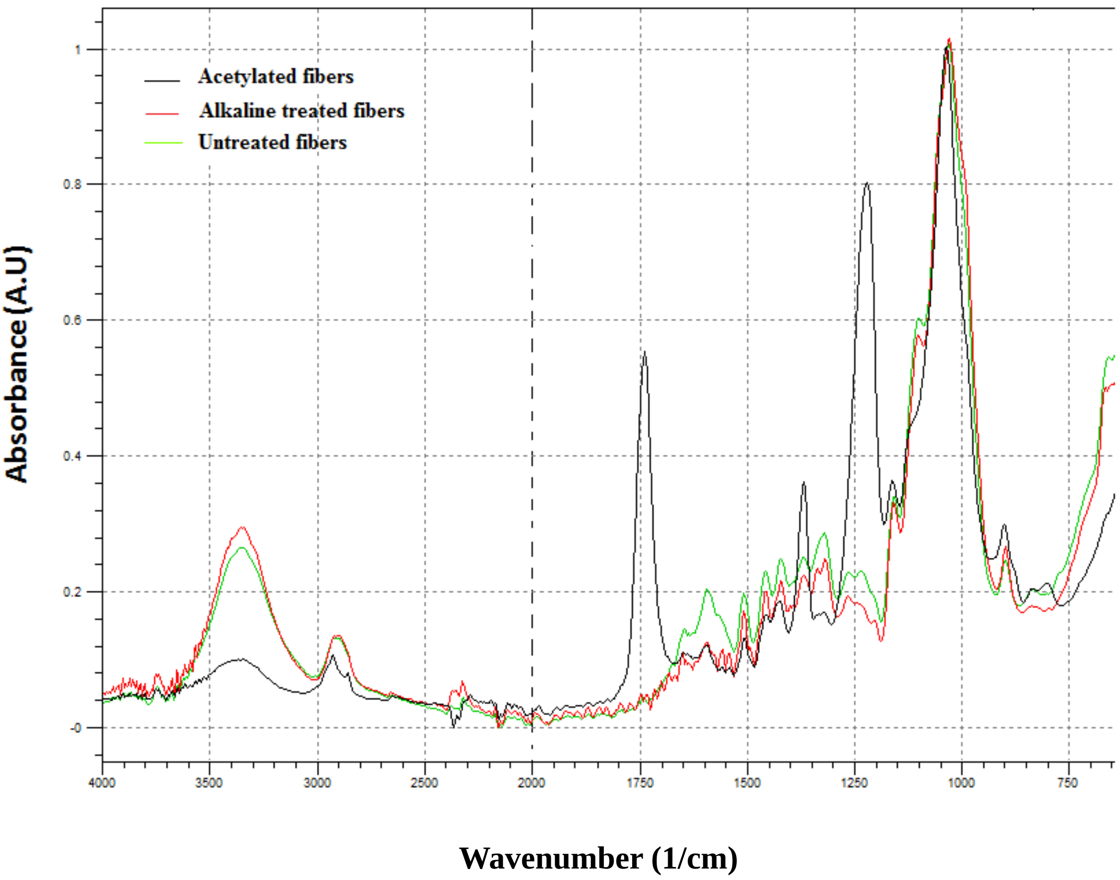


Figure 44: Effect of acetylated modification (normalization)

Obviously, the –OH group gradually disappear since it reacts and it is replaced by acetyl group. Also, the 3 typical groups which appear on the figure prove that the acetylation process was successful. For example, the appearance of C=O (at 1740 cm^{-1}), C-O (at 1221 cm^{-1}), CH_3 (at 1370 cm^{-1}) or the decrease in the height of the OH peak confirm the success of acetylation treatment. The peak at 1600 cm^{-1} wavenumber is attributed to the conjugated carbonyl present in the lignin. At this wavenumber, the peak of untreated bamboo fibers is much higher than that of fibers obtained from alkaline treatment or acetylation treatment because lignin was partly removed after the treatments.

II.2.3. Degree of acetylation

In a glass Erlenmeyer flask, 100 mg of sample was suspended in 40 mL of 75% ethanol 99.8% and 25% distilled water by volume. The flask, loosely stoppered, was heated to 50 – 60° C in a water bath for 30 min for better swelling of the material. Then, 40 mL of 0.5 N NaOH solution was poured to the sample flask (loosely stoppered), and the mixture was heated to 50 – 60°C in a water bath for 15 min. The flask was stoppered tightly and allowed to stand at room temperature for 72 hours. Blank flasks were also prepared according to the same procedure, with the exception that no sample was added to the blank flasks [32, 33, 34, 35].

The excess alkali (the volume which was not used to saponify the acetyl groups) was then titrated with 0.5N HCl using phenolphthalein as an indicator. At the endpoint, 1 mL excess 0.5N HCl solution was added, and any remaining NaOH was allowed to diffuse from the fibers overnight. Any excess HCl was then titrated with 0.5 N NaOH solution using phenolphthalein as an indicator. The mixture was vigorously shaken to ensure all excess HCl was consumed, which was indicated by a persistent faint pink endpoint.

Percentage of acetylation is determined on the whole fibril fraction, not just for the surfaces. Also, the calculation is on a mass basis and can be defined as the ratio of acetyl group mass to the mass of the entire sample as the equation below:

$$\%\ \text{Acetyl} = \frac{mass\ of\ acetyl\ ester}{mass\ of\ sample} x100$$

It is important to calculate the level of substitution that the molar mass of the actual substitute group be used. For acetylation, the substitute group is the acetyl ester (containing 2 carbon atoms, 3 hydrogen atoms, and 1 oxygen atom), hence, its molar mass is equivalent to 43.05 grams. Thus, the mass of the acetyl ester can be found using Equation below:

Mol number of $COCH_3$ = Mol number of reacted NaOH = the difference between mol number of HCl used for blank and NaOH reagent in titration experiments = (V_{HCl} x N_{HCl})/1000 ml = (D-C) N_{HCl} /1000 ml

- ⇨ Acetyl mass/ Molecule mass = Acetyl mass /43.05 = (D-C) N_{HCl}/1000
- ⇨ Mass acetyl = (D-C) N_{HCl} 0.04305 /1000
- ⇨ % acetyl = ((D-C) N_{HCl} 0.04305 / mass of bamboo used for titration) x 10
  = ((D-C)N_{HCl} x 4.305)/ mass of bamboo used for titration

Where *C* = HCl solution required for titration of sample, mL
D = HCl solution required for titration of blank, mL

$$\%\ \text{Acetyl} = \frac{mass\ of\ acetyl\ ester}{mass\ of\ sample} x100$$

Degree of substitution (DS) was calculated as reported in the work of D.L. Philips et al . [44]

$$\%\ \text{DS} = \frac{162.acetyl\ \%}{4300-(42.acetyl\%)}$$

Or

$$\% \text{ Acetyl} = \frac{43.DS}{162+42.DS} x100$$

where,
mass of acetyl ester = 43 grams
number of acetyl esters per anhydrous glucose = DS (degree of substitution)
mass of anhydrous glucose unit = 162 grams
additional mass from esterification with acetate = 42 grams [32, 35]

The first experiments were conducted with fibers which are modified in 3 conditions (in 3 hours at 3 different temperatures 60, 70 and 80^{o}C respectively). The results were similar to what can be observed from FTIR spectra and the condition for experiment at 70°C in 3 hours is confirmed to be the optimum one.

Table 17: Acetylation results (for bamboo treated in 3 different temperatures) (my result)

Temperature (^{o}C)	**Duration time (hours)**	**% Acetyl (%)**	**DS**
60	3	14.96	0.66
70	1	9.65	0.40
	2	16.06	0.72
	3	18.68	0.86
	4	17.88	0.81
80	3	17.97	0.82

Table 18: Acetylation results

Type of fibres	**% Acetyl (%)**	**DS**	Quote
Bamboo (70^{o}C)	18.68	0.86	This study
Banana fibres (>50% cellulose)	14.25	0.69	[32]
Bacterial cellulose (70^{o}C in 1 hour)		0.87	[30]
Bacterial cellulose (Annealed at 200^{o}C)		0.37; 1.44	[33]
Cellulose nanofiber		0.2	[36]

II.2.4.Thermal property

In this study, experiments were carried out on machine NETZSCH, TG 209F3 at the starting temperature of 24°C to 600°C, the heating rate was 10°C/min in the inert nitrogen environment.

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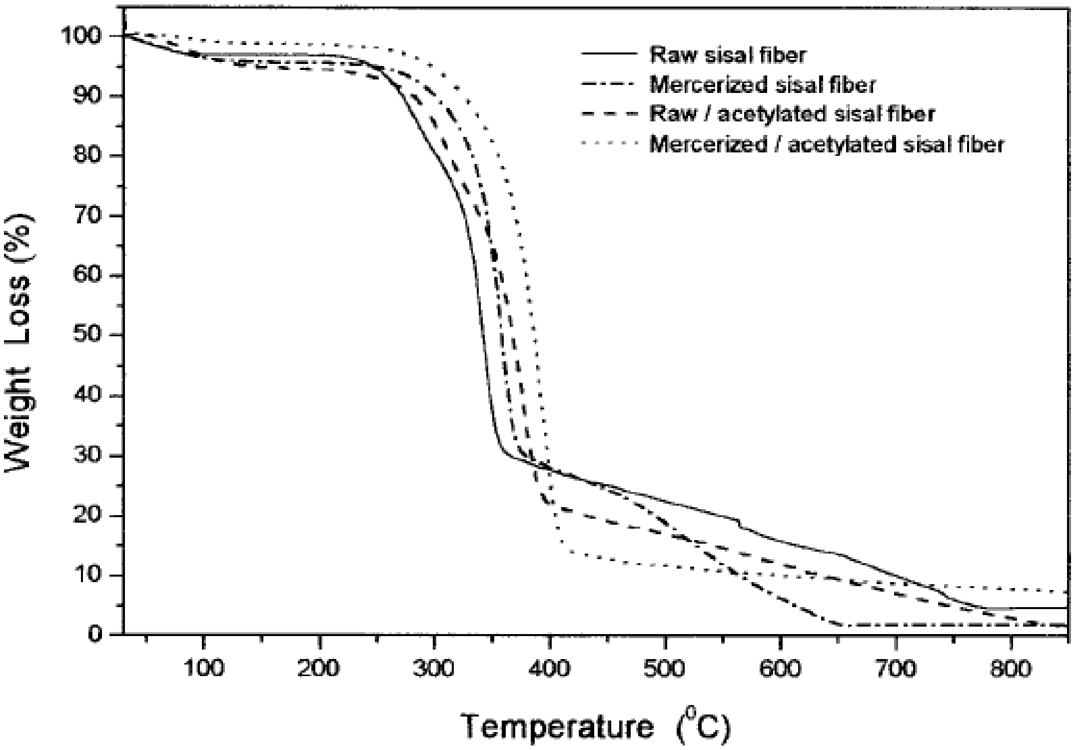


Figure 45: Thermogravimetric analysis (TGA) of raw and treated sisal fibers [39].

Temperature range: 25–800°C, 3 °C/min, argon atmosphere and duplicate results are coincident [39].

As for M. A. Martins [39], as it is showed in figure 45, the first decomposition peak at about 280°C is attributed to thermal depolymerization of hemicelluloses and the glycosidic linkages of cellulose; the second decomposition peak at about 340°C is attributed to -cellulose decomposition (weight loss 70%); the small peak at 570°C may be attributed to oxidative degradation of the charred residue.

The thermogram shows an improvement in the thermal stability of the modified fibers in relation to the raw fiber. The main decomposition temperature increases from 340°C (raw) to 350°C for the mercerized fibers and to 395°C for the mercerized/acetylated fibers.

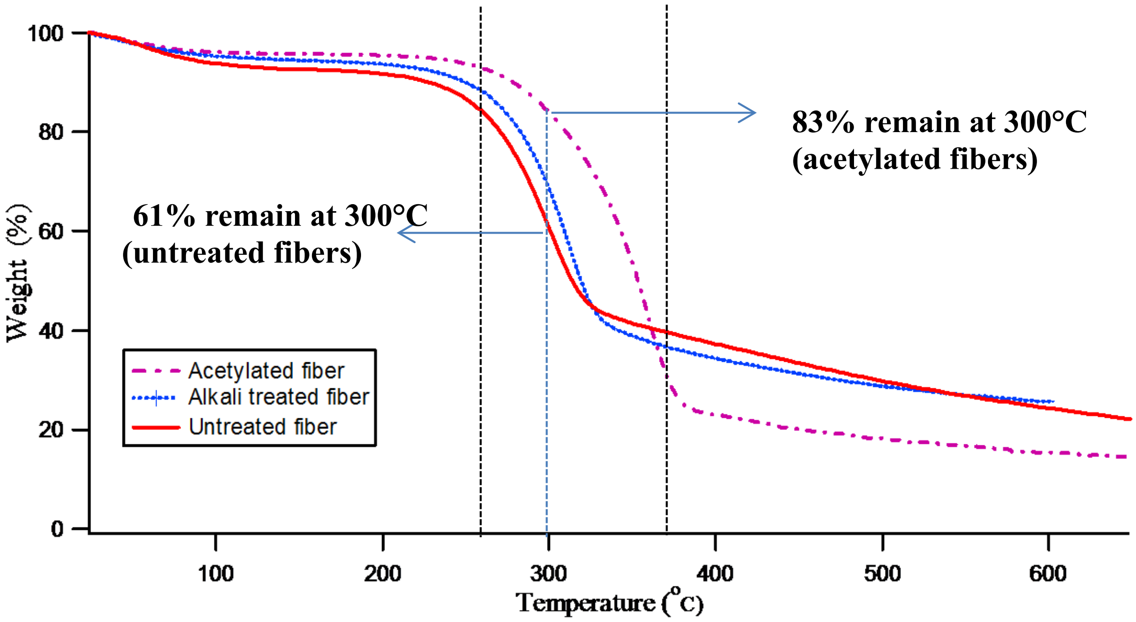


Figure 46: Behavior of bamboo fiber under temperature

Similarly, in our study, the results reveal that there are 3 periods of degradation. In the first period (to approximately 280°C), the low molecules and volatile compounds evaporate quickly when the temperature is raised. The second period is attributed to the thermal polymerization of hemicelluloses and the glycosidic linkages of cellulose and the last period is caused by the cellulose degradation. In the first period, untreated fibers and alkali treated fibers show the loose of weight, from 100% weight remain to approximate 80% and 75%, (by 20 and 25%) respectively while the remain weight of acetylated fiber is 90% at the temperature around 280°C. The untreated fibers show the most tremendous decrease due to the significant accumulated moisture in the fiber. Also, in the beginning process, the weight loss of untreated fiber is more significant than acetylated fiber indicating that acetylated treatment (following the alkali treatment) removed a part of the adsorbed molecules like fats and waxes, pectins [109, 110]. In the second period of degradation, the weight remain of untreated fibers is still less than the treated ones. For example, at 300°C, 61% weight remain is recorded for untreated fibers while it is 83% weight remain for acetylated fibers. In the last period of degradation, the acetylated fibers degrade more than the untreated fibers because in this period, not only cellulose degrades. For example, the acetylated bamboo fibers exhibited that they degraded more at the temperature higher than 380°C. This clearly indicates that the acetylated bamboo fiber showed relatively lower thermal stability as compared to the raw fiber. The plausible reason could be that the disintegration of intermolecular interactions such as hydrogen bonds between polymer molecules during acetylation [32].

II.3.Silane treatment

Firstly, the fibers were modified with alkali and followed by silane treatment. We expected that the mechanical strength of the fibers could be improved, and the hydrophobic properties would be better due to the better compatibility between fibers and matrix. The silane used for the modification is 3-aminopropyltrimethoxysilane (APS), during the treatment, the hydrolysis was induced. The treatment was conducted as following [62]:

The time for hydrolysis is 2 hours at room temperature with the presence of acetic acid to maintain pH =4. After that, the fibers were immersed for another 3 hours and were washed by distilled water until pH=7. Finally, the fibers were kept in the air before moving to the oven and dried for 12 hours at 80°C.

Then, the grafting process will be induced.

II.3.1. FTIR result

Similarly to acetylated method, FTIR was performed to investigate the effect of the treatment, using FTIR- 8400 S, Shimadzu, the wavenumber ranged from 600 cm^{-1} to 4000 cm^{-1}, and 150 scans were taken per measurement. The stretching vibrations of some main groups are summarized in table 19.

Table 19: Summary of vibration modes [74]

Wavenumber (cm^{-1})	**Group**	**Source**
3356 – 3349	O-H	Polysaccharide
2930-2923	C-H	Polysaccharide
2868	CH_2	Wax
1742	C=O (ester)	Hemicellulose
1630	OH	Water
1514	C=C	Lignin
1432	CH_2, C=C	Pectine,lignin, hemicellulose
1370	CH_2	Polysaccharide
1335	C-O	Cellulose
1252	C-O	Lignin
1162	C-O-C	
895	Glycoside	Polysaccharide
841 and 768	-Si-O-Si	Silane
670	C-OH	Cellulose

Since the amino group of silane and Si-O-Si group exhibits the peaks overlap with that of fibers, it is difficult to observe silane peak on the spectra of fibers modified with silane [74].

Deák et al. also used silane for fiber modification [67], their FTIR results showed that the presence of coupling agent on the surface of basalt with the wavenumber range between 2700 and 3100 cm^{-1}. The figure is shown below (in their study GF80 is 3-Glycidoxypropyltrimethoxysilane) [67].

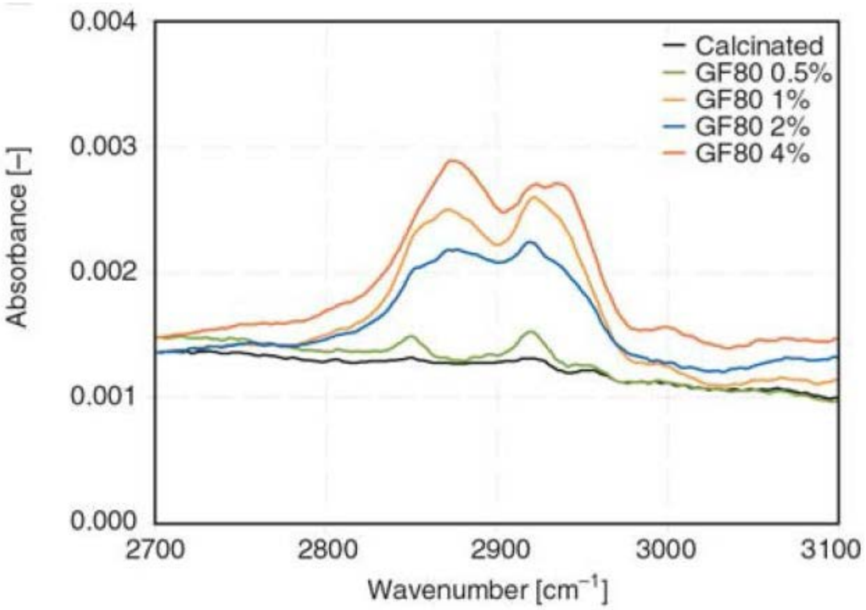
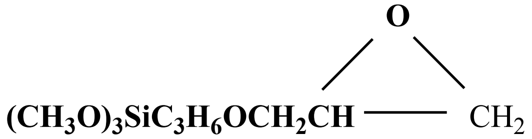


Figure 47: FTIR absorbance spectrum of basalt fibers sized with GF80 silane with different concentrations in the wavenumber range between 2700 and 3100 cm^{-1} [67]

In Figure 47, the “calcinated” legend refers to the basalt fiber which were untreated, and the peaks at 2850 and 2925 cm^{-1} were in connection with C-H bonding in aliphatic carbon chain and no distinct peaks could be seen on the curves of calcinated fiber.



$$(CH_3O)_3SiC_3H_6OCH_2CH \overset{O}{\text{———}} CH_2$$

Figure 48: Structure of GF 80

In that study, the fibers were modified as the process mentioned above. The structure of 3-aminopropyltrimethoxysilane is as follow:

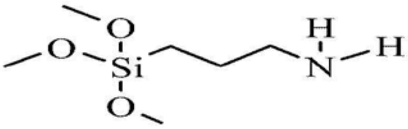


Figure 49: Structure of 3-aminopropyltrimethoxysilane

In our study, 10% to the fibers (by weight) of silane was used. The hydrolysis in ethanol/ distilled water (60/40 by weight) was conducted for 2 hours in the presence of acetic acid as the catalyst. Acetic acid was dropped into the mixture until pH=4. Here below shows the FTIR results (the fibers treated with silane was previously treated with NaOH solution).

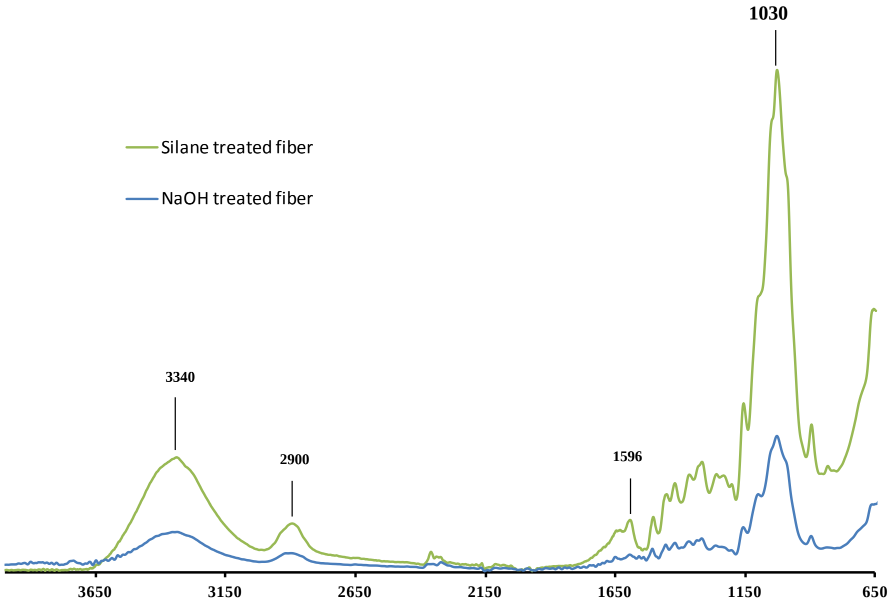


Figure 50: FTIR spectra for bamboo fibers: Silane treated fiber and alkaline treated fiber

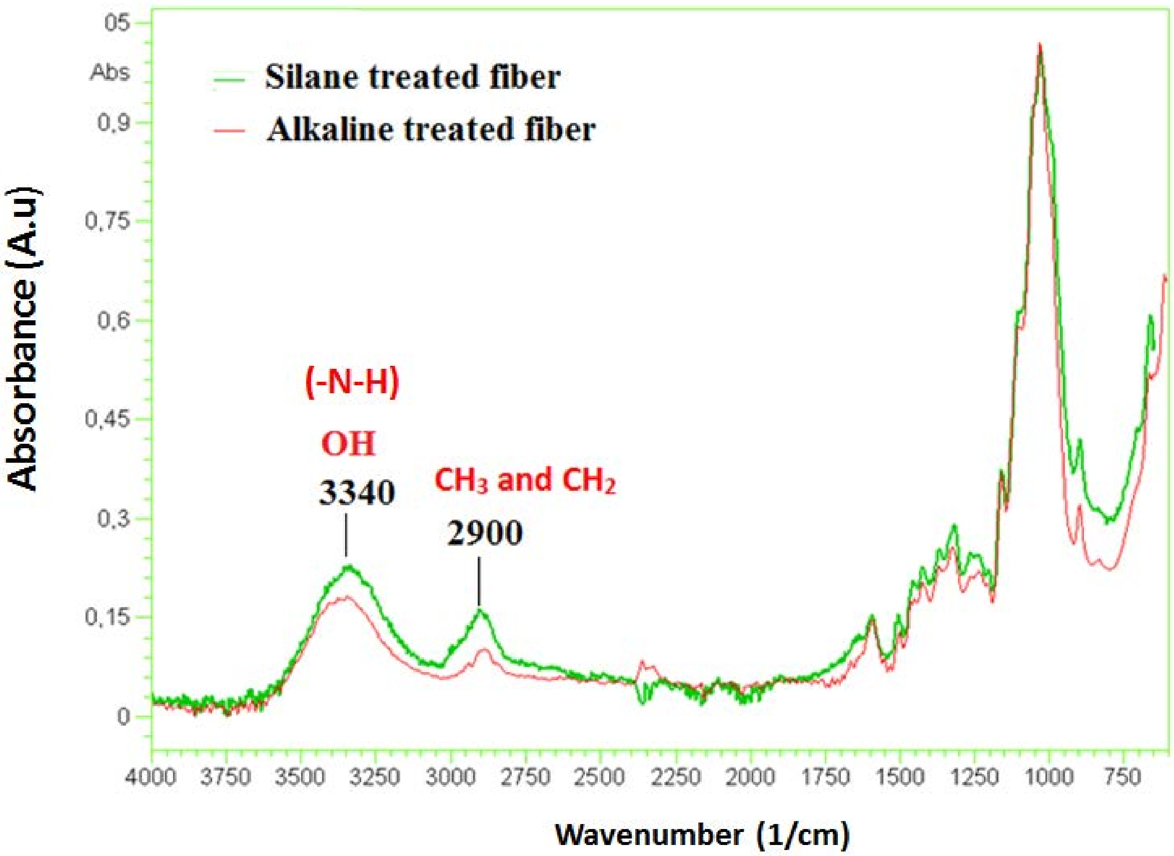


Figure 51: FTIR spectra (normalization) for bamboo fibers: Silane treated fiber and alkaline treated fiber

For silane treated fibers, it is difficult to observe because the functional groups of Siloxane show the similar FTIR peaks with those of the groups in some compositions of bamboo fiber. For example, amine group has the peak of around 1596 cm^{-1} wavelength; and 750-850 cm^{-1} is the area of –O-Si-O-. Those peaks are overlap with the groups CH and CO of fibers; more over they all have CH group. In Figure 51, a broad absorption band around 3340 cm^{-1}, characteristic of hydrogen bonded O–H stretching vibration, is observed in the spectra of all samples. After the surface treatment with silane, this absorption band was broadened. It is attributed to an overlapping of absorptions of the O–H stretching vibration and amino group N–H stretching vibration. It also indicates that the coupling agent has bonded to the fiber surface. The peak at 2900 cm^{-1} belongs to the –CH_3 stretching vibration of cellulose and silane [65, 67, 75].

II.3.2. TGA result

Thermal property of bamboo fiber modified by silane

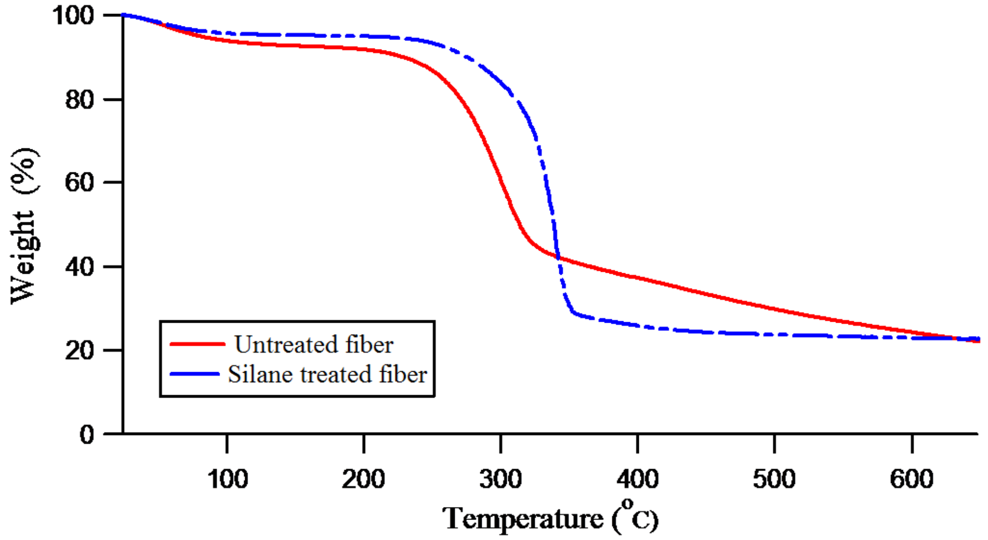


Figure 52: Behavior of silane treated fiber under temperature

Similarly, a TGA experiment was conducted to investigate thermal degradation of silane treated fiber. There are also three periods of degradation (as referred above) for silane treated fibers. At low temperature (lower than 340°C, the first and second period)) the silane treated fiber degraded less than untreated bamboo fibers. Because this range of temperature corresponds to the thermal degradation of pectins and hemicelluloses and these compositions were removed from silane treated fibers due to the ethanol/water extraction [110]. The partly removal of hemicelluloses and pectins, thus, increased the percentage of cellulose and it is attributed to the tremendous weight loss of silane treated fibers compared with untreated fibers at high temperature [110]. Also, the plausible reason for the more significant of silane treated fibers compared to the untreated ones in the third period of degradation might be due the disintegration of intermolecular interactions such as hydrogen bonds between polymer molecules caused by silane treatment.

Probably, it is difficult to determine the effect of silane treatment via FTIR method, however, the TGA behavior clearly showed the difference between untreated fibers and treated fibers.

II.4. Modification of fiber by acetylation followed by silane treatment

In an attempt to improve the adhesion between the fibers and matrix, we developed a modification method that combines acetylation treatment and silane treatment. It is expected that the combination will make the most of the advantage of each separate method. In this method, firstly the fibers were treated by alkali. After that, the fibers were treated with acetic acid and anhydride acetic as presented above. And finally the fibers would be modified by silane treatment.

III. Characterization and comparison of fiber properties

III.1. Thermal property of bamboo fibers by TGA analysis

Thermal properties of bamboo fiber under TGA (Thermogravimetric Analysis) method

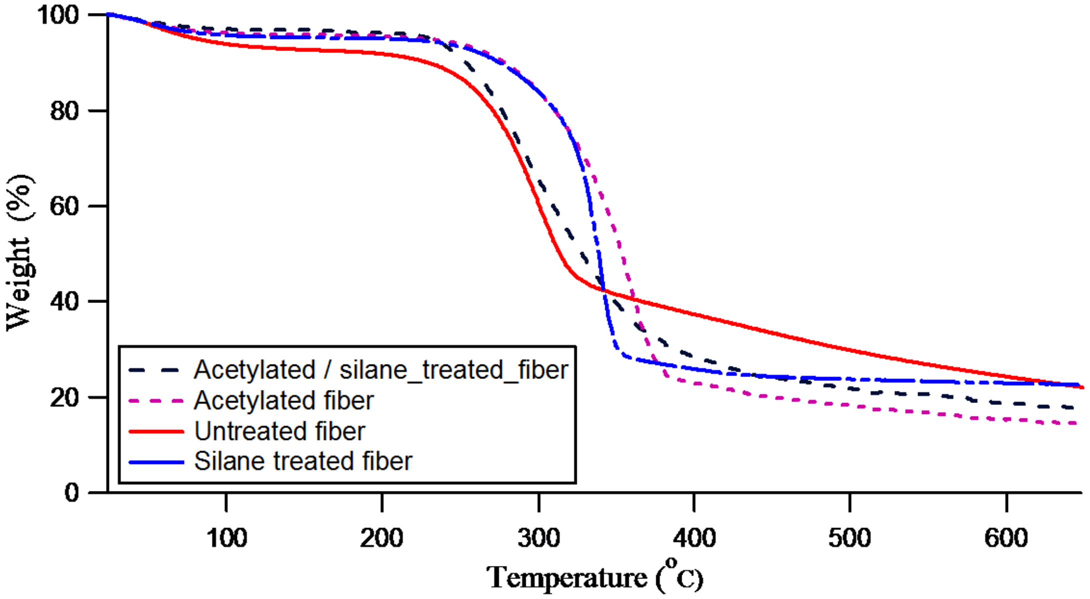


Figure 53: Behavior of untreated fiber and fiber treated with different methods under temperature

Acetylated/ silane treatment is the combination method of silane treatment and acetylated treatment that may help to improve the adhesion between fiber and matrix. We also conducted a TGA experiment to investigate the behavior of thermal curve. The results reveal that using this new treatment can remove moisture, pectins and hemicelluloses, thus, at low temperature the weight loss is less significant than that of untreated fiber. However, at high temperature (more than 340°C) it degraded more than untreated fiber because of the high percentage of cellulose caused by the removal of pectins and hemicelluloses and because of the disintegration of intermolecular interactions such as hydrogen bonds between polymer molecules.

III.2. Water absorption of fiber

In this experiment, the fibers were kept in the desiccator that contained of saturated salt KNO_3, the humidity recorded after 1 day was 91 %. In this method, the fibers were moved out and then the weight was measured. The ratio of the weight gain and the original weight is the water absorption.

Figure 54: Water absorption measurement

The drawback of natural fibers, as mentioned above, is their high moisture absorption. Moisture absorption can result in swelling of the fibers, and concerns about the dimensional stability of the agro-fiber composites cannot be ignored. The absorption of moisture by the fibers is minimized in the composite because of encapsulation by the polymer [64]. As referred above, acetylated treatment is one of the methods to reduce water absorption, however, it may result in increasing in the cost of the fiber. Thermoplastic will be used as a coat for fibers and this will significantly reduce the absorption and also it will and improves the durability of the end product. Also, by silane treatment, the fiber absorbed less moisture than the untreated one. Means that all the modification methods improve the moisture proof, thus make the fibers less hydrophilic and more compatible with the matrix.

In Figure 55, it can be seen that all the water absorption of all 5 kinds of bamboo fibers level off after a certain times, 3 or 4 days (72 or 96 hours). Firstly, the absorption increased quickly on the first day. It still increased on the second and third days but the speed became slowly. And after a time that is long enough, the values are stable.

One thing to note is that the untreated bamboo shows the highest value of absorption and the following ones respectively are the ones treated with NaOH only, with acetylated modification, with silane treatment and with acetylated treatment followed by modification by silane. It is supposed that by the treatments, the water absorption was reduced.

The changes in mass (water sorption) were calculated as following equation:

$$W = \frac{m_2 - m_1}{m_1} 100\%$$

m_2 : mass after immersion

m_1 :mass before immersion

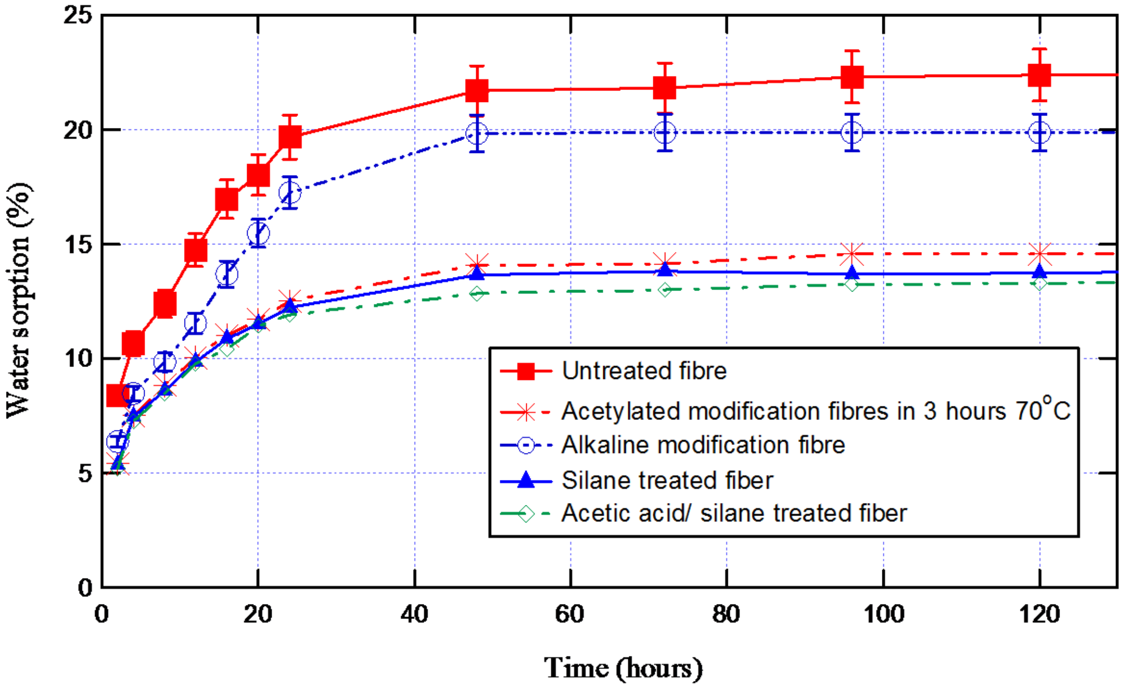


Figure 55: Water sorption of bamboo fibers

From the graph, it is seen that the water sorption was decreased by using acetylation method since the OH and ONa groups in the fibers were replaced by acetyl groups. If necessary, the moisture absorption of the fibers can be dramatically reduced through the acetylation of some of the hydroxyl groups present in the fiber [64]. Similarly, the fibers treated with silane method showed the significant decrease in water absorption since the –OH group of the cellulose fibers reacts with silanol which is produced by hydrolysis process. Fibers treated by silane method even showed its better water proof. Fibers treated with both acetylated modification and silane treatment revealed the best water proof since more –OH groups could react with either acetyl group or silanol. In conclusion, fibers treated with the method using acetylated treatment and followed by silane method show the minimum value of moisture (water) absorption while untreated fibers have the maximum one. This parameter is very important because it reflects the compatibility between fibers and matrix. We aim to improve the adhesion between the fibers and hydrophobic matrix and we aim to modify the fibers, make the fibers less hydrophilic. The lower water absorption reflects the less hydrophilic property. Therefore, the results prove that the modifications give the less hydrophilic property and those kinds of fibers promise to be better compatible with polymer matrix and fibers modified with the method using the combination of acetylated treatment and silane method is expected to be the optimum fibers to reinforce the polymer matrix.

III.3. Mechanical properties of fibers

The measurements were carried out at 20^{o}C and the RH (relative humidity) was 70%. The mechanical properties were performed under Test 108.5kN - Testwell machine using the 2kN sensor, the speed of the movement is 10 mm per minute.

Numerous of fibers were measured to obtain the average values. Fibers were treated with several methods (with NaOH, acetylated treatment or silane treatment). However, it is not easy to get the exactly values to compare since the values fluctuate. Moreover, the treated fibers were stirred during the treatment process, making them broken. (And the fibers were cut in to very short fibers before being mixed with polymer). The general mechanical properties of fibers were obtained and showed in Table 20.

Table 20: Mechanical properties of bamboo fibers

References	**Young modulus (GPa)**	**Tensile strength (MPa)**	**Strain (%)**
[23]	27-40	500-575	1.9 – 3.2
[6]	11-17	140-230	----------
[37]	27	575	----------
[38]	18-55	391-713	----------
Bamboo fibers	12 -15.78	314.64 -379.88	2.94 - 3.19

The obtained results show that tensile strength and young modulus of bamboo fibers are pretty good and in the range of the conventional bamboo fibers.

III.4. Morphology of fiber

The morphologies of fibers were observed via Scanning Electron Microscope (SEM) method using HITACHI TM-1000 machine. The settings were “observation mode” and “reduced mode”. In the images shown below, there are 3 types of bamboo fibers: untreated bamboo fibers, bamboo fibers mercerized in NaOH solution and bamboo fibers modified by acetylated method.

The obtained images indicate that probably there were still accumulated pectin or wax ‘(as we supposed) on the surface of the untreated fibers while this phenomenon could not be seen on that of fibers modified with any treatment. In general, the morphology of bamboo fiber revealed that the surface of all kinds of fibers were clean with no apparent damage. The modified fibers also exhibited the smoother surfaces as some compounds were removed during the treatment. The method confirms the success of fiber treatments.
Here are some images taken with different magnifications:

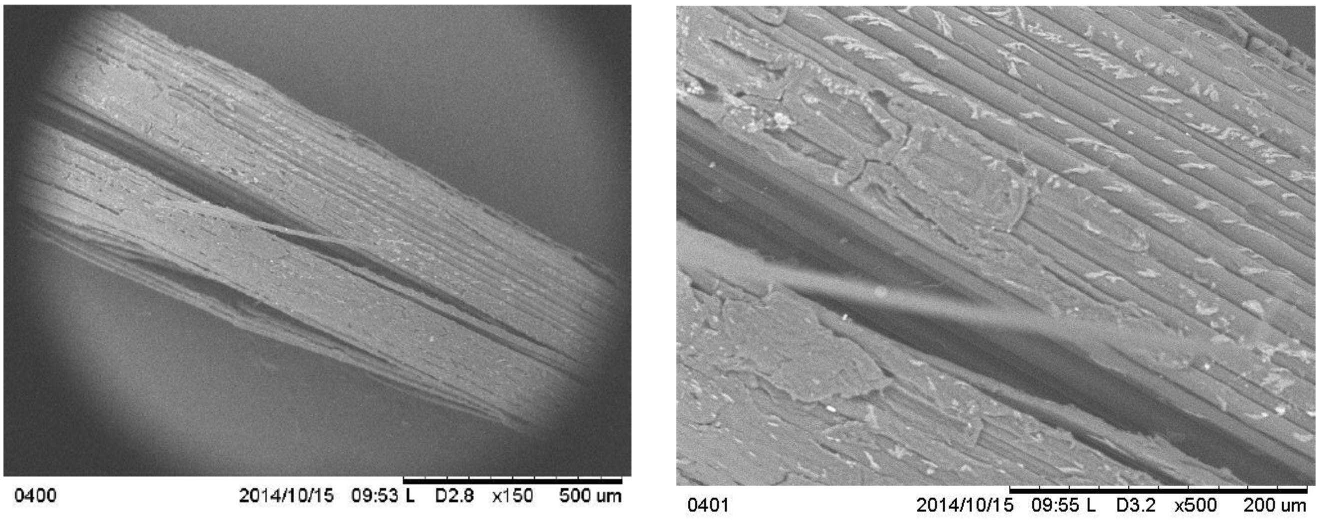
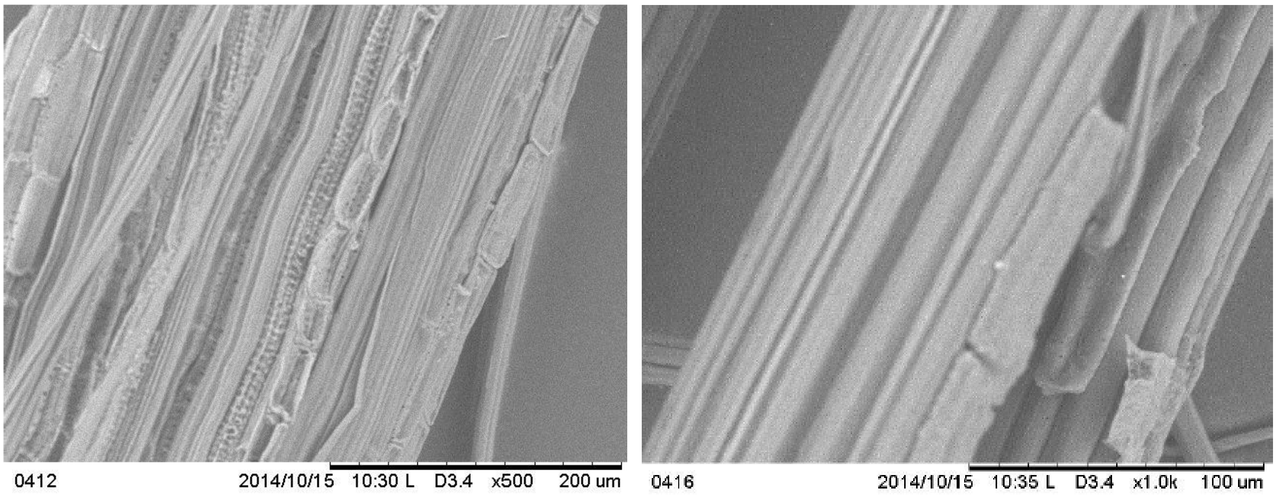


Figure 56: Morphology of untreated fibre (Magnifcation: x150 (left) and x500 (right))



(a) (b)

Figure 57: Morphology of bamboo fibers

(a) Morphology of fiber mercerized in NaOH 0.1N (Magnification: x500)

(b) Morphology of fiber modified by acetylated treatment (Magnification: x1000)

IV.Conclusions

In this chapter, bamboo fibers were modified with chemical treatments such as: alkali method, acetylated method, silane treatment and a method using acetylated method followed by silane treatment. Some tests were conducted to confirm the effect of those modifications. Using the chemical modifications, some substances in the fibers were removed, such as: lignin, pectin, wax … and new function groups were grafted. By modifying the fibers, we expect to improve the compatibility of the hydrophilic bamboo fibers and hydrophobic polymeric matrix. And thus, the compatibility will contribute to the improvement of composite material. Of all the treatments, a treatment using both acetylated method and silane treatment reveals to be the best one.

CHAPTER 3: Composite based from P34HB matrix

Chapter 3: Composite based from P34HB matrix

I. P34HB (Poly 3 hydroxybutyrate – co –4 hydroxybutyrate)

I.1.SEC experiment

SEC (Size exclusion chromatography) experiment was conducted using pump injection model: Varian 390-LC and column oven Varian Model 510 to determine the molecular weight and the poly-dispersity index of polymer P34HB. The solvent used for the experiment was chloroform.

Two kinds of P34HB (PH34B) were investigated. They are: the original P34HB pellets and P34HB obtained from internal mixer and compress molding process.

The original samples was prepared in Chloroform with the concentration of 0.6 g/L while the samples from the PHB plate (prepared by compressing molding at 8 minutes at 180^{o}C), the concentration was 0.9 g/L (those were the maximum concentration that the solution passed through the filter, because the higher concentration will give the better response signal). The result is shown in the table below:

Table 21: Molecular weight of PH3B –co- PH4B

Samples	**M_n**	**M_w**	**P_D**
Original P34HB pellets	87367	165417	1.8960
PH34 plate	84308	190894	2.2642

The molecular weight changes after the proces. Mn of P34HB after the process (Mn=84308) is smaller than that of the original polymer because there was a thermal degradation during the process and the polymer chain might be cut into the smaller chains. These smaller chains could react together forming new longer chains and probably a few crosslinks. Both events lead to the transformed polymer insolubility in chloroform and results to the higher Mw of the soluble polymer chains.

I.2.FTIR experiment

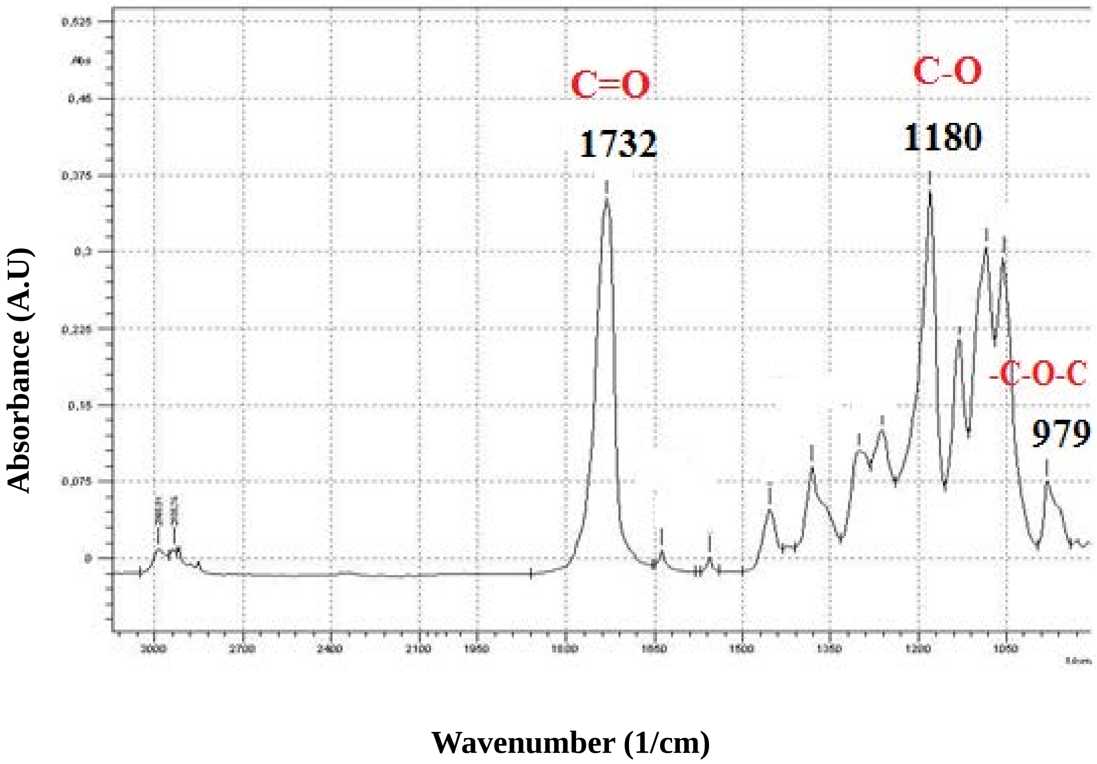


Figure 58: FTIR result of P34HB

FTIR experiment were performed on FTIR- 8400 S, Shimadzu, the wavenumber ranged from 800 cm^{-1} to 4000 cm^{-1}, and 40 scans were taken per measurement. The obtained result is similar to that of Shah KR [40]. Shah KR indicated that the polymer PHA was confirmed as C=O groups by FT-IR spectroscopy. The result obtained by this is exactly similar to that of other researchers (De Smet et al., 1983; Castillo et al., 1986). For example, the stretching vibrations were recorded at 2933 and 1162 cm^{-1} (CH, CH_2, CH_3); 1720; 1162 cm^{-1} (ester C=O valence); 1162 cm^{-1} (ester C-O).

A summary of some FTIR results from several papers were presented on the table below:

Table 22: FTIR results

Wavenumber (cm^{-1})	Wave number (cm^{-1}) (references)	Group	Reference number
979.87	979	-C-O-C- and -C-C- stretching frequencies (between 800 and 1400 cm^{-1})	[41]
1261.49	1260; 1270 ; 1279	_CH$_2$_R	[40]; [41]; [42]
1180.47	1162	Ester C_O	[40]
1381.08; 1301.99	1380; 1302	_CH$_2$_R	[40]
1732.13	1720	ester C=O valence	[40]; [42]
2935.76	2933	CH, CH$_2$,CH$_3$	[40]
2985.91	2983	CH,CH$_2$,CH$_3$	[40]

Y.Kann et al. showed the IR result for P3HB. In the figure, there exist 3 peaks at 1275, 1180 and 979 cm^{-1}. In our study there are also peaks at 1261, 1180 and 979 cm^{-1} [41].

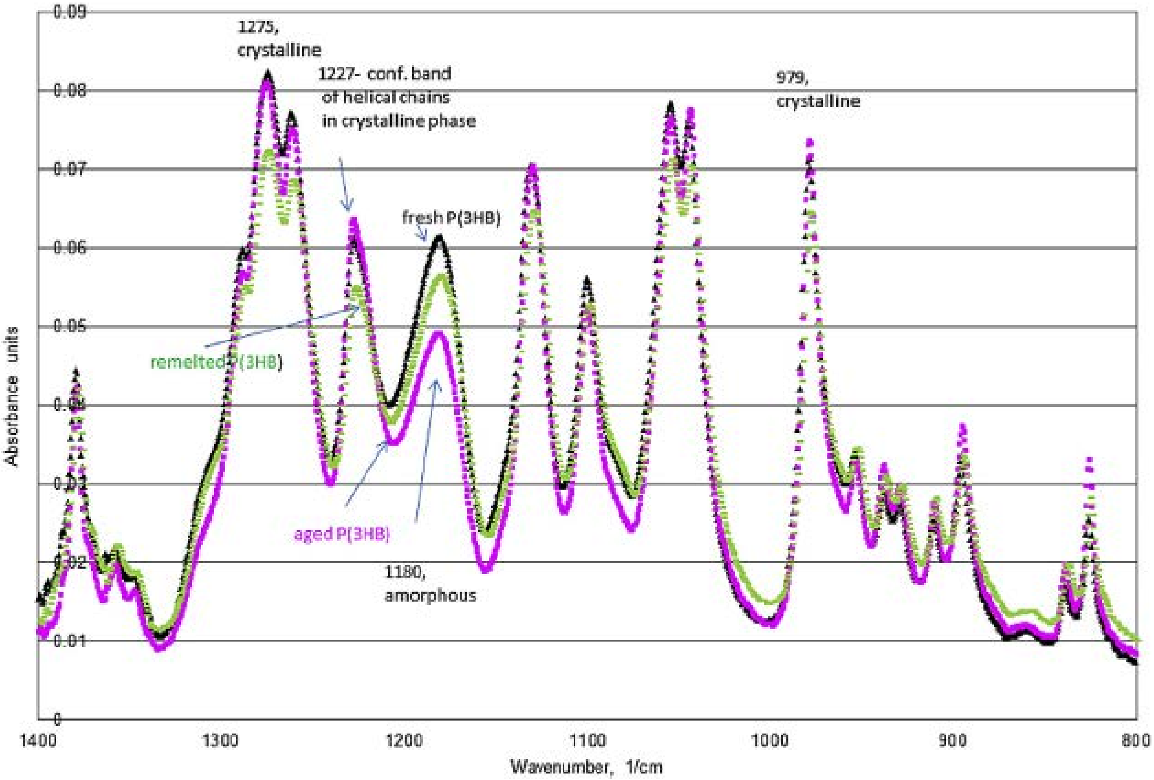


Figure 59: FTIR of fresh, aged and re-melted P(3HB) [41].

Figure 59 indicates that with aging, the crystallinity increases and the amorphous decreases. The growth of the crystalline phase corresponds to the peak at 1227 cm^{-1} while the reduction of the amorphous phase can be observed at the peak of 1180 cm^{-1}.

I.3. Thermal Properties

I.3.1. TGA experiment

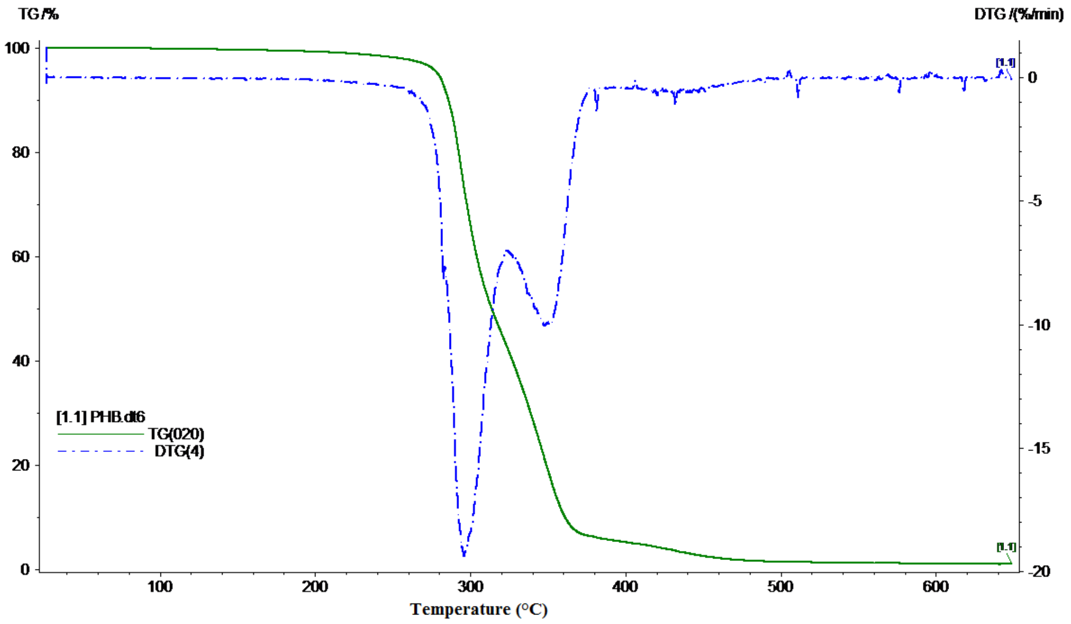


Figure 60: TGA result for P34HB

TGA experiment was carried out using NETZSCH, TG 209F3 at the starting temperature of 24°C to 650°C, the heating rate was 10°C/min in the inert nitrogen environment. From 140°C, polymer started to thermally degraded and quickly lost the mass at around 230°C. The mass loss matches with the result of P3HB shown in the publication [43] and [49]. In the figure, there are 2 periods of thermal degradation and the first period (below 300°C) is assigned to the degradation of P3HB phase while the second period of degradation is attributed to P4HB phase [129] or the miscible P34HB phase. It is very clear that there exist 2 phases inside the copolymer. The result can also be described via DSC experiment.

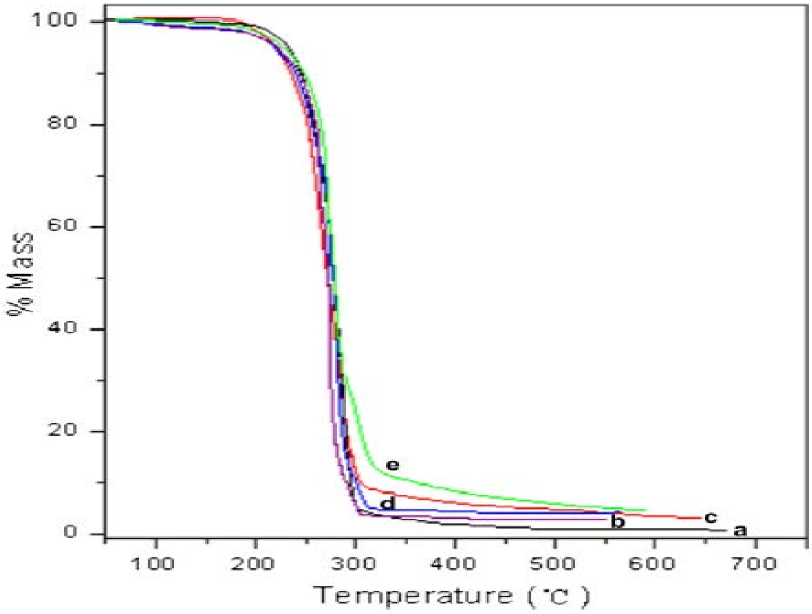


Figure 61: TGA curves of P3HB and P3HB/PEG grafting copolymers.

(a, PHB; b, c, d, e, P3HB/ PEG grafting copolymers responding to graft% ¼ 7.5%, 13%, 15% and 20%, respectively) [43]

Rosaria Abate et al. [130] also investigated the thermal property of P4HB and gave the result of TGA test. As can be seen in the Figure 62, the second degradation period of our P34HB (in Figure 60) is very similar to the weight loss curve of P4HB alone (in Figure 62).

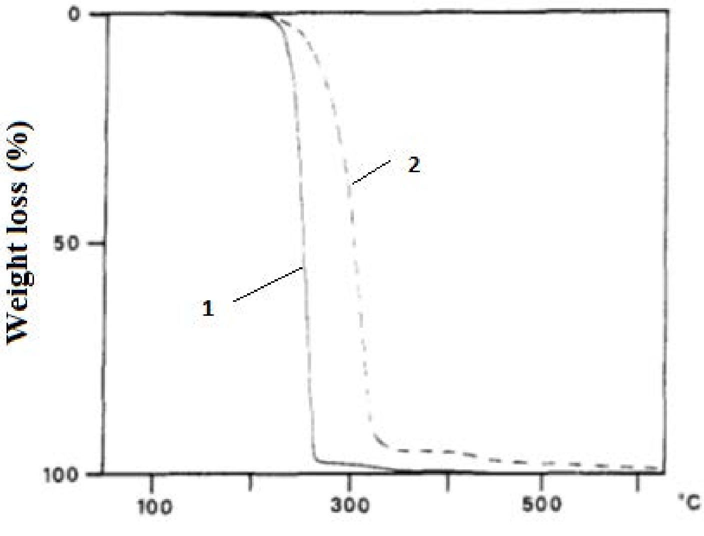


Figure 62 : Weight loss curves for P3HB (1) and P4HB (2) under a nitrogen atmosphere

X.Wang et al. [129] showed the TGA result of P34HB as Figure below and it is quite similar to our obtained result, and the figure is consistent with our conclusion of the behavior of weight loss curve.

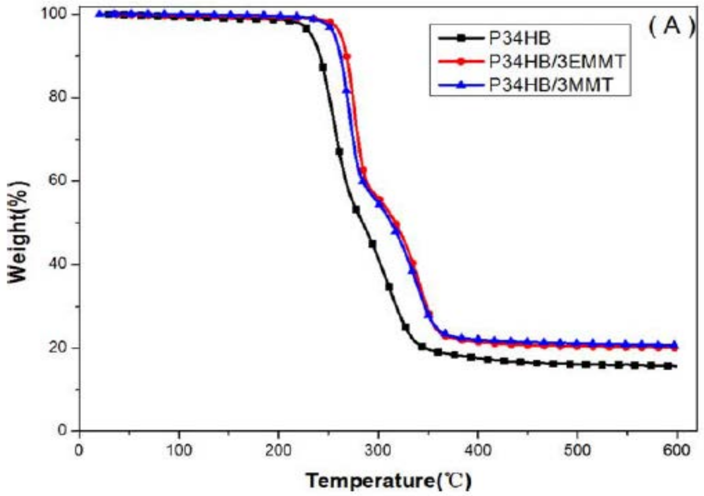


Figure 63: TGA curves of P34HB/3EMMT [129]

From the bottom to top: P34HB; P34HB/3EMMT and P34HB/3MMT
where : EMMT: modified montmorillonite; MMT: montmorillonite

I.3.2.DSC experiment

The thermal properties of copolymer P3HB – co –P4HB and composites were characterized by performing a NETZSCH, DSC 204 F1 instrument under nitrogen atmosphere. The specimens were heated from the room temperature to 185°C at the heating rate of 10°C/min. All analyses were performed with a 10 mg sample in aluminum pans. More specifically, the process was performed as follow:

1. Isothermal process: at room temperature (about 24°C) in 10 minutes
2. Cooling process: to -30°C, cooling rate: 10°C/min
3. Isothermal process: at -30°C in 15 minutes
4. Heating process: to 185°C, heating rate: 10°C/min
5. Cooling process: to -30°C, cooling rate: 10°C/min
6. Heating process: to 185°C, heating rate: 10°C/min
7. Cooling process: to 24°C, cooling rate: 10°C/min
8. Isothermal process: at 24°C in 5 minutes.

The results were read from the second heating traces. From the behavior of the curve, information about glass transition temperature (Tg), the melting temperature (Tm), and melting enthalpy were known.

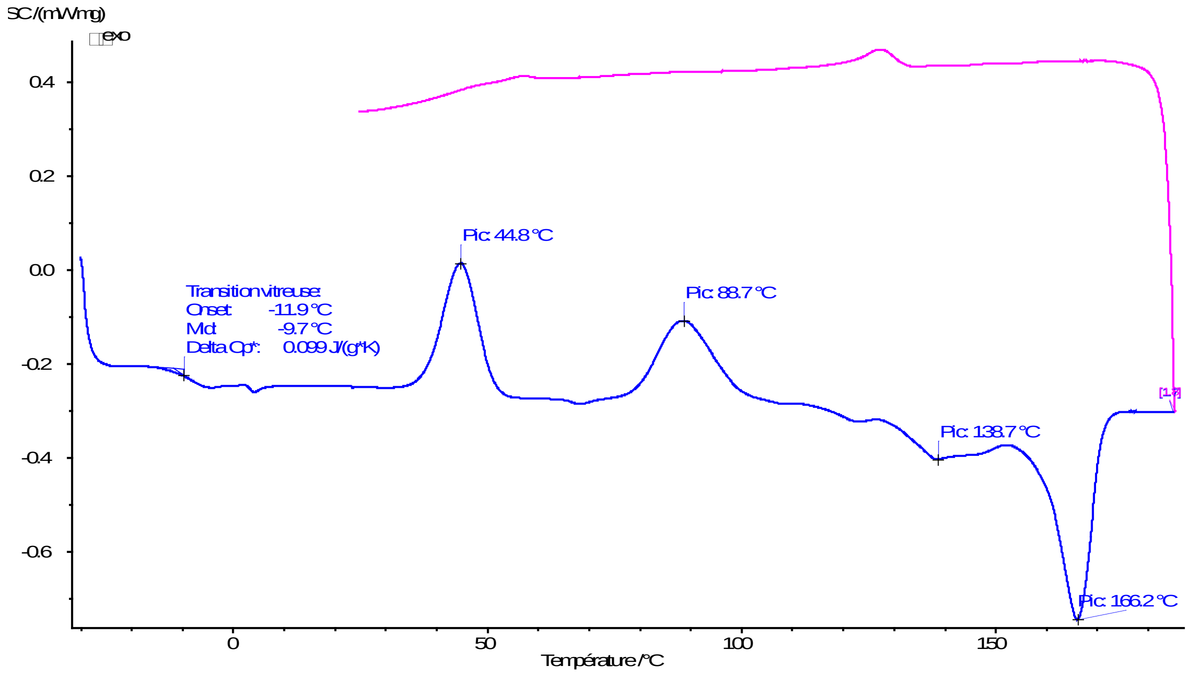


Figure 64: DSC heating curve of P3HB – co – P4HB copolymer

The melting temperature supplied by Tianjin Green BioMaterials (Tianjin, China) provider is 170^{o}C which represents the fusion of the copolymer phase. The result obtained from the figure showed two melting points at 138.7^{o}C; and 166.2^{o}C respectively. The lower temperature peak can be attributed to the melting of imperfect crystal, while the higher one corresponds to the more perfect crystals, produced by recrystallization on the second heating run [43]. Two cold crystallization temperatures (T_{cc}) were recorded at 44.8^{o}C and 88.7^{o}C can be attributed to the presence of the two phases P3HB and P4HB respectively. The peak at temperature of 44.8°C can also be caused by the combination of the glass transition and cold crystallization as referred later in DMA (Dynamic Mechanical Analysis) test. It was reported that P3HB (or PHB) is a highly crystalline (about 60 to 70% crystallinity) and linear polymer, if the heating rate of the measurement is fast then the crystallization temperature (Tc) is between 80°C and 100°C while Tc can also be below 60°C if the rate is slow [125]. For example Shinn- Gwo Hong et al. [126] performed DSC experiment with the heating rate of 10°C/min and the obtained Tc was 95.6°C. Similarly, X. Wen et al [127] conducted DSC experiment at the same heating rate (10°C/min). The crystallization temperature (Tc) for PHB neat (P3HB) was 69°C while the cold crystallization temperature revealed at 48°C. It should be noted that, the presence of P4HB in the copolymer gave to the rise of cold crystallization temperature (Tcc) as it showed in the following table:

Table 23: Values of T_{m1}, Tg, T_c, T_{cc}, T_{m2}, ΔH_{m1} and X_c of PHB and P34HB copolymers [127]

Samples	First heating process			Cooling process		Second heating process		
	T_{m1} (°C)	ΔH_{m1} (J/g)	X_c (%)	Tg (°C)	T_c (°C)	Tg (°C)	T_{cc} (°C)	ΔH_{m2} (J/g)
Neat PHB	172.3	98.16	67.23	2.6	69	3.8	48	173.6
P34HB (5% P4HB)	150.4	76.98	52.73	-3.5	63.1	0.4	52.0	153.1
P34HB (10% P4HB)	128.4	71.53	48.99	-6.4	50.7	-2.5	63.7	142.1
P34HB (15% P4HB)	101.6	41.03	28.10	-11.2	_	-7.1	78.2	130.5
P34HB (20% P4HB)	91.8	38.43	26.32	-12.1	_	-8.1	_	_
P34HB (30% P4HB)	69.7	3.04	2.08	-22.5	_	-18.8	_	_
P(4HB) [128]	54.0	_	_	-50.0	_	_	_	_

Table 23 indicated that the presence of P4HB unit, the crystallization ability of PHB is strongly reduced. When P4HB fraction is up to 20 mol %, the crystallization ability of copolyesters markedly decreases and Tc, Tcc of copolymers could not be detected [127]. Moreover, it also revealed that Tc and Tcc could not be either detected for P4HB only [128]. These results give interesting information to explain our DSC result. For example, it is observed that there are two Tcc in our result as referred above. And these two Tcc are attributed to the two phases of the copolymer as it can also be seen in TGA result. The first Tcc (44.8°C) is assigned to the cold crystallization temperature of P3HB phase only while the second Tcc at 88.7°C is probably caused by P34HB miscible phase. In general, the influence of 4HB unit on the copolymer is complicated. The crystallization of P34HB copolymer is determined by the competition between two factors: one is the existence of 4HB unit that undermines the crystal regularity of neat P3HB and the second factor is the improvement of the macromolecular chains mobility (which is beneficial to crystallization) caused by the introduction of P4HB unit also [127]. X.Wen et al [127] gave the result with only one Tcc, it is probably that there was only one phase in the copolymer as it is showed in Figure 59 below:

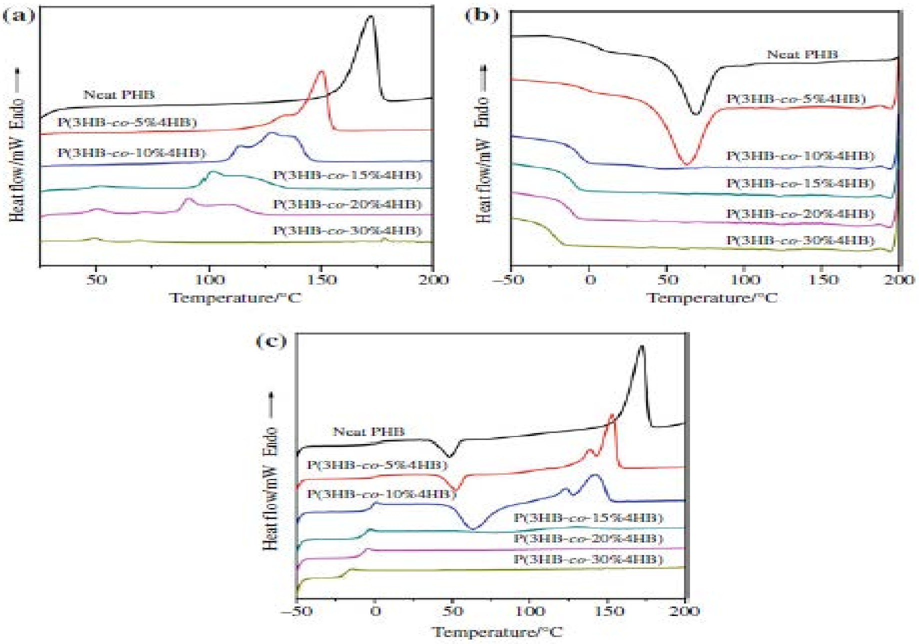


*Figure 65***:** DSC result for P3HB and P34HB [127]

a: First heating curve b:Cooling curve c: Second heating curve

In our experiment, the glass transition temperature is recorded at -9.7°C, however, the glass transition temperature of PHB is supposed to be difficult to determine by the conventional DSC experiment, owing to its high crystallization [43].

C. Zhijiang et al. [43] showed the Tg for PH3B and melting point in the Figure 66 below. As for them, for pure P3HB, melting temperature is about 180°C and it shows double melting peaks, which could be explained in terms of melt/recrystallization process.

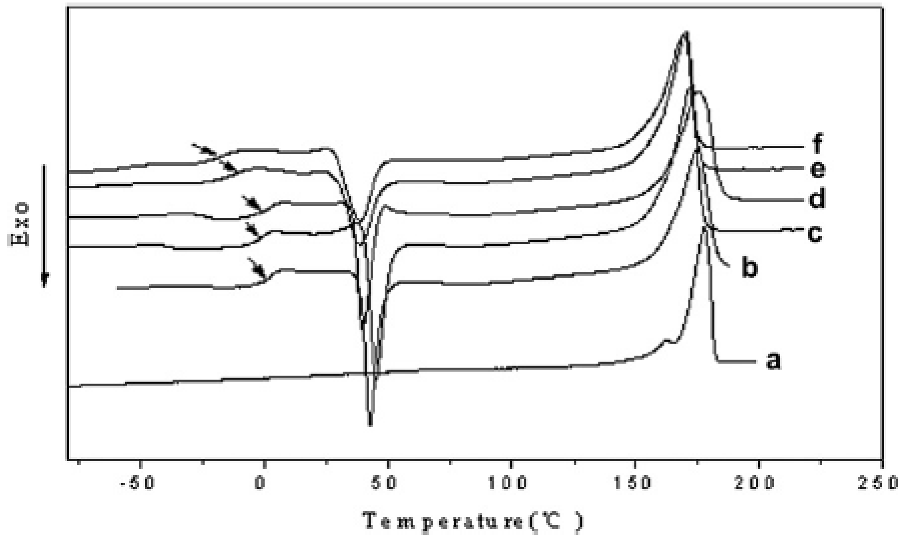


Figure 66: DSC heating curves of PHB and PHB/PEG (polyethylene glycol) grafting copolymers (II run). (a, PHB; b, c, d, e, f, PHB/PEG grafting copolymers responding to graft% ¼ 5%, 7.5%, 13%, 15% and 20%, respectively) [43].

The crystalline peaks at around 40°C (PH3B) and melting peak at 180°C is pretty similar to what can be observed from our obtained result. Hence, those peaks could be attributed to the P3HB component in P34HB.

Another publication by Dazhu Chen et al. stated that there was a peak on the cooling curve at 6.68 °C (Crystallization peak) [10].

II.Composite based from P34HB

II.1. Preparation

The major factors that govern the properties of short fiber composites are fiber dispersion, fiber length distribution, fiber orientation, and fiber matrix adhesion. In this study, the length of the fiber was cut to 2 mm. The efficiency of the composite also depends on the amount of stress transferred from matrix to fibers or in other words, it depends on the compatibility between fibers and matrix. This can be maximized by improving the interaction and adhesion between the two phases, and also by maximizing the length of the fibers retained in the final composite.

The uniform fiber dispersion is of great importance and a careful selection of processing techniques. Several types of compounding equipment have been used for blending lignocellulosic fiber and plastics. The ultimate fiber length present in the composite depends on the type of compounding and molding equipment used. The level of fiber attrition depends on the used type of compounding and molding equipment, level of loading, temperature, and viscosity of the blend. The properties of the agro-based thermoplastic composites are thus very process-dependent [64].

II.1.1. Internal mixer processing

Firstly, resin and bamboo fibers (10, 20 and 30% by weight) were introduced into the Haake Rheomix 3000 laboratory internal mixer via funnel, fitted with high intensity rotors and operated at a nominal speed N=100 rpm. The processing chamber was 70% full in all cases and the walls were kept at the temperature of 160^{o}C during each test. The test revealed that it required 5 minutes for processing time. At first, only resin was introduced and kept inside the chamber for 3 minutes at 160°C, after that fibers were gradually introduced. After the process, the mixer of fibers and resin was well mixed and the fibers were well distributed in the resin.

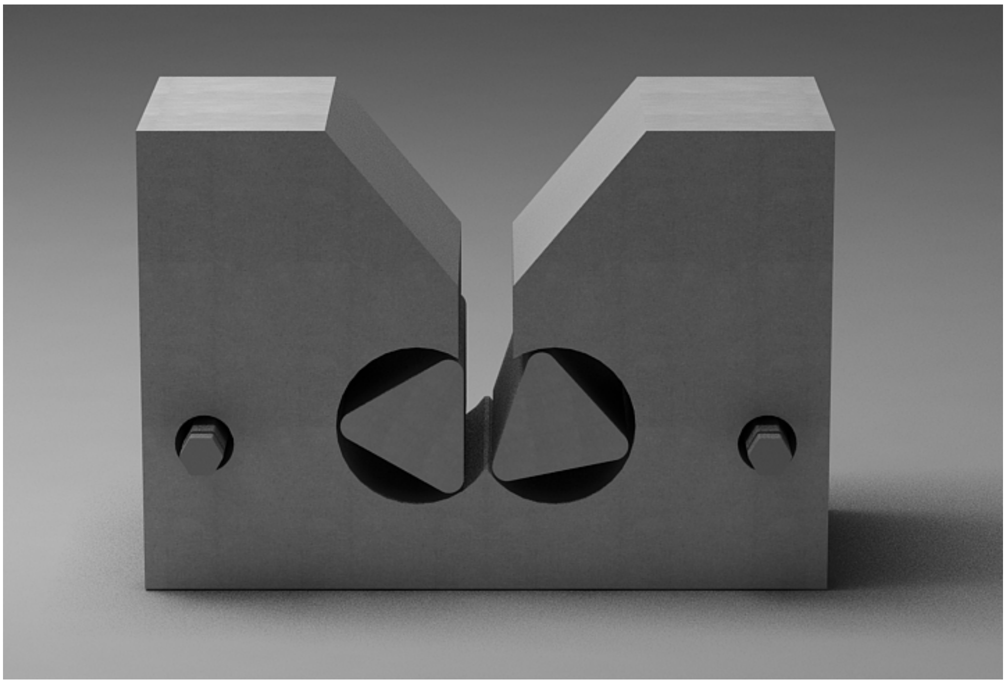


Figure 67: Scheme of the chamber of internal mixer

II.1.2. Compress molding method

In general, the processing methods of polymer only and polymer composite are similar including the method of injection molding, compression molding or extrusion. Besides, there are other techniques that are unique only to polymer composite processing namely filament winding pultrusion and hand lay-up. Even for those methods that are both used for polymer processing and polymer composite processing, the conditions can be very different.

There are many methods to elaborate polymer composite. In this case, composite of P34HB thermoplastic reinforced with bamboo fibers were prepared using compression molding.

Figure 68: Composite process

Compression molding uses a press to compress either the dough of resin and fiber mixture, or the layers placed by a hand lay-up method or mechanical means, typically at an elevated cure temperature. With the compressive force, the void content is lower than the ordinary atmospheric pressure processing method. We took advantage of this method to make composite plates with the thickness adjusted by the designed frames.

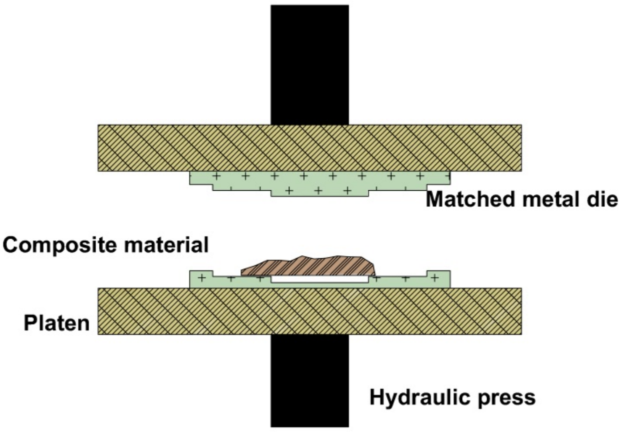


Figure 69: Schematic diagram of a compression molding press [17]

This is a popular and simple method. The productivity and working period is short. The by-product can be introduced into the die mold in terms of prepreg or hot melt liquid.
The hot melt compression molding method can be used for composites with various kinds of polymer matrix like PP, PET or ethylene- propylene.

In this case, a mixture of P34HB matrix and bamboo fibers were placed on the metal die with the thickness adjusted by using the frame as can be seen in Figure 70. The metal die was pressed under the force (5000 kg) over the area of 25x25cm for 10 minutes, at 180°C.

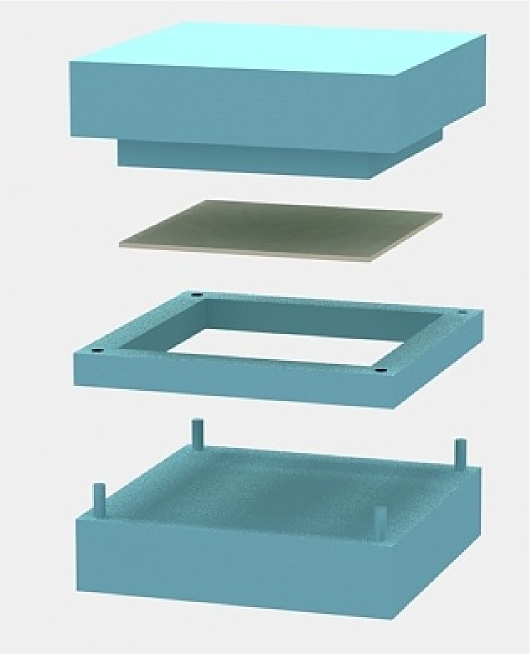


Figure 70: Fabrication procedure of the bio-composite

The composite plates obtained from these preparations will be cut into the specimens in different shapes for the certain tests.

Figure 71: Samples from the obtained polymer composite plates

The rectangular specimens were designed for flexural test, DMA test and to determine the water uptake property while the dumbbell specimens were used for tensile test.

II.2.Composite reinforced with acetylated bamboo fibers

II.2.1. DMA (Dynamic Mechanical Analysis) experiment

Dynamic Mechanical Analysis is among the thermal analysis for measuring mechanical properties at various temperatures. DMA is a tool where damping capacity of a material is measured which is dissipated in the material during mechanical vibrations under cyclic loading [134]. Identifying the glass transition and how various system modifications affect Tg is a major application for DMA [69]. DMA is a powerful test method for investigating the viscoelastic behavior of the bio-composites [71]. In this method, a device (DMA Q800 –TA instrument) was used at the typical heating rates ranged between 1 and 5 K/min and a compromise rate must be found. The higher the heating rate, the more the real sample temperature deviates from the temperature registered by the thermocouple in the chamber. In our experiments, the heating rate was 2°K/min and the amplitude was held constant at 20 µm. During the measurement run, the specimens were vibrated with a dual-cantilever fixture at a frequency of 1Hz [70] and the temperature was from 30^{o}C to 120^{o}C. The samples used for the test were shaped into a strip of 2.5 mm (thickness) x 13 mm (width) x 60 mm (length).

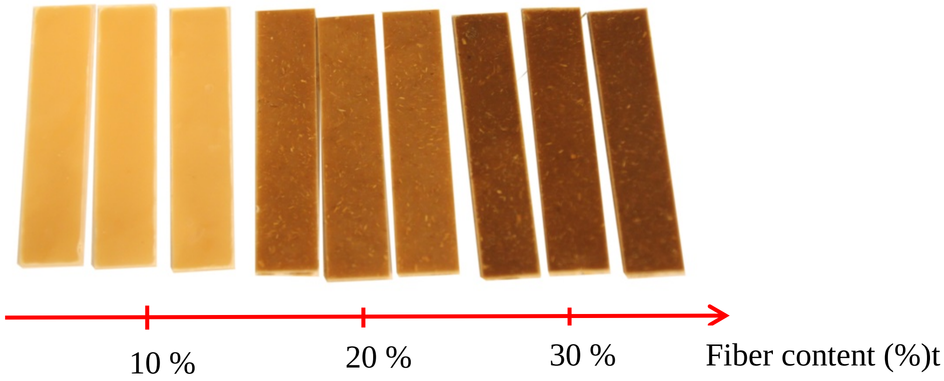


Figure 72: Samples for DMA

From left to right, the specimens are gradually darker, corresponded to the weight percent of bamboo fibers ranging from 10%, 20% to 30%.

Storage modulus

Visco-elastic storage modulus (E’) is defined as the stress in phase with the strain in a sinusoidal shearing deformation which is divided by strain [131] and it is also a measure of stiffness of a composite [132]. Storage modulus is influenced by inherent stiffness of fiber which allows effective stress transfer between fiber and matrix and directly proportional to interfacial bonding [133]. The temperature dependence of storage modulus of composites is presented in Fig.73 below. In this experiment, fibers modified with acetylated method were used as the reinforcement. As can be seen from the graph, the storage modulus E’ tends to decrease with the increase of the temperature because of increased chain mobility of the matrix P3HB –co- P4HB [71, 131] and lose the tight packing arrangement which gradually decreases the E’ value [132]. Storage modulus is associated with the elastic response of the composite and indicates the stiffness of the material [96]. The drop in modulus is precipitous near the α-relaxation temperature of P34HB (around 45 to 50^{o}C). This α-relaxation may indicate the polymer segments, however in most cases the polymer segments reveal α-relaxation at lower temperature. Therefore it probably reflects the glass transition temperature. On DSC results, at that range of temperature, only peak of cold crystallization temperature can be observed and we assumed that there should be glass transition temperature and cold crystallization temperature at that range of temperature area. This phenomena seems to be the same with all kinds of composites reinforced with acetylated fibers and neat P34HB, it suggests that there is slight influence of the amount of the bamboo fibers added in. Moreover, there appears another peak on the storage modulus. The lower peak of each storage modulus curve corresponds to the cold crystallization temperature of the matrix as it can be seen on the DSC results (corresponds to the second cold crystallization temperature which can be observed in DSC results). Also, the storage modulus of bio-composites is considerably higher than the pure P34HB over the whole temperature range, a clear indication of the reinforcing of bamboo fibers. And the more considerable amount of fibers were added, the higher values of storage modulus were obtained. It means that bamboo fibers enhance the storage modulus of bio-composites, the increase of storage modulus should be associated with the fiber/matrix interaction and the high modulus of fiber [131]. Moreover, since storage modulus indicates the stiffness – an inherent property of a material, this can give a better estimation of fiber to matrix interaction. In this case, probably there exists an interfacial interaction caused by the dipolar nature of hydroxyl group on cellulose and carbonyl group on P34HB [98]. The result reflects that by increasing fiber content, the storage modulus is improved because of the mechanical limitation posed by increasing fiber content embedded in the viscoelastic matrix thereby reduced the mobility and the deformation of the matrix with increasing temperature [96,97]. Also, the well dispersion of fiber in matrix plays an important role in increasing the storage modulus [97].

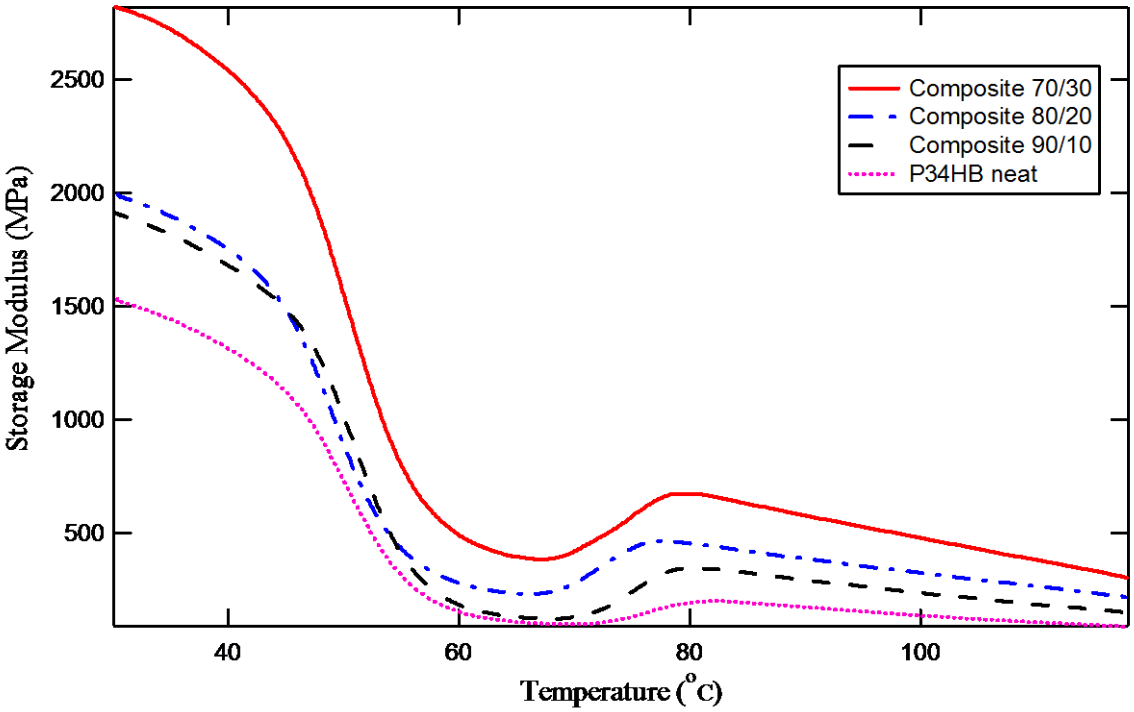


Figure 73: Storage modulus of composite reinforced with bamboo fibers (acetylated fibers)

Although bamboo fiber contributes to the increase of storage modulus, if the amount of fiber introduced to composite is too much, it is impossible to prepare the composites since the matrix is not significant enough to cover all the fibers.

Loss modulus

The loss modulus of the material reflects the viscous response or the dampening effect of the material. E” is known as the loss modulus and is a measure of the viscous character or liquid-like nature of the material [69]. Loss modulus is also an indication of dispersed relaxation mechanism and shows similar trend as in the case of storage modulus in variation in relative weight fraction bamboo fiber [132]. Figure 74 shows the effect on loss modulus of fiber content. As it is depicted, loss modulus increased with the increasing fiber content. A higher peak height may be associated to a poor interface. However, in general, it may also be attributed to an increase in the mobility of the polymer chains [96, 131]. There exist 2 peaks which are assigned to the α-relaxation temperature and cold crystallization temperature, respectively.

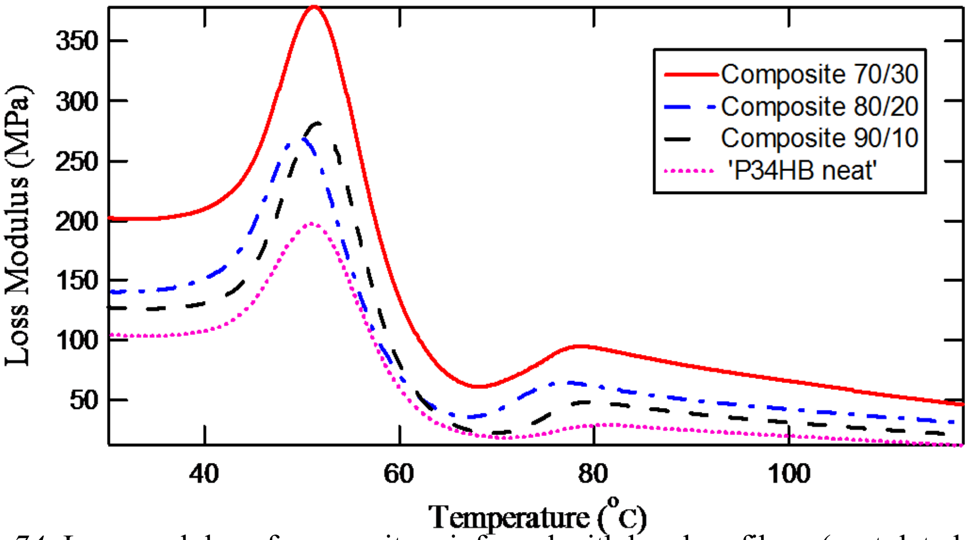


Figure 74: Loss modulus of composite reinforced with bamboo fibers (acetylated fibers)

Tan delta

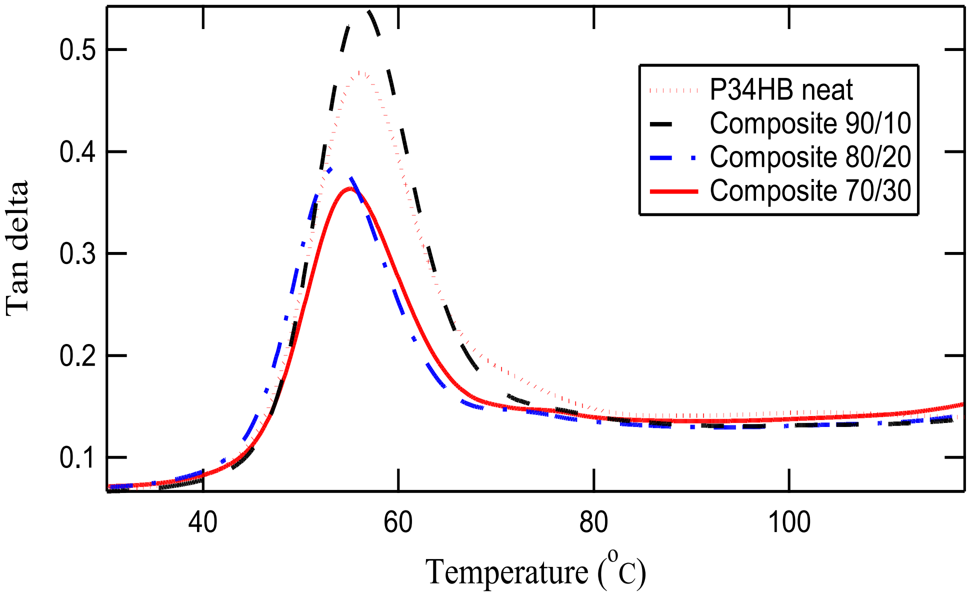


Figure 75: Tan delta of composite reinforced with bamboo fibers (acetylated fibers)

Tan delta (δ) is defined as the ratio of the loss modulus to the storage modulus [98].

$$tan\delta = \frac{sin\delta}{cos\delta} = \frac{E"}{E'} \text{ [69]}$$

Tan δ is also known as the material loss factor or loss tangent. Tan δ ranges from 0 for an ideal elastic solid to infinity for an ideal liquid [69]. Tan δ is also regarded as an indication of balance between elastic and viscous phase in a polymeric material [135].

Tan delta peak height decreased with the increasing bamboo fiber loading in bio-composite. Generally, composites containing less fiber content exhibit higher peak heights. One reason for this may be that there is less matrix by volume with higher content, and there is more energy at the interface in the interfacial area. The matrix dissipates more energy than composites, because the fibers carry a greater amount of the load, dissipating a small of it to strain in the interface [96]. Tan δ gives a peak in a region in which rate of decrease of storage modulus is higher than that of loss modulus. And the tan delta peaks had a little shift to the low temperature, which indicated that the presence of fibers had a modest effect on the change of relaxation temperature and that the mobility of polymer is increased. As can be seen in the figure the height of tan δ decreases when adding more fiber; means that there exist a connection between fibers and matrix. However, the incorporation is not so good because the peak shift to lower temperature at higher fiber content. If the adhesion is good, the tan δ shifts to higher temperature which indicates that the heterogeneity is generated inside the material [98]. The fibers are packed inside matrix results in stress transfer from matrix to the fibers [96]. The peaks of tan δ become narrow can be attributed to the increase the fiber content.

II.2.2.Tensile test

The plates were cut into standard dumbbell samples, using the sharp knife.

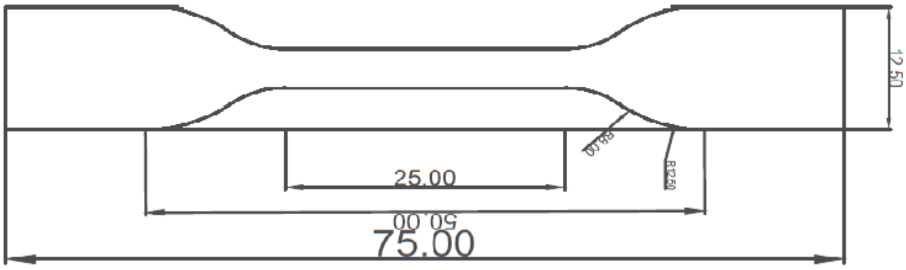


Figure 76: Standard sample for tensile test

The distance between the 2 points that were kept in the clamps is 5 cm, the width is 4 mm and the thickness of the sample is around 0.3 mm. Tensile test was performed according to ISO 527 -2 by using MTS Adamel Lhomargy – DY35XL equipped with a 500N load cell and connected with a computer using Testwork 4 software (by MTS systems Corporation). Test specimens were applied to the test at a cross head speed of 10 mm/ minute. For each type of sample, at least 30 specimens were performed to guarantee the reliability. Figure 77 indicates the tensile strength and strain of P34HB neat and composites reinforced with bamboo fibers (treated with acetylated method).

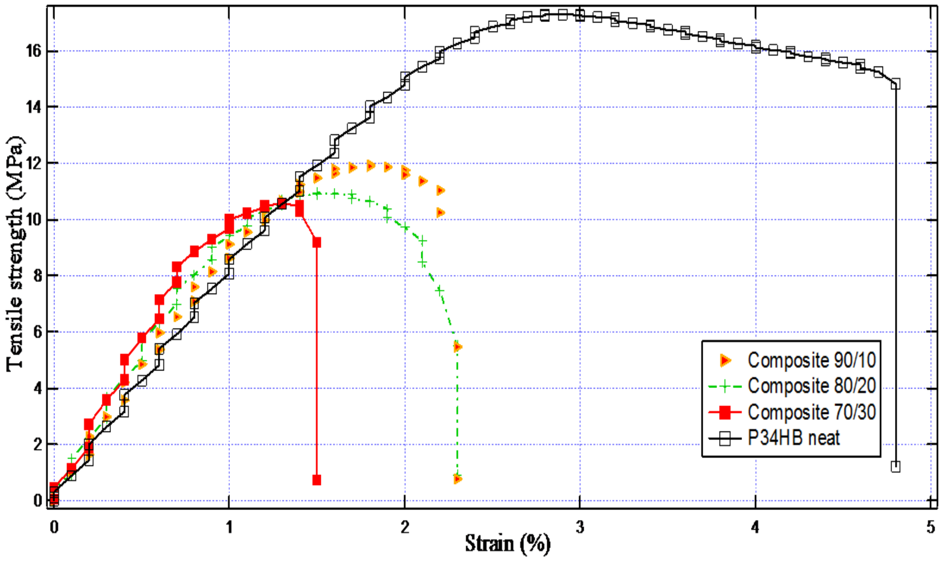


Figure 77: Tensile strength of the composite

The results show that the modulus increases upon the increase in the fiber loading, means that the rigidity property was improved with the presence of bamboo fiber. This result is consistant with the increase of storage modulus obtained from DMA results.

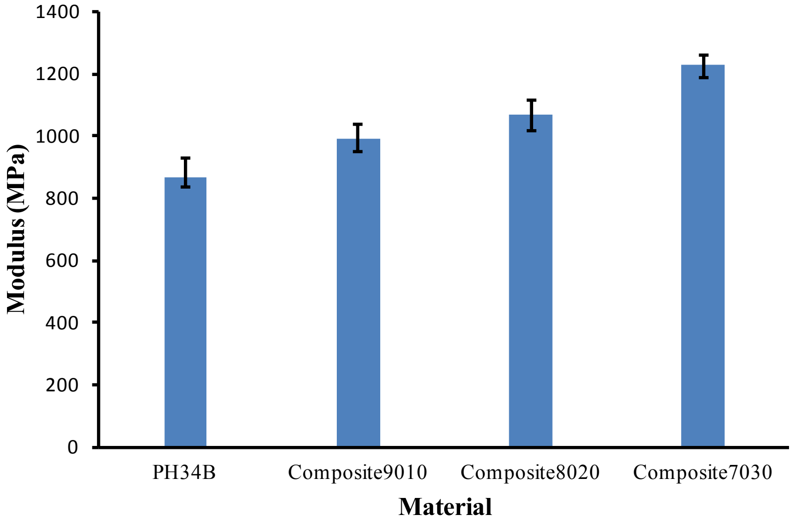


Figure 78: Dependence of modulus on the composition of composites

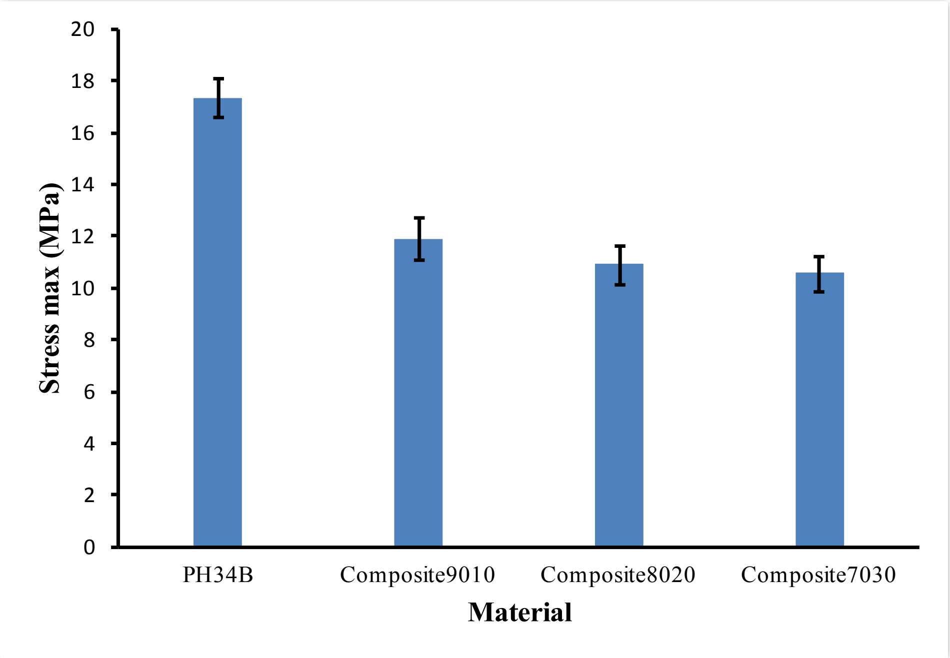


Figure 79: Dependence of tensile strength on the composition of composites

The tensile strength (stress max), however, decreases when adding the fibers. Although fiber itself has a much higher tensile strength (314.64 -379.88 MPa compared with nearly 17 MPa of P34HB) than that of the polymer alone, the bio-composites seem to exhibit lower tensile strength than P34HB. It is because of the poor adhesion between the matrix and the fibers.

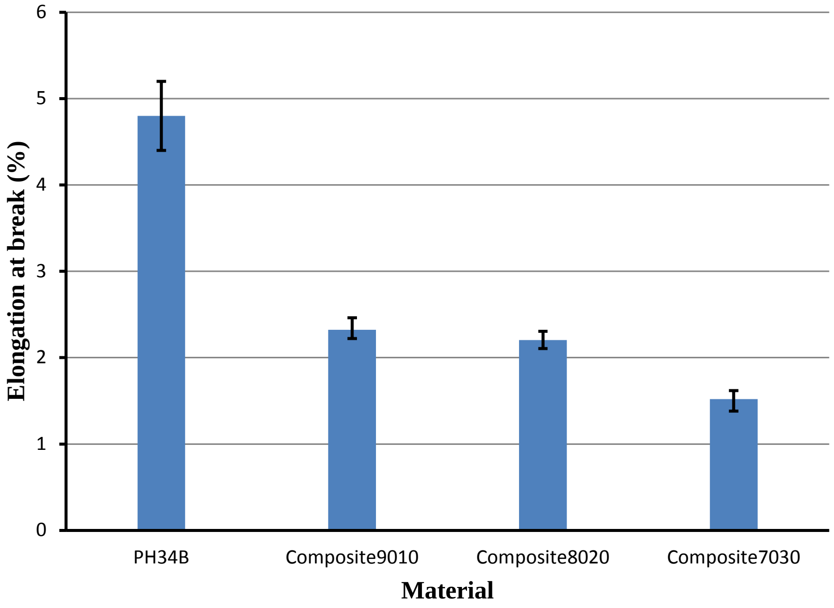


Figure 80: Dependence of elongation at break on the composition of composites

The elongation at break decreases with the increasing of fiber loading and this phenomenon is quite popular and almost observed with composites. Especially, P34HB is a unique polymer whose strain (nearly 5%) is higher than that of bamboo fibers (2.94-3.19%) and the adhesion between fibers and matrix was not good. In most cases, elongation at break decreases when adding fibers, probably fibers are also failed points that can generate a crack or there is a sliding of the fibers in relation to the matrix. Hence, the composites tend to break more quickly when being pulled than the pure polymer.

II.2.3.Flexural test

Flexural test was also performed to determine the mechanical property of the material. Unlike tensile test where stress spreads throughout the specimen, in flexural test the stress is focused in the area of applied load [96].

A flexural test was conducted by INSTRON machine, with the cross head speed of 10 mm/minute and the test was conducted following ISO 178:2010.

R_1 =5.0 mm ± 0.2mm

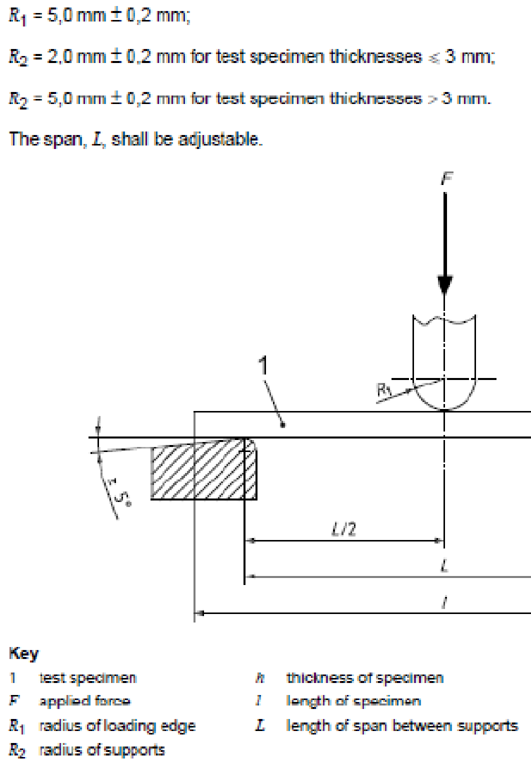
R_2= 2.0 mm ± 0.2 mm for test specimen thickness ≤ 3mm

R_2= 5.0 mm ± 0.2 mm for test specimen thickness >3 mm

The span, L, shall be adjustable

Key

1 test specimen F: applied force; R1 radius of loading edge ; l : length of specimen L:length of span between supports; R_2: radius of supports



R_1 = 5,0 mm ± 0,2 mm;

R_2 = 2,0 mm ± 0,2 mm for test specimen thicknesses ≤ 3 mm;

R_2 = 5,0 mm ± 0,2 mm for test specimen thicknesses > 3 mm.

The span, L, shall be adjustable.

Key

1 test specimen
F applied force
R_1 radius of loading edge
R_2 radius of supports
h thickness of specimen
l length of specimen
L length of span between supports

Figure 81: Position of test specimen at start of test

In this test, the samples were cut into rectangular and the dimension is 2.2 mm in thickness and 13 mm in width, the length of span between supports is 40 mm.

For a rectangular sample under a load in a three-point bending setup, the flexural strength is calculated as the following equation:

$$\sigma = \frac{3FL}{2bd^2}$$

F is the load (force) at the fracture point (N); L is the length of the support span; b is width and d is thickness.

Calculate the flexural modulus, E_f, expressed in MegaPascals, using the following equation:

$$E_f = \frac{\sigma_{f2} - \sigma_{f1}}{\varepsilon_{f2} - \varepsilon_{f1}}$$

Where σ_{f1} is the flexural stress, in Megapascals, measured at deflection s_1

σ_{f2} is the flexural stress, in Megapascals, measured at deflection s_1

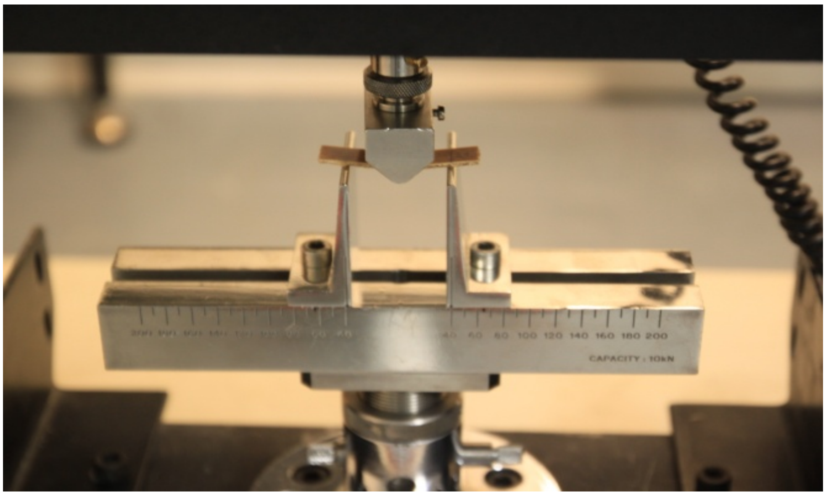


Figure 82: Flexural test on INSTRON machine

Firstly, the composite plates were prepared. The compositions of fibers were 10, 20 and 30% respectively. (40 % of fiber was considered too much for 60% of P34HB to cover).

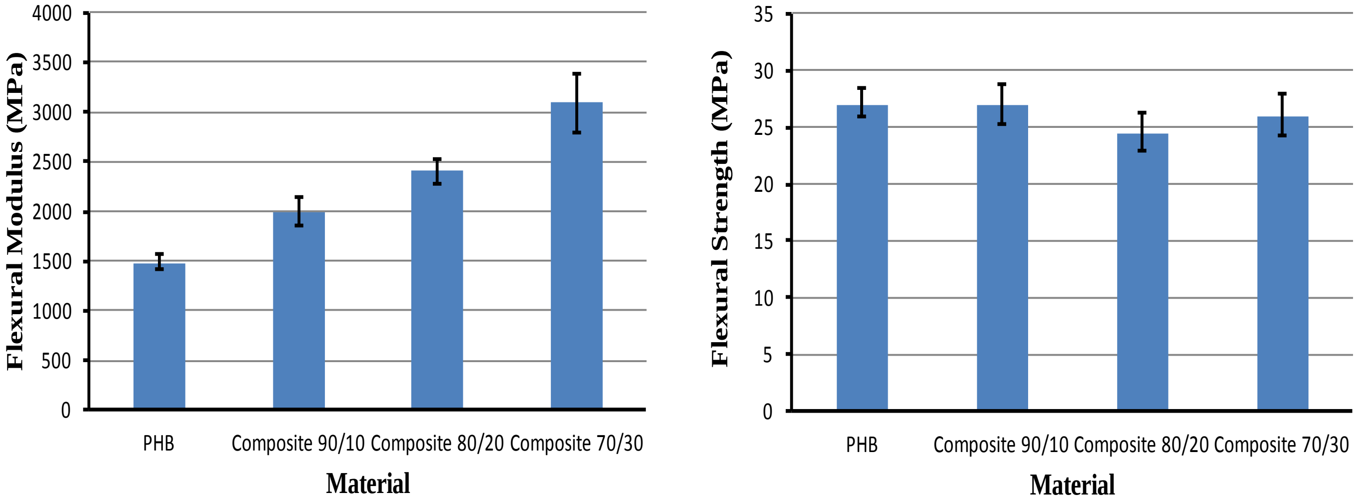


Figure 83: Flexural properties of composite reinforced with acetyl treated fibers

Similarly to the tensile test, the modulus was tremendously increased with the increase of fiber content. The modulus doubles when adding 30% acetylated bamboo fibers compared to the neat P34HB. It contributes to the conclusion that there exists the adhesion between the matrix and fiber that allows the transmission of stress from matrix to fibers leading to the improvement of stiffness [96]. The flexural strength, however, seems to be stable. It does not show any improvement with the increase of bamboo fiber in P34HB – bamboo composition. Bamboo fiber alignment also plays an important role in determining the flexural strength.

II.3. Composite reinforced with Silane treated bamboo fibers

II.3.1.DMA experiment

Storage modulus

The temperature dependence of storage modulus, loss modulus and tan delta of composites reinforced with silane treated fibers is presented in Figure 84, Figure 85 and Figure 86. Similarly, the storage modulus E' tends to decrease with the increase of the temperature because of increased chain mobility of the matrix P3HB –co- 4HB [71]. Also, it can be observed the drop at nearly 50°C that corresponds to the α relaxation temperature while the peak at around 80°C is assigned as the cold crystallization temperature of the matrix [117]. The increase of storage modulus with the fiber content indicates that the fibers increase the polymer capacity to support mechanical constraints with recoverable viscoelastic deformation. The storage modulus, therefore increases with fiber loading which is proved by tensile modulus and flexural modulus.

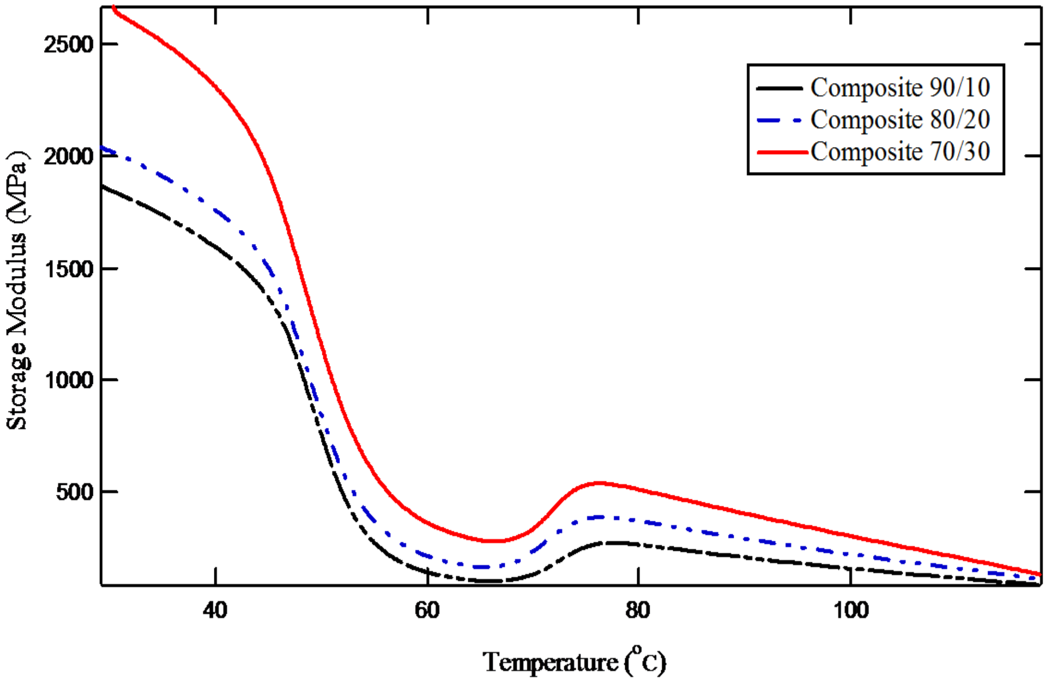


Figure 84: Dependence of storage modulus on temperature

Loss modulus

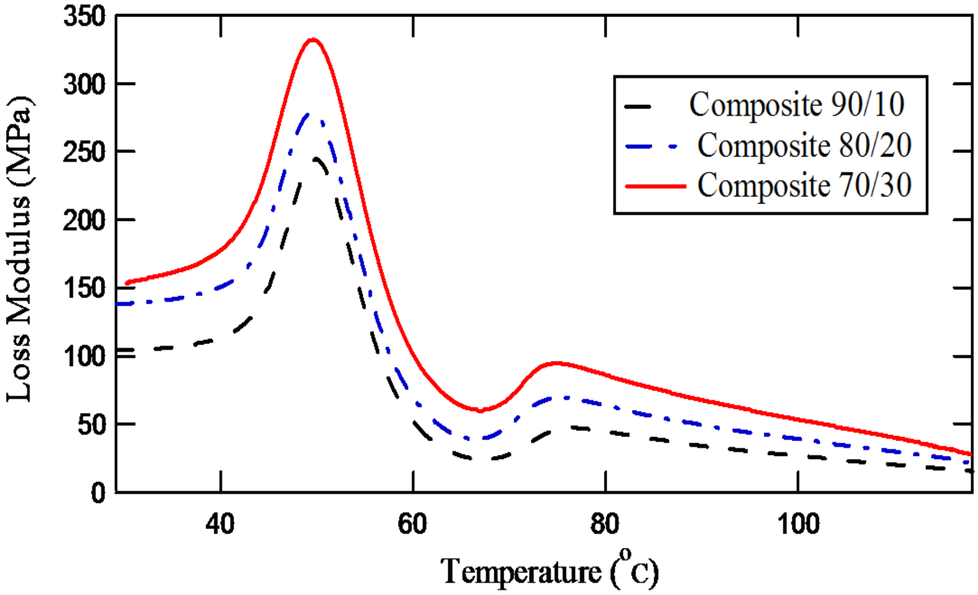


Figure 85: Dependence of loss modulus on temperature

The loss modulus of the material reflects the viscous response or the dampening effect of material. As it is shown in Figure 85, loss modulus again increased with the increasing fiber content. There exist 2 peaks which are assigned to α relaxation temperature and cold crystallization temperature.

Figure 85 depicts that the broader peaks were obtained with the increase of fiber and that the peaks tended to at the similar temperatures with the increase of fiber. If it shifts to lower temperature, the reason can be attributed to an increase in the flexibility of P34HB chains induced by the incorporation of bamboo fibers [117].

Tan delta

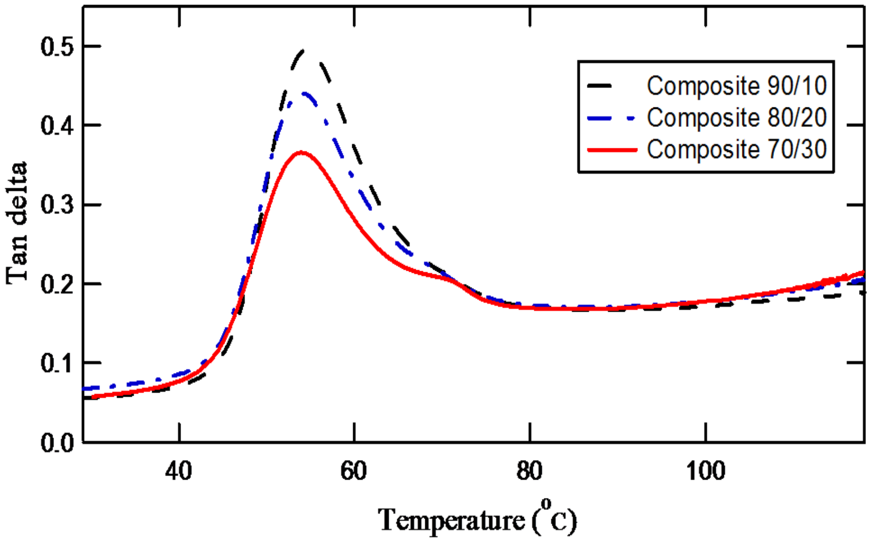


Figure 86: Dependence of tan delta on temperature

Similarly, the tan delta peak height decreased with the increasing bamboo fiber loading in bio-composite. The tan delta peaks had a slight shift to the low temperature (but insignificant), which indicated that the presence of fibers and this presence allow the increase of the mobility of the polymer chains. In fact, tanδ also indicates the composite damping capacity which has a maximum value at the glass transition [118].

As can be seen in the figure the height of tan δ decreases when adding more fiber; means that there exist a connection between fibers and matrix. The fibers are packed inside matrix results in stress transfer from matrix to the fibers [96]. The broadening phenomena of tan δ can be explained that when increasing the fiber content, the molecular relaxation is increased or the mobility of the chains is improved [98,118].

In conclusion, similarly to the results obtained from composite reinforced with acetylated fibers, the storage modulus and the peak of loss modulus increase upon the increase of fiber loading while tanδ decreases. As explained above, there exists an interaction between matrix and fibers. The combined attenuation of bamboo fiber reinforced composites could be mainly caused by the molecular motion of P34HB and the interaction at the bamboo fiber/P34HB matrix interface.

II.3.2.Tensile test

The tensile test was also conducted with composite reinforced with silane treated fibers.

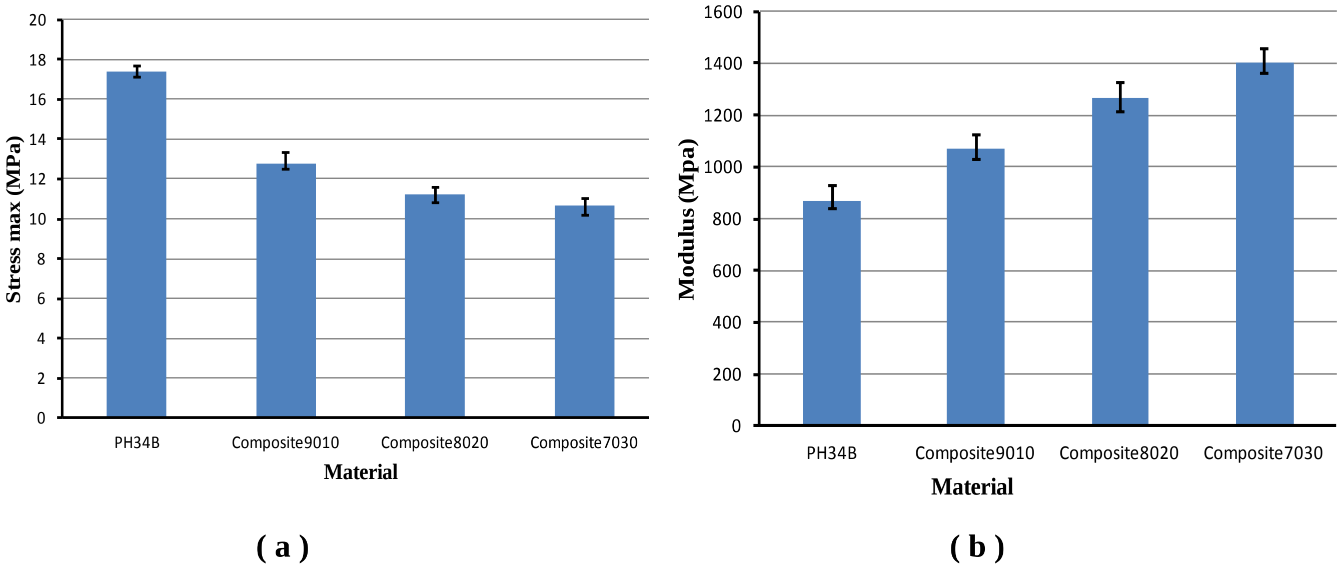


Figure 87: Tensile test for composite reinforced with silane treated fibers

Similarly to the results obtained from composites reinforced with fibers which were modified with acetylated fibers, in this test, the results show the increase in modulus and decrease in stress max (tensile strength) with the increasing of fiber load. Especially, the modulus increases tremendously from approximately 850 MPa of P34HB to 1400 MPa when adding 30% fibers. Increasing trend of tensile modulus of P34HB based composites can be assigned to the compatibility between bamboo fiber and P34HB. Bamboo fiber contains of polar groups that can react with moderate groups of P34HB, thus, provide some opportunity of having a reasonable interaction at the interface between fiber and matrix [96]. On the other hand, the decreasing trend in tensile strength can be attributed to the dewetting effect. According to the theory, under external loading, the interface region of the fiber and matrix undergoes the stress concentration around the bamboo fibers, making the interaction between the fiber and matrix weakens up, and results to debonding at the interface [96]. In summary, the tensile strength decreases and tensile modulus increases with the increasing of fibers. It is explained that tensile strength is more dependent on the matrix and the compatibility between fiber and matrix while tensile modulus is influenced more by the fiber impregnation and fiber aspect ratio [99].

This phenomenon can also be seen with composites reinforced with acetylated fibers.

Elongation at break

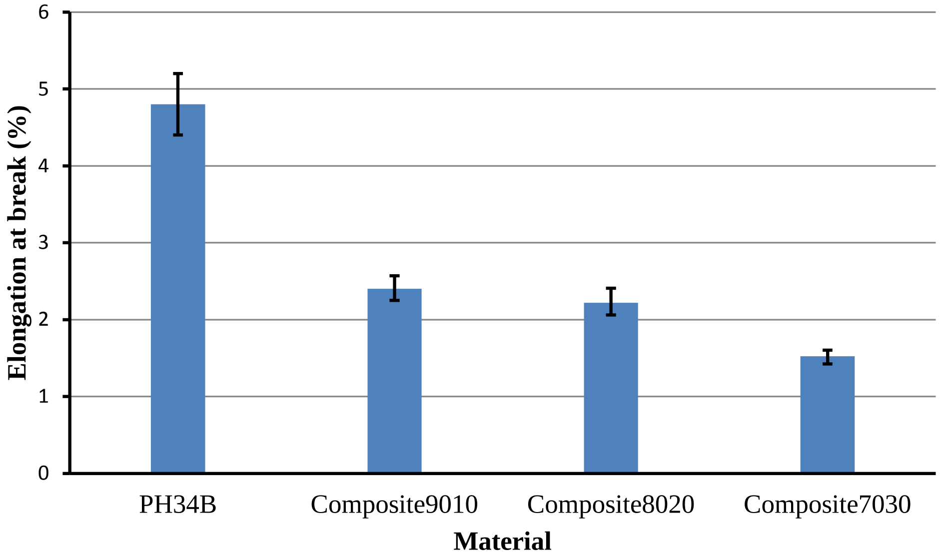


Figure 88: Elongation at break for composite reinforced with silane treated fibers

As can be seen in Fig.88, apparently, the elongation at break decreased with the loading fibers. Long Jiang et al. [70] indicated that in many other natural composites, the strength and elongation usually decreased with fiber content and are lower than those of the neat polymers. The decrease of elongation at break with the increase of fiber content also implies the ductility with improved interfacial action.

II.3.3.Flexural test

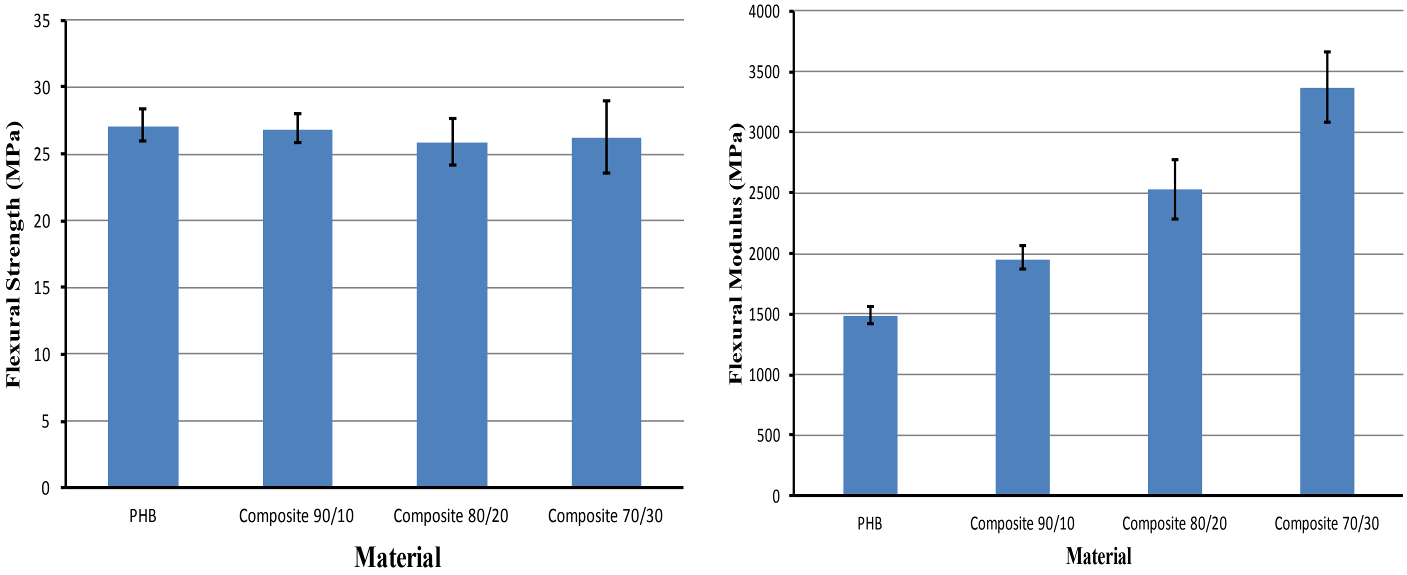


Figure 89: Flexural test for composite reinforced with silane treated fibers.

Similarly to the result that obtained from tensile test, flexural modulus increases tremendously with fiber loading. The flexural strength, however, shows a little declivity when adding more fibers. As explained above, the results indicate that there exist a connection between fibers and matrix that allows the transmission of stress from matrix to fiber thereby increasing the stiffness of the specimen. The flexural strength is stable and does not reveal any improvement. The uniaxially aligned fibers can give a better strength property than the random oriented fibers [96].

We observed that the flexural strength was not improved. In fact, without the presence of coupling agent, it is difficult to improve the strength as the fibers act as the fillers and in most case the strength decreases. However, the modulus increases tremendously. At 30% of fiber, the modulus is approximately two and half times that of neat polymer. This result agrees with other study [119].

II.4. Composite reinforced with acetyl – silane treated fibers

Acetylation and silane treatments have their own advantages. They both help improve the interaction between fibers and matrix. In this study, we think of making a combination of these 2 methods with the aim to improve some properties for the material. In this method, the fiber was firstly immersed in NaOH 0.1N for 3 days and then they were treated with acid acetic. In the last step, those fibers were treated by silane method.

II.4.1. DMA experiment

Storage modulus

We also conducted DMA experiment for composites reinforced with bamboo fibers treated with both acetic acid and silane. The result obtained were quite similar to those with composites reinforced with silane treated fibers or acetylated fibers. For example, the storage increased with the content of fibers and the curve also showed the peaks at nearly 80°C.

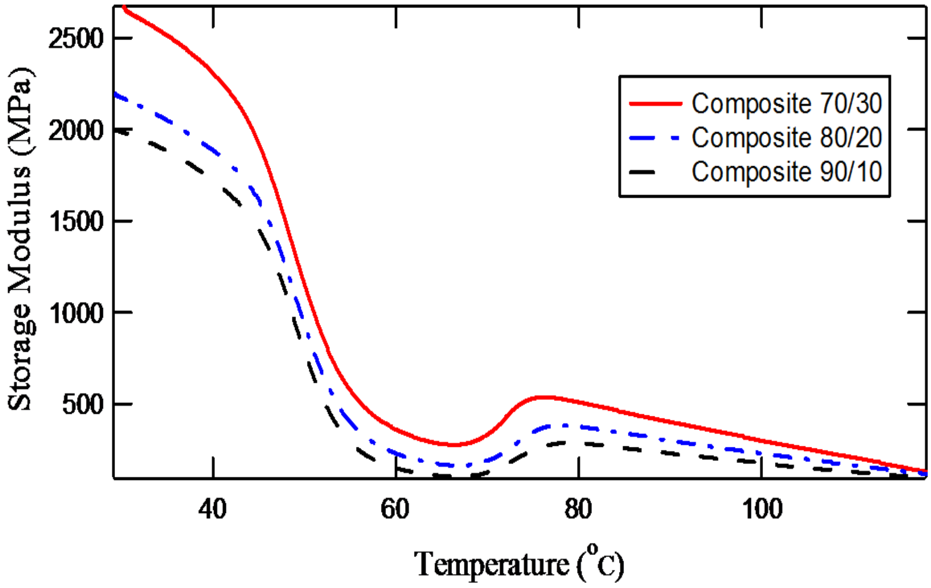


Figure 90: Dependence of storage modulus on temperature

Loss modulus

Similarly, the loss modulus increased when adding more fibers and the peaks are broader. It's clear that there should be an incorporation of fiber and matrix and the broader phenomenon can be attributed to the inhibition of the relaxation process within the composite as a consequence of a higher number of chain segments upon fiber addition [131].The increase of loss modulus with higher fiber content is caused by the more flexibility of polymer.

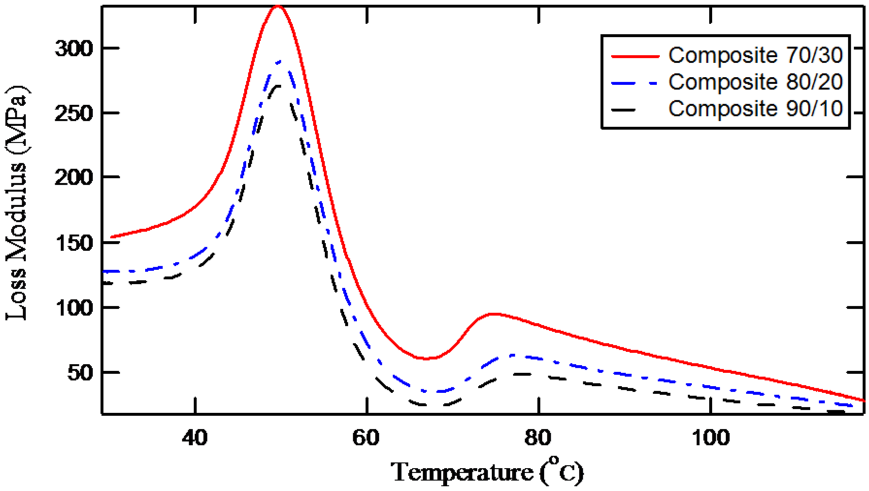


Figure 91: Dependence of loss modulus on temperature of composite

Tan delta

Again, tan δ decreases when adding more fiber proves the existence of a connection between fibers and matrix. Generally, composites containing less fiber load will show the higher peak heights because there is less matrix by volume and there is more energy at the surface because of the increase in the interfacial area [131].

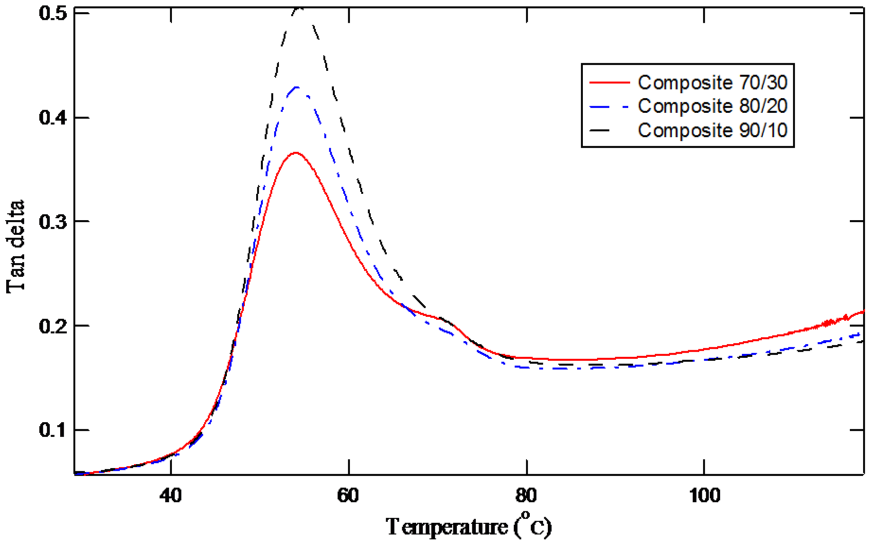


Figure 92: Dependence of tan delta on temperature

In general, the loss modulus and storage modulus increased with the increase of fiber loading while tan delta decreased. As explained above, there exists an interaction between matrix and fibers. The results are consistence with those obtained by composites reinforced with acetyl treated fibers and reinforced with silane treated fibers. All of these methods help to trigger the interaction between matrix and reinforcement.

II.4.2.Tensile test

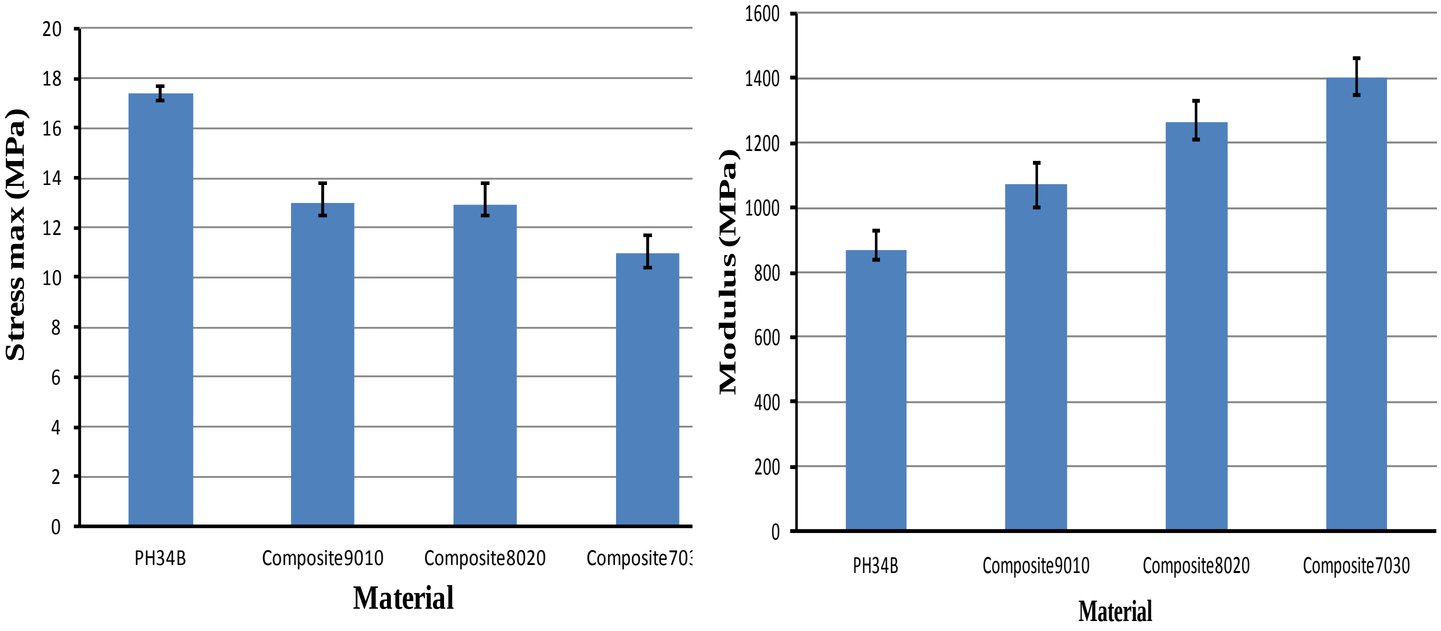


Figure 93: Tensile test for composites reinforced with bamboo fibers treated with both acetic acid and silane

We have used both acetylated method and silane treatment with the aim of improving the compatibility between the fibers and matrix. We expected that there would be more hydroxyl group or –ONa (as the fibers were treated with NaOH) react with acetyl group or silanol.

The tensile test was performed to determine the influence of bamboo fibers to the mechanical properties of the composites. And in fact, only modulus showed the improvement with higher fiber contents. The tensile strength (or stress max), however, showed the decrease with the fiber loading while the modulus increased significantly. The phenomenon is the same as composite reinforced with bamboo fibers which were treated with silane or acetic acid. It suggests that maybe the coupling agent is needed to improve the adhesion between matrix and fibers. The influence of fiber treatments will be presented after.

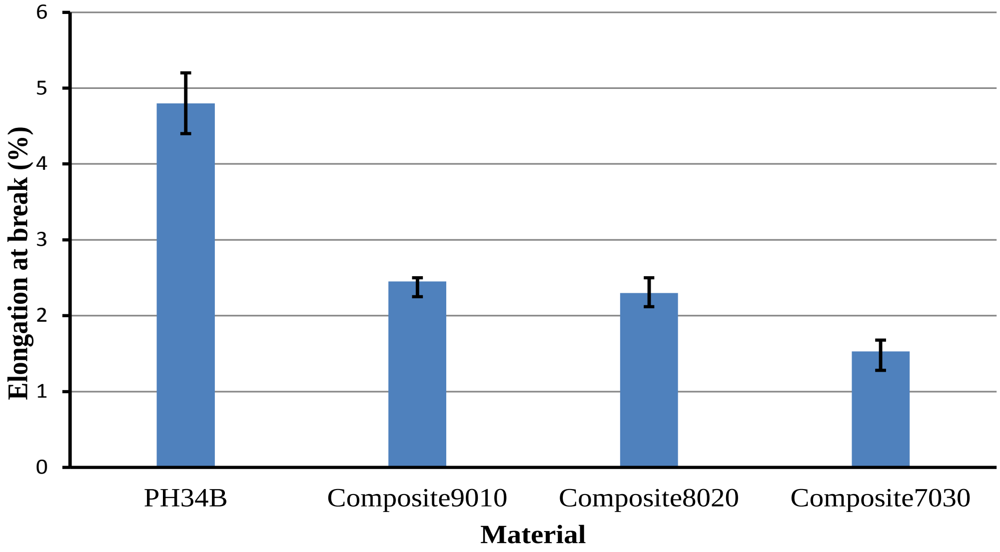


Figure 94: Elongation at break of composites reinforced with bamboo fibers treated with both acetic acid and silane

Similarly, the elongation at break decreased with the loading fibers. Long Jiang et al. [70] indicated that in many other natural composites, the strength and elongation usually decrease with fiber content and are lower than those of the neat polymers. Silane treatment does not help an effect to improve the elongation at break of the composites and this value of composite is lower than that of neat polymer.

II.4.3. Flexural test

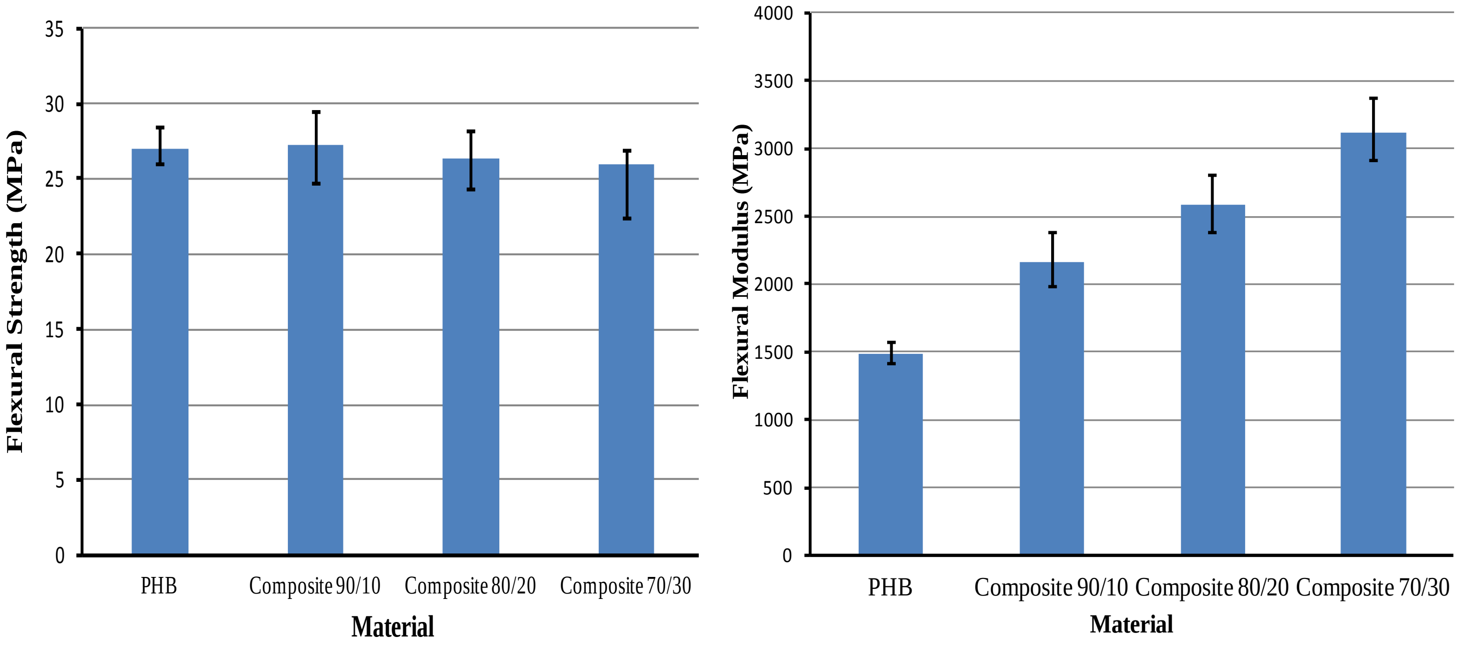


Figure 95: Flexural test for composite reinforced with bamboo fibers (treated by by both acetylated method and silane method)

Flexural test was performed to examine the mechanical property of composites reinforced with bamboo fibers treated with acetic acid and silane. The results showed that flexural strength had a slight increase when adding 10 percent of fibers, indicated that matrix could transfer the stress to fiber. As more fibers were added, the flexural strength slightly decreased because the fibers could not truly compatible with the matrix to achieve the very good adhesion. Improved adhesion between fibers and matrix could make it possible for stress transfer from the weaker matrix to the stronger fiber during loading and thereby improving the strength of the composites [120].

Flexural modulus, however, always revealed the significant improvement with the increase of fiber loading. At 30% of fiber loading, the modulus doubled, in comparison with the neat polymer.

III. General characterization of composite based from P34HB

III.1.Thermal properties

III.1.1. DSC experiment

The crystallinity of the polymer component can be determined by:

$$X\text{c (\% crystallinity)} = \left(\frac{\Delta H_f}{\Delta H_f^0}\right).\frac{100}{w}$$

Where ΔH_f^0 is the enthalpy of 100% crystalline polymer in the composite and ΔH_f is the heat of fusion for the PH3B-co-PH4B phase. The crystallinity depends on the crystallization conditions of polymer matrix [43,102].

$$\Delta H_{of} = \frac{\Delta H_f}{w}.100$$

Where w is the percentage of polymer in composite.

In this study, we compared the crystallinity of the composites only (the composition of P3HB and P4HB unit is unknown thus ΔH_f^0 was impossible to be found). Since ΔH_f^0 is fix, the composites with higher ΔH_f (or ΔH_{of} in the table below) reveal the more crystallinity.

Table 24: DSC result

Composites (Fiber modification methods) (Matrix (wt%)/fiber (wt%))	ΔH_f (J/g)	ΔH_{of} (theory ,assume that composite contain 100% P34HB) (J/g)	Tcc (^oC) (T_{cc1}/T_{cc2})	Tm (^oC) (T_{m1}/T_{m2})
Acetyl-silane 90/10	32.21	35.79	44.1/ 79.6	135.7/ 163.9
Acetyl-silane 80/20	29.32	36.65	42.3/ 78.2	134.4/ 162.7
Acetyl-silane 70/30	27.39	39.13	42.2/ 76.2	133.5/ 161
Silane 90/10	30.79	34.21	42/ 85.7	138.5/ 165.6
Silane 80/20	26.57	32.21	45.1/ 86.2	138.9/ 166
Silane 70/30	21.37	30.53	44.7/ 86.1	138.9/ 166.3
Acetyl 90/10	30.54	33.93	46.5/ 86.2	138.9/ 166.2
Acetyl 80/20	26.11	32.64	44.3/ 86.1	139.4/ 166.3
Acetyl 70/30	22.84	32.63	44.4/ 89.6	138.8/ 166
P34HB neat	***32.21***	***32.21***	***44.8/ 88.7***	***138.7/ 166.2***

According to table 24, as the loading of fiber increases, enthalpy of fusion decreases. It is the reduction in the free volume of PHB that caused the decrease of enthalpy of fusion [102]. Also, the appearance of fibers leads to the limited growth of P34HB spherulite [99]. In the table, ΔH_{0f} is defined as the ratio between ΔH_f and the percentage of P34HB (by weight).

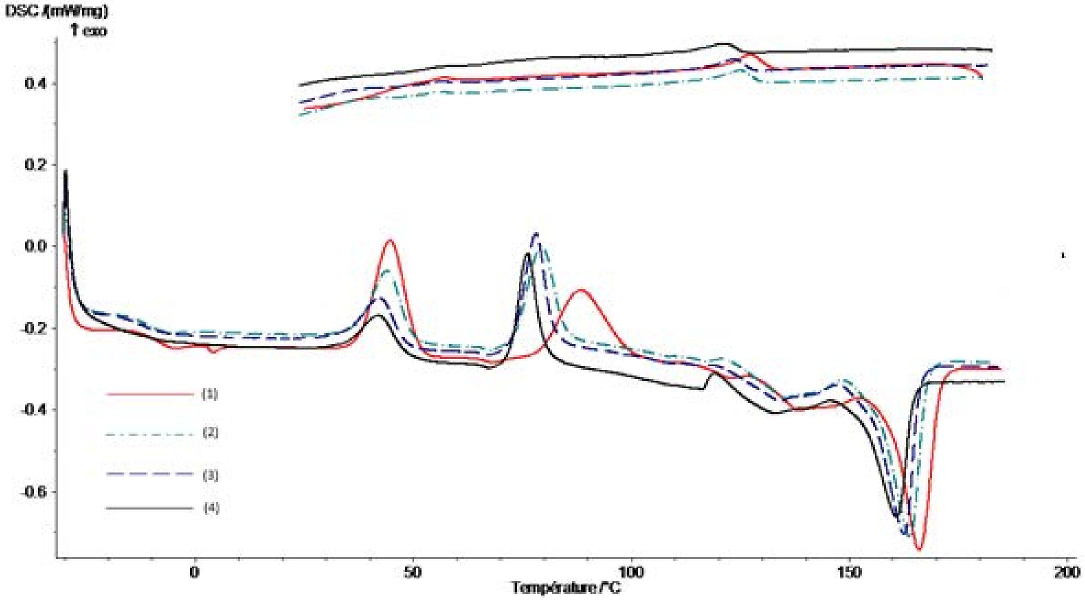


Figure 96: DSC results of composites from P34HB reinforce with bamboo fibers (treated by both acetic acid and silane)

Where (1): P34HB neat; (2): P34HB- acetic acid/silane treated fibers 10% (by weight); (3): P34HB- acetic acid/silane treated fibers 20% (by weight); (4): P34HB- acetic acid/silane treated fibers 30% (by weight)

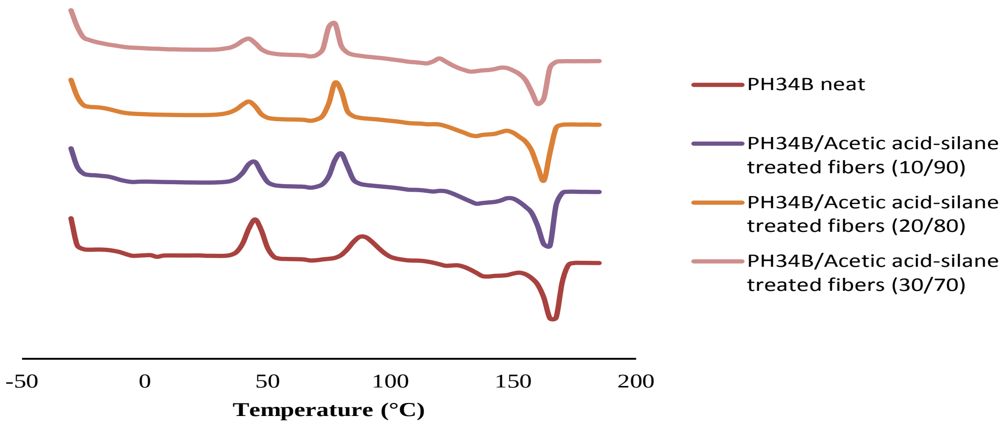


Figure 97: DSC results (heating process) of composite from P34HB reinforced with bamboo fibers (treated by both acetic acid and silane)

As can be seen from the figure, when bamboo fibers are added to the matrix to produce polymer composite, the basic information of P34HB has not changed much. The two cold crystallization temperatures and the two melting points remain at around 44^{o}C; 86 – 89^{o}C and 135-140°C and 166^{o}C, respectively.

According to the results obtained, for composite reinforced with acetyl- silane treated fibers; the calculated enthalpy increases with the increase of loading fibers and higher than that of P34HB neat. It suggests that the degree of crystallinity increase, the result matches with the reference [114]. For fibers modified with silane and acetic acid separately, the calculated enthalpy shows the insignificant decrease. The degree of crystallinity is decided by the competition between two processes. One is the nucleation effect of fillers which improves the crystallization and the other is the hindering effect of fillers that leads to the restriction of the polymer movement [105]. Fibers treated with the combination of two methods (both by acetic acid and silane methods) improve of crystallinity of composites since enthalpy of fusion increases with fiber loading. It proves that in this case, the nucleation effect dominates the competition. The increase in crystallinity might result in the better stiffness of composite.

The Tc and Tcc seem not to be significantly affected by adding fibers, the Tc, Tcc of composites are slightly smaller than that of the neat polymer. Wulin Qiu et al. gave the result with the increase of Tc, they explained that a remarkable increase in the crystallization temperature (*Tc*) was due to the cellulose fibers acting as an efficient nucleating agent for the crystallization of polymer (Poly Propylene in their study) [115]. In another publication, Daniel T. Q insisted on the importance of surface treatment of cellulose fibers, cooling rate and filler content on the crystallinity process and that the surface treatments of the cellulose can remarkably reduce the transcrystalline nucleated structure [116]. Seung Hwan Lee insisted that by adding LDI (Lysine-diisocyanate) (a coupling agent) and bamboo fibers, the crystallinity of the composite was higher than the neat polymer and also his results showed that the Tc shifted to the higher values. He explained that it was caused due to the nucleation effect of the BF (bamboo fiber) and LDI [87].

The fiber modification methods may act a role to the crystallinity of polymer composites. In this case, 3 methods are compared. The same quantities of fibers (20% by weight) were used for the composites in all cases. It reveals that fibers treated with acetic acid and followed by silane contributes to the higher crystallinity of composite (by comparing the enthalpy of fusion) as it acts as the nucleating agent. It is appropriate with the results obtained from mechanical tests because normally composites with higher crystallinity give better mechanical properties.

Table 25: DSC results for composite reinforced with bamboo fibers (treated with different methods)

Composite	ΔH_f (J/g)	ΔH_{of} (theory ,assume that composite contain 100% P34HB) (J/g)	Tcc (°C) (T_{cc1}/T_{cc2})	Tm (°C) (T_{m1}/T_{m2})
Acetyl-silane 80/20	29.32	36.65	42.3/ 78.2	134.4/ 162.7
Silane 80/20	26.57	32.21	45.1/ 86.2	138.9/ 166
Acetyl 80/20	26.11	32.64	44.3/ 86.1	139.4/ 166.3
P34HB neat	***32.21***	***32.21***	***44.8/ 88.7***	***138.7/ 166.2***

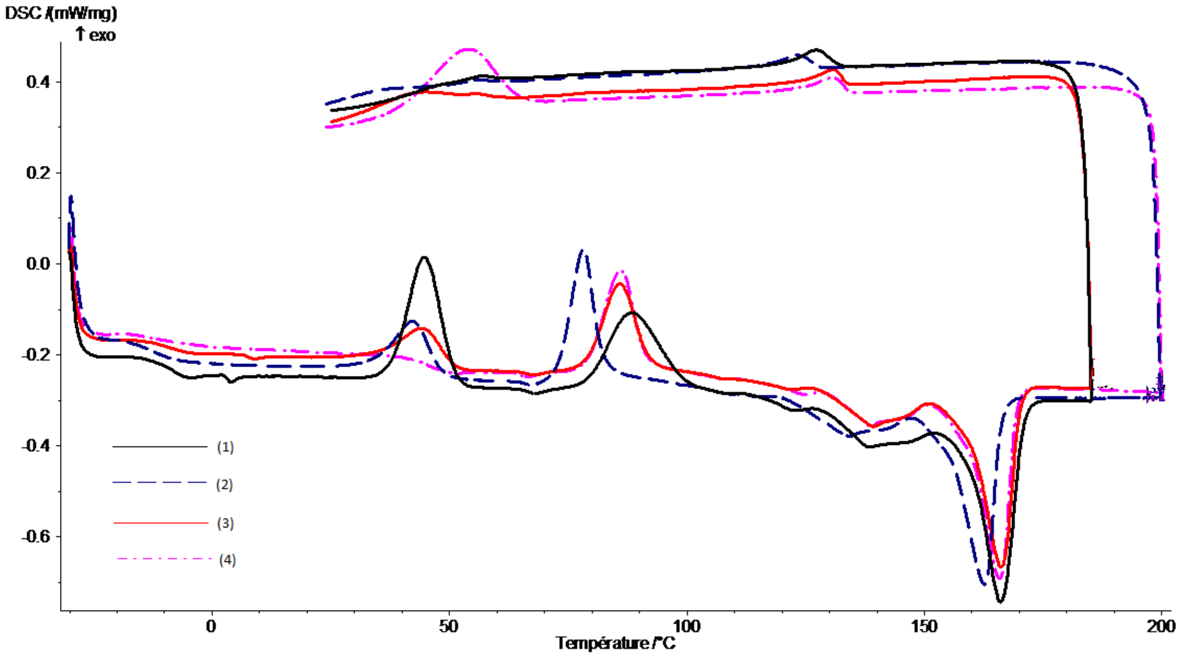


Figure 98: DSC results of composite from P34HB reinforce with bamboo fibers (treated by different methods)

Where (1): PH34B neat; (2): composite from P34HB and fibers treated with acetic acid and silane ; (3) composite from P34HB and fibers treated with acetic acid; (4): composite from P34HB and fibers treated with silane.

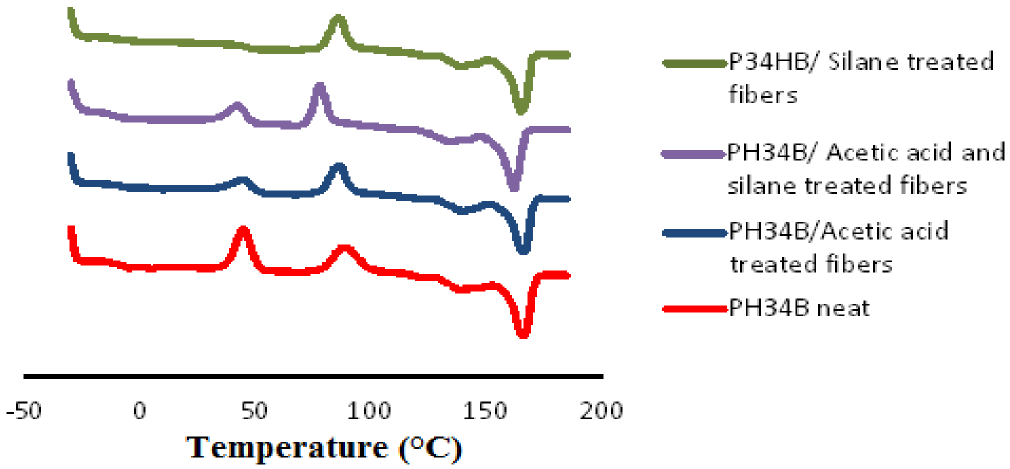


Figure 99: DSC results (heating process) of composite from P34HB reinforced with bamboo fibers (treated by different methods)

III.1.2. DMA experiment

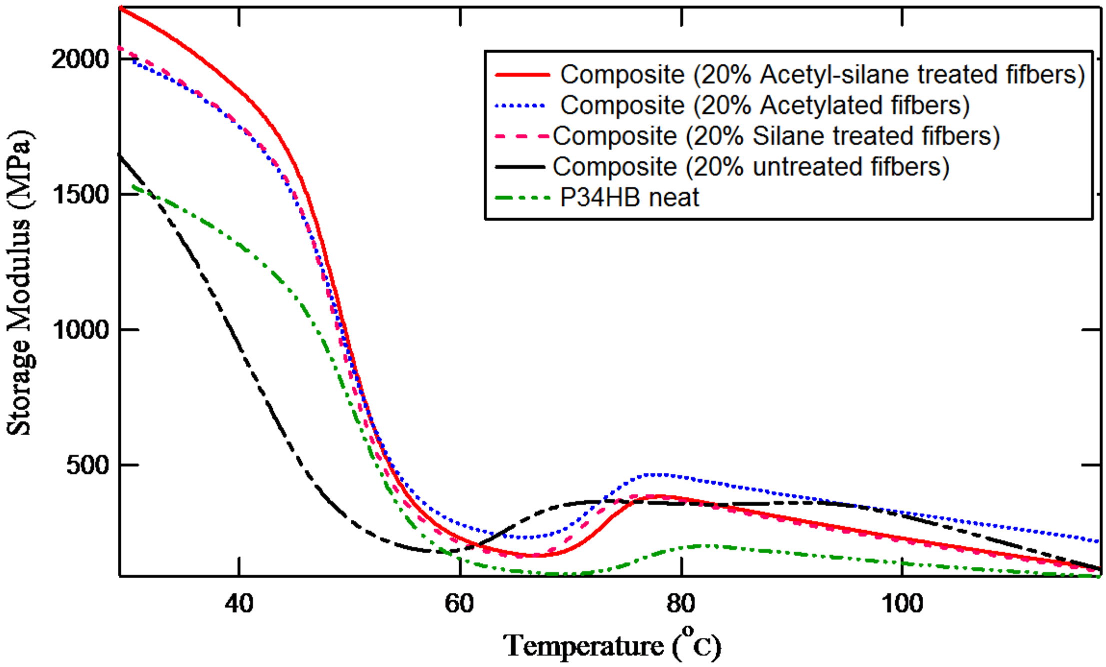


Figure 100: Storage modulus

Figure 100 shows the storage modulus of composites 80/20 reinforced with different kinds of fibers. The results allow us to understand that the fibers treated with aceyl-silane or silane nearly the same and have the highest values.

As can be seen, the composite reinforced with Acetyl – silane treated fiber shows the highest value of storage modulus while that of the composite reinforced with untreated fiber is the lowest. It suggests that the adhesion between P34HB matrix and bamboo fiber was much improved by the treatment. This DMA result shows variation of main relaxation temperature, which can be linked to interactions resulting in a decrease of chain mobility and to a regular reinforcing effect [66].

III.1.3. TGA experiment

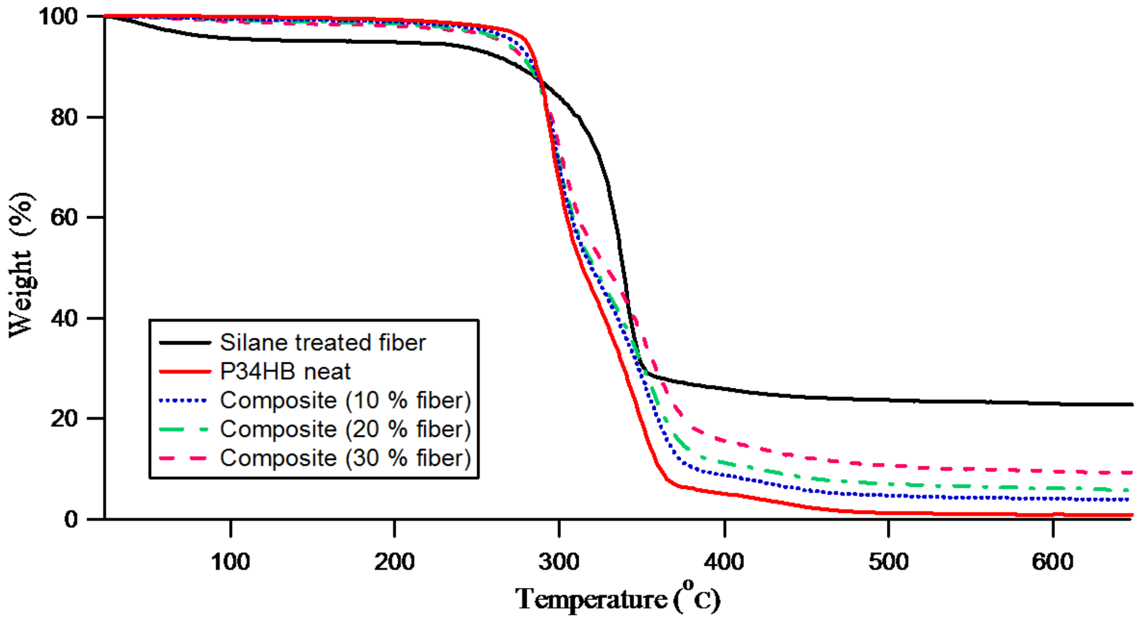


Figure 101: Dependence of thermogravimetric analysis (TGA) curves on fiber compositions of composites based from PBS matrix.

The TGA curve reveals that P34HB undergoes thermal degradation in 2 processes at 300°C and 360°C and almost achieve 0% (almost degraded) at approximately 500°C. Above 500°C, P34HB almost decomposes, thus, a plateau curve was obtained.

According to the behavior curves from Figure 101, when the fibers were added in the matrix, the TGA curve shifted upward, to the fibers neat curve. Means that, the more fibers were added, the closer the behavior curve approached to fiber curve. The curve of 20% fiber composite is in between the curves of 10% and 30% fiber composites and all these curves are between the curves of fiber and P34HB neat. The composite curves reached the plateau of between 5 to 10% mass remain depending on the fiber contents, the more fibers were added the more composites remained. It matches with the degradation of fiber and P34HB neat under temperature. At 650°C, P34HB almost decomposed while the thermal degradation of fibers was stable at around 20% mass remain. As referred, the fibers undergo the process of degradation at around 280°C which is characteristic of low molecular weight components, such as hemicelluloses [87] (it is the thermal depolymerization of hemicelluloses and glycosidic linkages of celluloses) and 340°C corresponding to the cellulose decomposition. Composite is perhaps the combination of the thermal property of fiber and PHB neat. In the curves of composites, the degradation is more than that of fiber and less than P34HB. It was verified that the degradation temperature was shifted to a lower temperature of around 350°C showing that the presence of silane treated bamboo lowered the thermal stability of the polymer [108]. The composite curves showed the higher residue of composites at the end of process than the matrix and lower residue than fibers [82], [87]. In this case, the silane functionalization probably formed siloxane bridges between fibers and matrix during the degradation [107, 108]. And perhaps, these siloxane bridges enhanced the interfacial interaction which favored higher thermal stability [107]. It proves the effect of bamboo fibers to the thermal property of matrix.

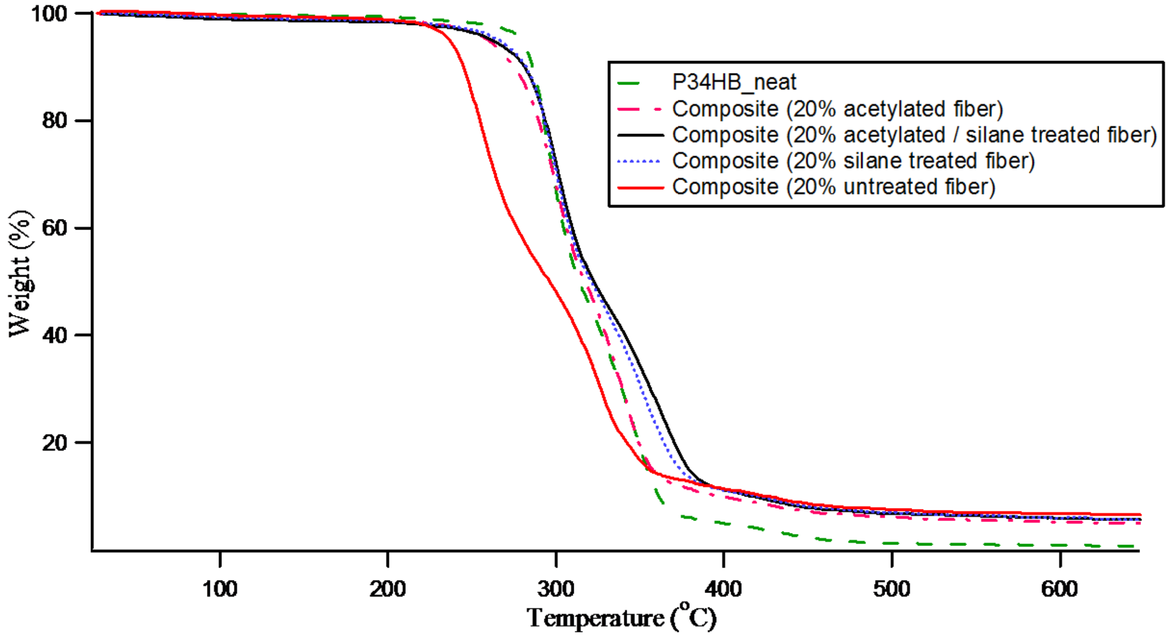


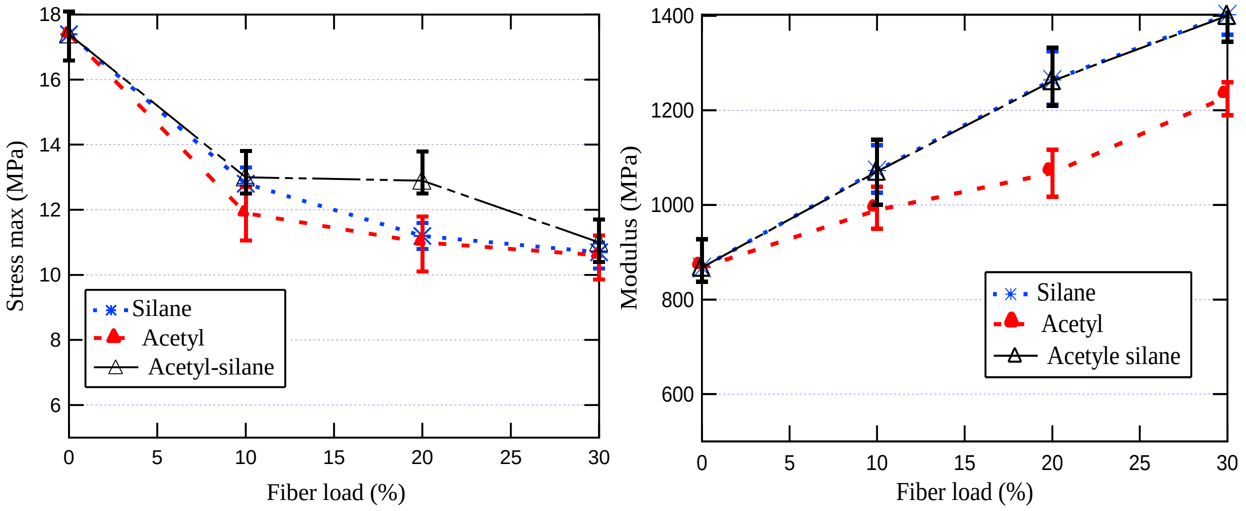
Figure 102: TGA curves of composite with fibers treated from different methods.

The TGA behavior curves for 4 kinds of composites showed consistently with the curves obtained from 4 kinds of fibers. For example, the relative location of untreated fibers and treated fibers are the same with that of composite reinforced with untreated fibers and composites reinforced with treated fibers. As usual, the TGA curves showed that P34HB-based composites undergo quick thermal degradation above 340°C, similarly to the neat polymer because the matrix dominate in composites. The composite curves are always in between the curves of polymer neat and the corresponding bamboo fibers. Composites degraded less than the neat of P34HB and after the process, there is still the residue of composites. The more fibers were added, the more composite curves shift to the curves of corresponding fibers. In the figure, the composites started to degrade at around 260 -280°C.

III.2. Mechanical properties

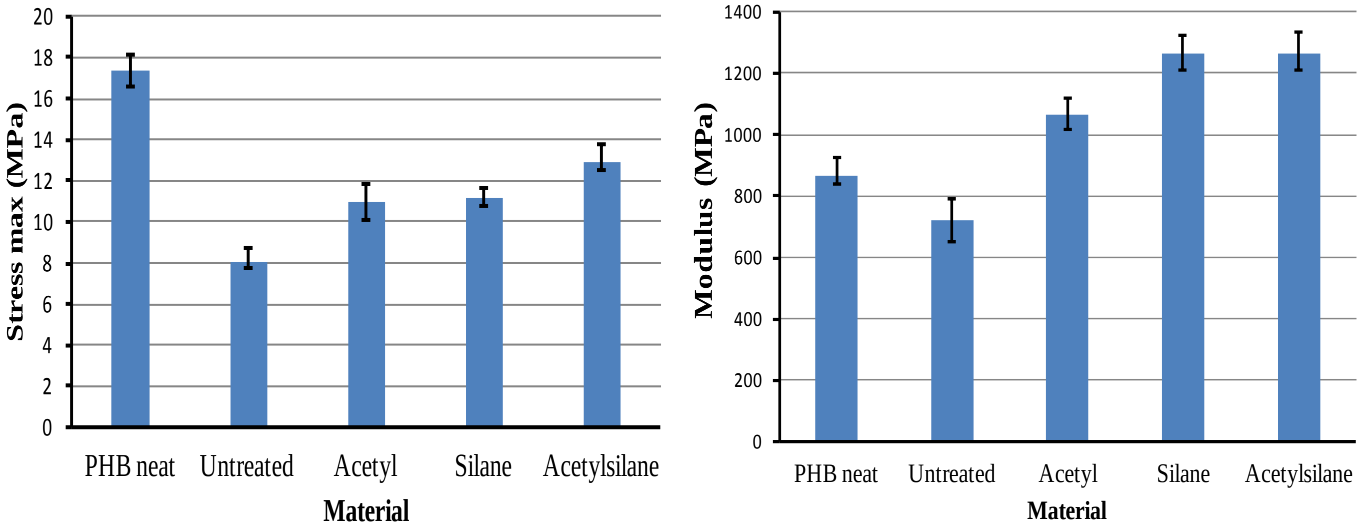
III.2.1. Tensile property

Tensile test was conducted to determine the mechanical property of material. As mentioned above, there are some decisive factors in determining this property, including the characteristic of fibers, preparation method, fiber orientation and interfacial adhesion. In this study, we focus on modifying the fibers, means that we improved the adhesion between fibers and matrix [70, 99]. Comparing to the untreated fibers, composites reinforced with treated fibers showed the better strength and modulus. Fig.104 (b) showed that the modulus composite (20% fibers by weight) reinforced with bamboo treated by both acetylated method and silane was two times as much as the one reinforced with untreated fibers (20% fibers by weight). Similarly, the strength (stress max) was significantly improved (Fig.104 (a)). These results prove that the modification of fibers play a role to improve the strength of composite. Besides, of all the using methods were used, the method combining both acetylated treatment and silane treatment exhibited the best results. However, except for modulus, the strength was not improved by adding fibers compared with the neat polymer. The strength was even worse when adding short bamboo fibers suggested that the adhesion needed to be further improved even that there is an interaction between fibers and matrix since they both have the polar groups [94]. The modulus increased tremendously, it is due to the presence of fibers because the fibers have much better modulus than the matrix. However, the interface region of fibers and matrix was weak, resulting to debonding at the interface. Hence, the tensile strength decreased with the increase of loading fibers. The compatibility between matrix and fiber is the decisive factor to the tensile strength while the modulus depends mostly on the fiber aspect ratio [99]. In the Figures 103 and 104, composites reinforced with 30% fibers are the highest in modulus but lowest in strength.



(a) (b)

Figure 103: Influence of fiber load to the strength of composites by tensile test



(a) (b)

Figure 104: Influence of fiber treatments to tensile strength of composites (at 20% of fiber loading)

In Figure 106, tensile strain (elongation at break) showed a significant change, decreasing by nearly 2.4% when adding 10% fiber into the neat P34HB (by weight). The strain continued to decrease, but slightly, when more fibers were added. This is attributed to the adhesion between the matrix and the fiber and because P34HB itself has better strain than bamboo fibers as described above. However, the modification improved the elongation at break as showed in figure 105. According to the results, composite from untreated (20% fibers by weight) fibers had the lowest elongation at break while acetyl-silane treated fibers showed the higher value. It is because the treatment for fiber induced the better compatibility between fiber and matrix. The physical force could be migrated from the fiber surface into the matrix, hence, slightly increase the strain [65].

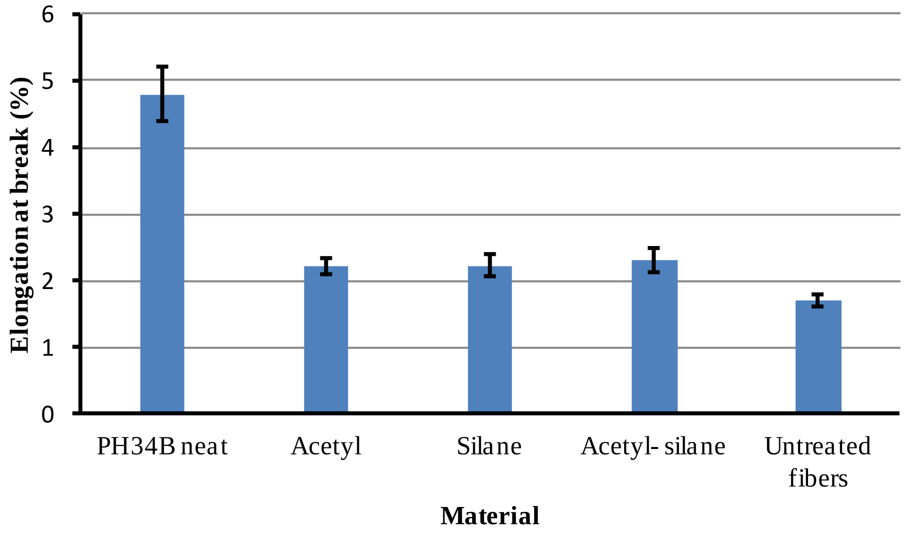


Figure 105: Influence of fibers to the strain of composites (at 20% of fiber loading) via tensile test

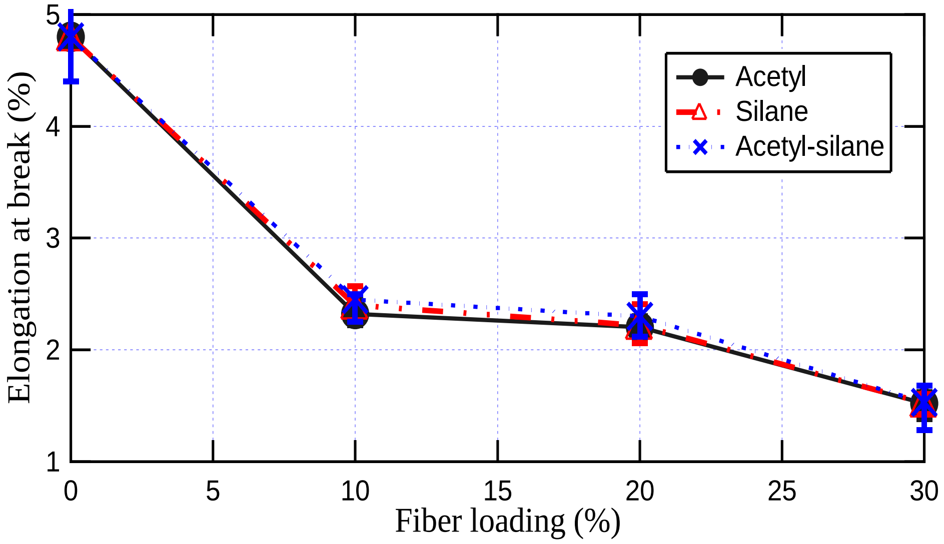


Figure 106: Influence of fiber contents to the strain of composites via tensile test

III.2.2. Flexural property

Flexural test was also performed to determine the mechanical property of the material. Unlike tensile test where stress spreads throughout the specimen, in flexural test the stress is focused in the area of applied load [96].

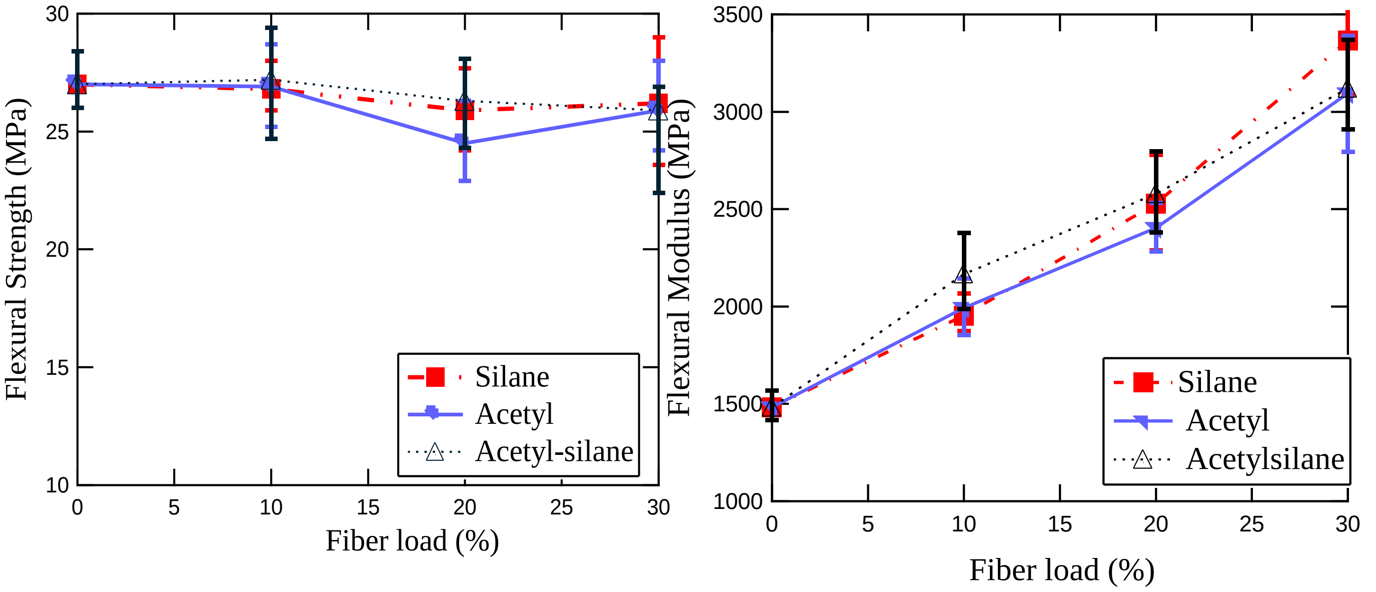


Figure 107: Influence of fiber contents to the mechanical property of composites via tensile test

Similarly to the tensile test, the modulus was tremendously increased with the increase of fiber content. The modulus even doubles when using 20% acetyl – silane treated fibers in the composite, compared with the neat P34HB or composite reinforced with 20% untreated fibers. It contributes to the conclusion that there exists the adhesion between the matrix and fiber that allows the transmission of stress from matrix to fibers leading to the improvement of stiffness [96]. The flexural strength, however, is nearly the same with P34HB neat when adding 10% of fiber and it slightly decreased when the fiber contents were 20% and 30%.

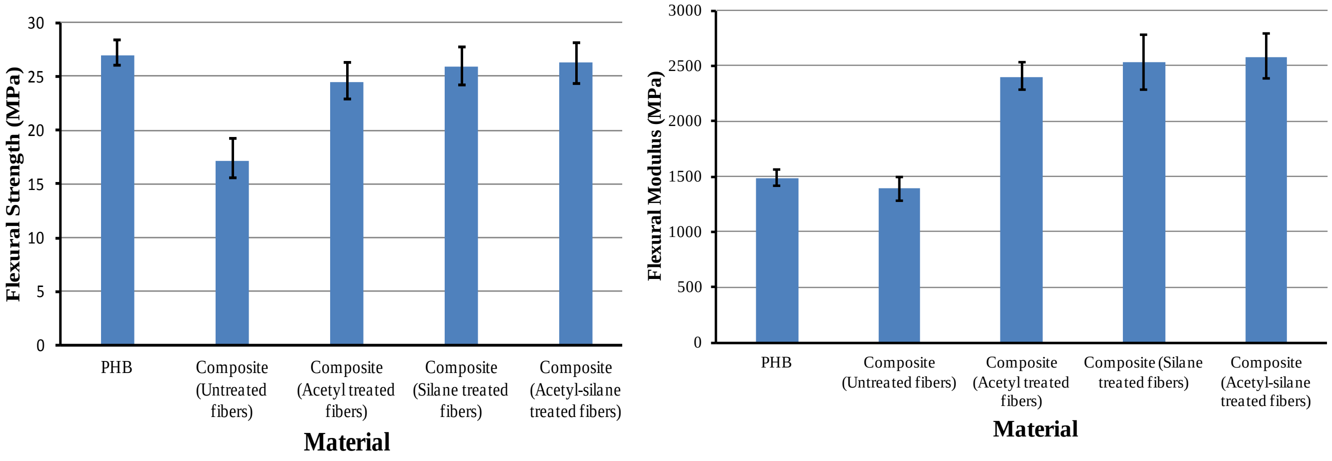


Figure 108: Influence of fiber treatments on flexural strength of composites

Again, composite reinforced by fiber treated with acetyl following by silane method allowed the much better strength than the one reinforced with untreated fiber. Modulus was even doubled by replacing untreated fibers by the treated ones. Also, 20% exhibited the good composite that is good for both strength and modulus.

III.3. Water absorption property of composite based from P34HB

Water absorption is an important property of the degradable composite reinforced with plant fibers. In this experiment, the composites were cut into specimens sized 60 x 13 x 2.2 mm. Then the samples were immersed in the capped bottles. There are 11 kinds of samples, they are:

- P34HB neat
- Composite reinforced with untreated fibers (80/20; P34HB/ fiber by weight)
- Composite reinforced with fibers modified with silane (90/10; 80/20; 70/30)
- Composite reinforced with fibers modified with acetyl (acetylated) method (90/10; 80/20; 70/30)
- Composite reinforced with fibers modified with acetyl-silane (90/10; 80/20; 70/30)

In the last step, the bottles with distilled water and samples were kept inside the oven at specific temperatures (30; 40 and 50°C).

Figure 109: Sample bottles in the oven

In this experiment, the rectangular pieces of composites were firstly weighed to determine the mass before immersion (m_1) then they were immersed for the certain time. After that, the composites were taken out and wiped carefully using the towel and tissues. Then, the specimens were weighed again to determine the mass after immersion process (m_2). The ratio of the difference mass and the original mass gives the value of water absorption as the following equation:

$$W = \frac{m_2 - m_1}{m_1} 100\%$$

The three following figures show the obtained results:

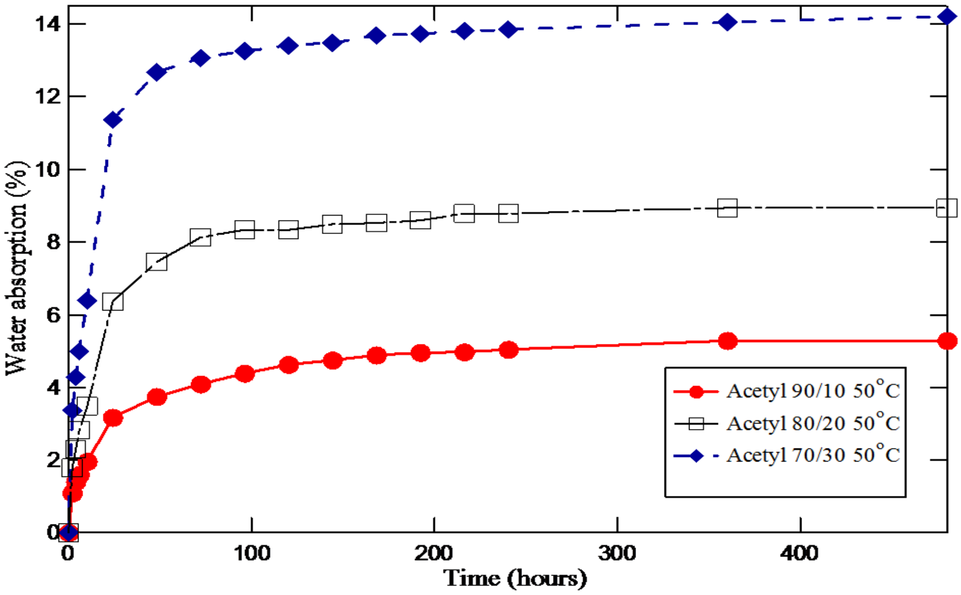


Figure 110: Dependence of water absorption on the compositions

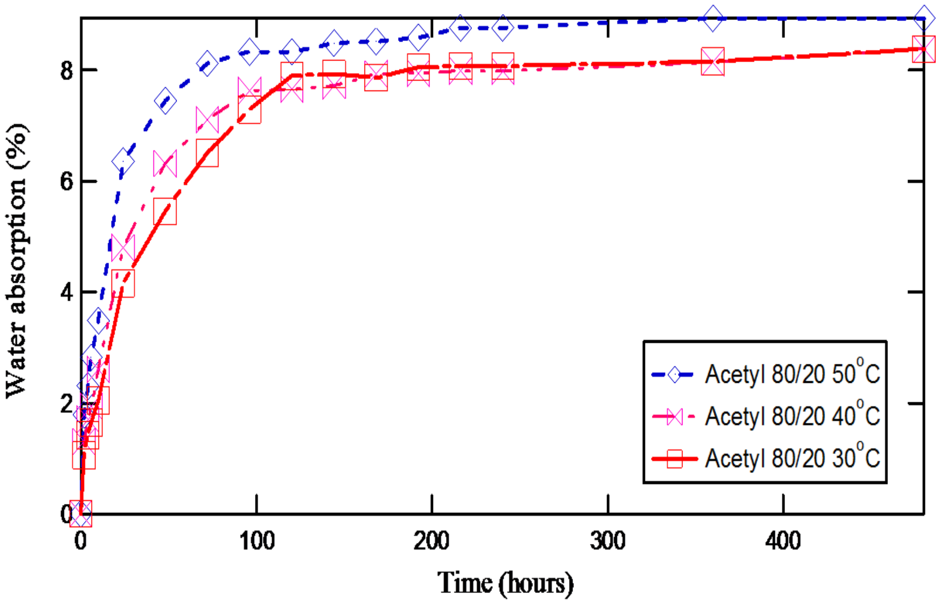


Figure 111: Dependence of water absorption on the temperature

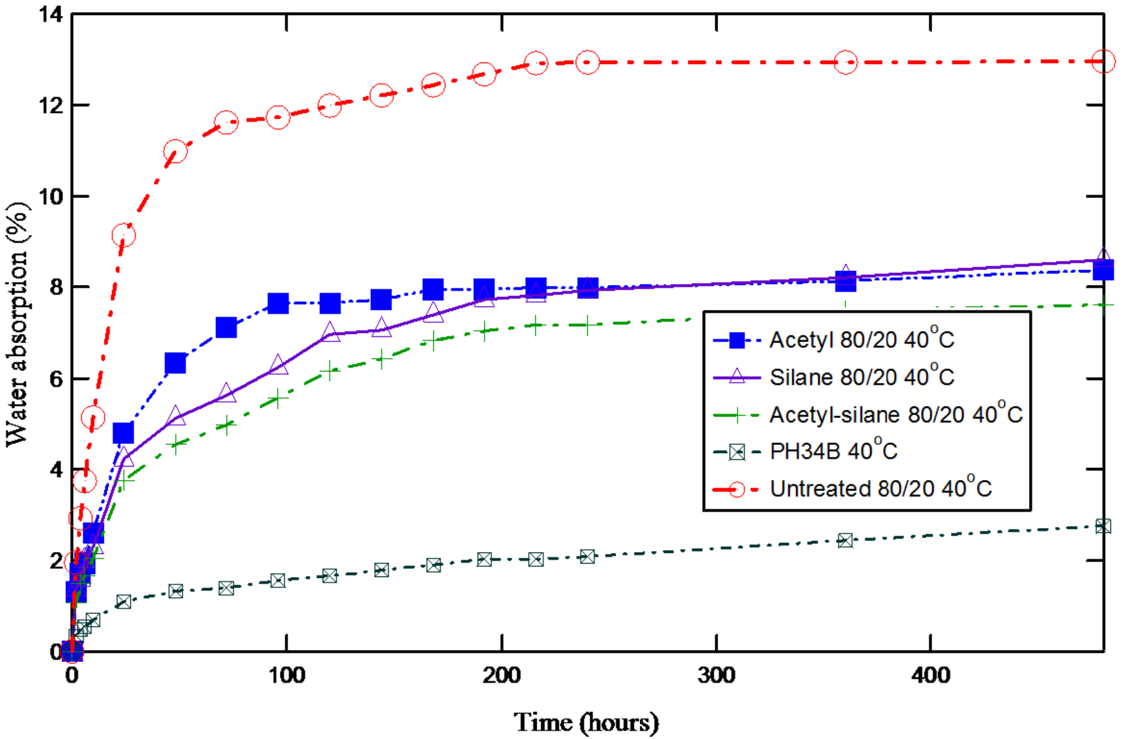


Figure 112: Dependence of water absorption of the composites and matrix

In this experiment, P34HB is more hydrophobic than bamboo fibers. Hence, the water absorption increases with the adding filler (bamboo fibers) into the composites as it is shown in Figure 110. Not only the hydrophobic property of bamboo fibers that cause the increase in water absorption, but it is also the addition of fibers leads to the formation of more holes, voids inside composites and these voids make good condition for water to leak in. Therefore, the increase of fiber content results in higher water absorption. For instance, the absorption triples from nearly 5% at 10% bamboo fibers to approximately 14% at 30% bamboo fibers (at equilibrium state). Also, the temperature affects to the water absorption. It is likely that the water absorption increases with the increase of temperature. It may be not clear with the case of 30°C and 40°C where the equilibrium state seems to be overlapped. However, it is clear that the temperature triggers the speed to achieve the equilibrium state (Figure 111). The higher the temperature is, the more quickly the water absorption of composites achieve to equilibrium state.

In Figure 112, it can be seen that the kinds of fibers affect a lot to the water absorption. The composite reinforced with untreated fibers absorbed much more water than the modified fibers. It also proved that the 3 kinds of modified fibers had the very similar water absorption property. P34HB also exhibited that it is much more hydrophobic than the reinforcement – bamboo fiber. It means that P34HB prevents the water from entering the composite and it restricts the impermeability or in another words, it makes bamboo fibers more difficult to swell inside the composite [71, 94, 95]. Composite reinforced with acetyl-silane treated fibers has the lowest value of water absorption, this result confirms the best adhesion between that type of bamboo fiber and P34HB and the more hydrophobic property of acetyl-silane treated fibers.

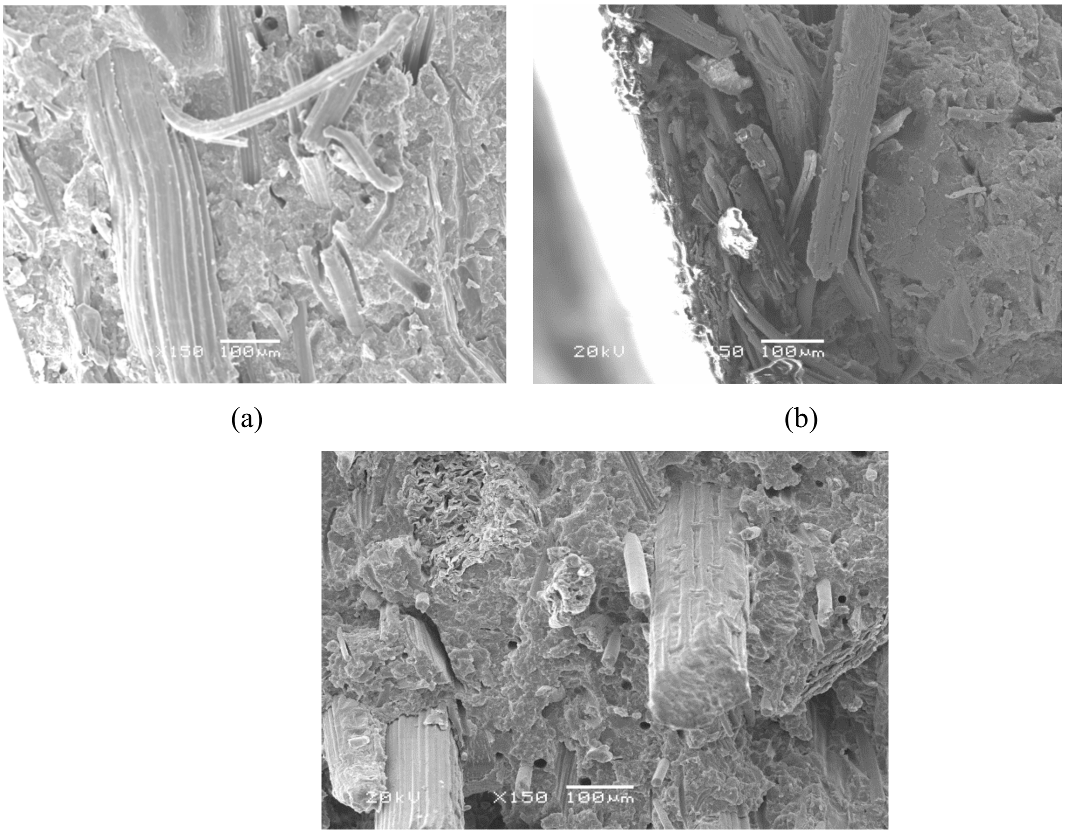
Also, the data proved that at 50^{o}C after 30 days, the composites tended to decompose due to the hydrolysis of P34HB. While at 30^{o}C or 40^{o}C, the sample mass was stable.

IV.Morphology of composite based from P34HB

Scanning Electron Microscopy (SEM) investigation

The morphology was investigated by observing the fractured surfaces via Scanning Electron Micrograph. The composite fragments were obtained by breaking the specimen in liquid nitrogen. Prior to the observation, the specimens were all coated with gold by plasma sputtering device.

The study of the sample morphology was conducted with a lanthanum hexaboride (LaB6) electron microscope (JEOL JSM-5400LV) operating at 0-30kV. To avoid the charging effects, the specimens were coated with a conductive gold layer (thickness ~10 nm). An accelerating voltage of 20 kV was used to collect SEM photomicrographs.



(a) (b)

(c)

Figure 113: SEM micrographs of fracture surfaces of P34HB/untreated fiber (UT) (a, b) and PH34B/Acetyl-silane treated fiber (AS) (c) composites.

In the Figure 113 (a) and (b): micrographs of P34HB/untreated fiber composite captured at different locations; (c): micrographs of P34HB/Acetyl-silane treated fiber composite.

Figure 113 shows the SEM micrographs of the surfaces after being broken in liquid nitrogen. The two specimens of composites contain the same quantity of bamboo fibers (20% by weight). The images reflect the mechanical properties of the composites. There are still holes inside. These holes maybe the breakages remained when the fibers were pulled out. Composites reinforced with AS fibers shows the better compatibility with the matrix, the leak between fibers and matrix is smaller. The fibers seemed to be well covered by the resin. In the case of treated fibers (AS fibers in the figure), it can be observed that fibers were embedded in the matrix and the links between fibers and matrix seem to be stronger than that of untreated fibers and matrix. It reflects the improvement of adhesion between AS fibers and matrix. Hence, the mechanical properties of AS composite are improved.

V. Conclusions

In general, poly 3,4 hydroxy butyrate (P34HB)/bamboo fiber composites were prepared by internal mixer and compression molding. The tensile strength, flexural strength, modulus and thermal properties were investigated. It was found that the modulus was significantly improved, however, the strength of the composite decreased and the elongation at break was lower than the neat polymer since the adhesion between matrix and reinforcement was not good enough. The study revealed that modifying the fiber with both silane and acetic acid would improve the adhesion, resulting to the better mechanical properties and water absorption of composite reinforced with this kind of fiber also exhibits the lowest value. The overall properties of composites reinforced with treated fibers are also much better than composites reinforced with untreated fibers. Also, 20 % of fiber content is regarded as the good composition to guarantee the good mechanical, water absorption and thermal properties. Moreover, the improvement of the adhesion between treated fiber and matrix (compared with that of untreated fiber and matrix) was verified by the morphology observed via Scanning Electron Microscopic (SEM).

CHAPTER 4: Composite based from PBS matrix and bamboo fibers

Chapter 4: Composite based from PBS matrix and bamboo fibers

I.Polybutylene succinate (PBS)

PBS preparation steps:

PBS was also chosen as another matrix for Polymer composite processing. Firstly, PBS was dried in the oven at 50°C for half a day. In the next step, the mold is heated to 150°C. Then PBS was poured inside the mold with the suitable quantity of 20 gram. Leave it without the pressure, at 150°C for 10 minutes. In the last step, the mold was pressed under 1000kg over the area of 20cmx20cm for 3 minutes. Then the thin PBS plate was obtained.

I.1. FTIR experiment

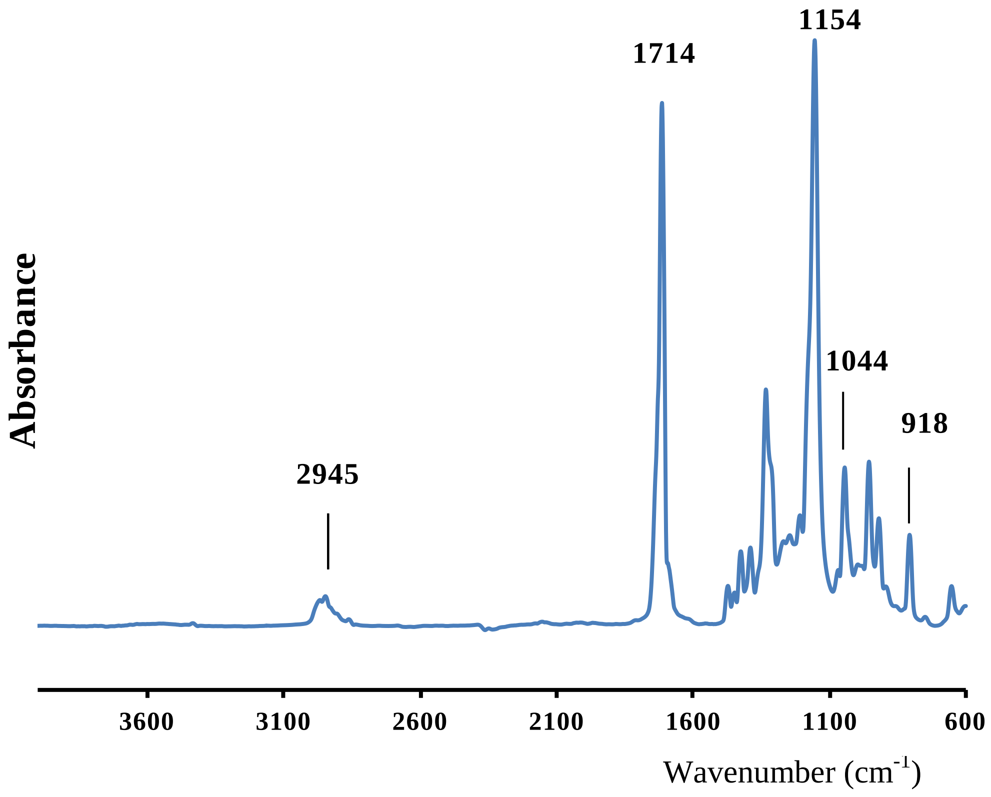


Figure 114: FTIR spectrum of PBS

FT-IR experiment was conducted on FTIR- 8400 S, Shimadzu. FTIR analysis was performed from 600 to 4000 cm^{-1} in wavenumber. The spectrum resolution was 4 cm^{-1} and the 40 scans were accumulated to determine the spectrum.

Figure 114 shows the FTIR spectra of PBS sample. The band at 2945 cm^{-1} wavenumber can be attributed to the vibration of CH_2 group in the main chain of PBS. The stretching vibration at 1154 corresponds to –C-O-C- bond in the ester group. The band at 1714 cm^{-1} relates to the stretching vibrations of the ester group in PBS, specifically in the C=O bonds of the carbonyl group. The bands at 1044 cm^{-1} can be attributed to the stretching vibrations of –O-C-C- bonds in PBS. Moreover, in the spectra, the 918 cm^{-1} band can be assigned to vinyl groups. The occurrence of terminal vinyl groups is also attributed to the degradation reaction of the PBS chain [76, 81, 72, 106].

I.2.Thermal properties of PBS

I.2.1. DSC experiment

The differential scanning calorimetry (DSC) of recycled cellulose fiber-reinforced PBS composites was carried out to investigate their crystallization and melting behavior. A DSC 204 F1 (NETZSCH) was served for calorimetric studies. The scanning temperature ranges from -50°C to 150°C at a heating rate and cooling rate of 10K/min in a nitrogen atmosphere.

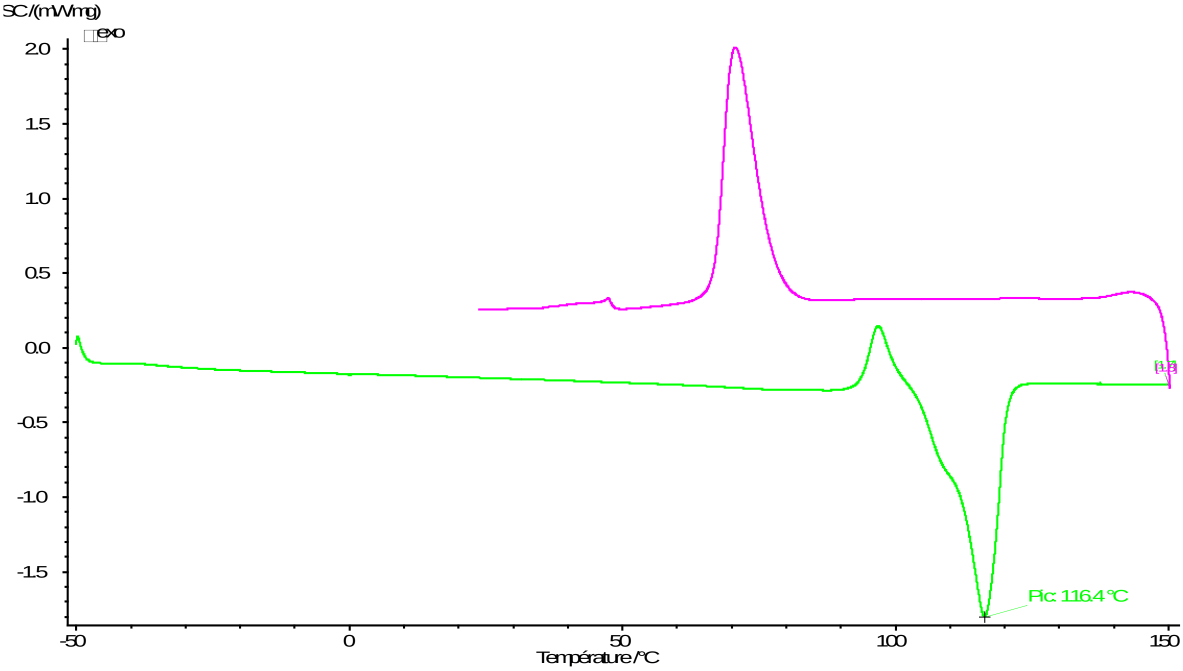


Figure 115: DSC thermograph of neat PBS

PBS has the melting point of 116.4°C and the T_C of 71°C

I.2.2. TGA experiment

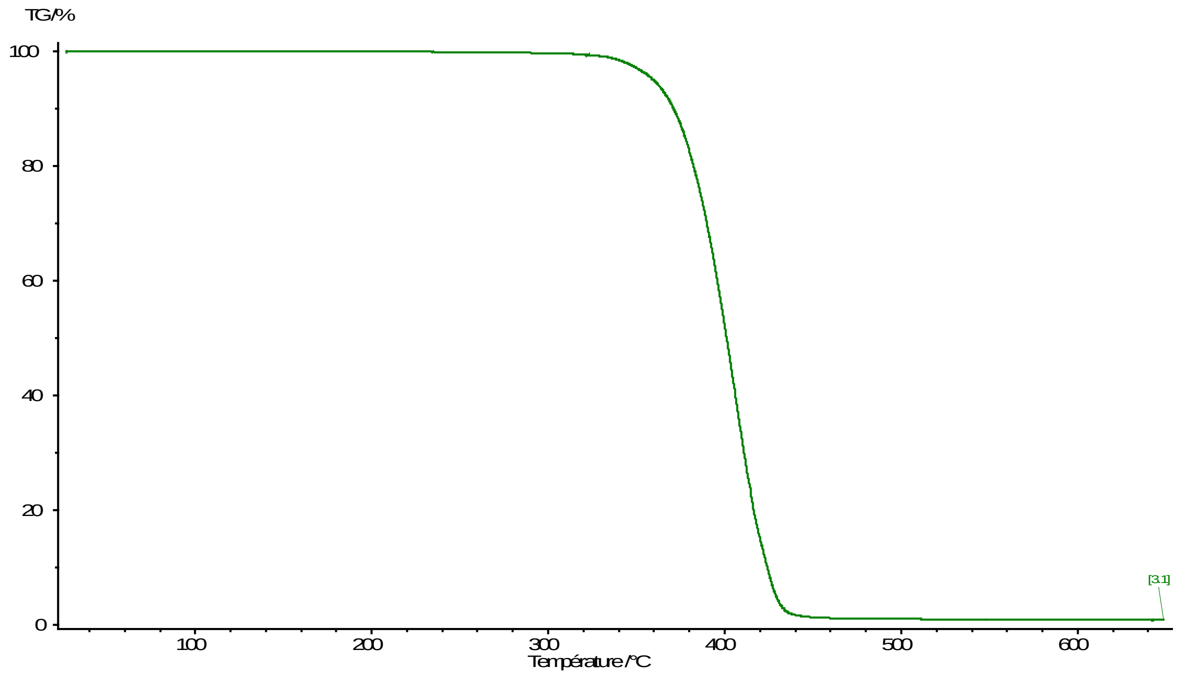


Figure 116: TGA trace of PBS

TGA measurement was performed using NETZSCH, TG 209F3 at the starting temperature of 24^{o}C to 650^{o}C, the heating rate was 10^{o}C/min in the inert nitrogen environment, to evaluate the thermal stability of PBS. The curve behavior revealed that at nearly 380°C, PBS quickly degraded. Unlike the result obtained from P34HB, PBS exhibited only one period of degradation because it is not copolymer like P34HB. The polyester almost thermally degraded to 0% at 420°C. This result is consistant with that of reference [82].

II. Composite based from PBS

II.1. Preparation

PBS itself flows quickly under high temperature. Hence, to mix it with fiber in batch mixer, the temperature was adjusted to 140^{o}C. The fibers and polymer were mixed during 5 minutes and the speed of rotor was 100 rpm. Then, the temperature was adjusted to 100^{o}C, the mixture became cool, the viscosity increased then the mixture will be obtained. Finally, the process to prepare the composite plate was exactly the same as the preparation of PBS plate. The mixture of PBS and fibers were pressed under the pressure of 1000kg over the area of 25x25cm at 130°C for 5 minutes.

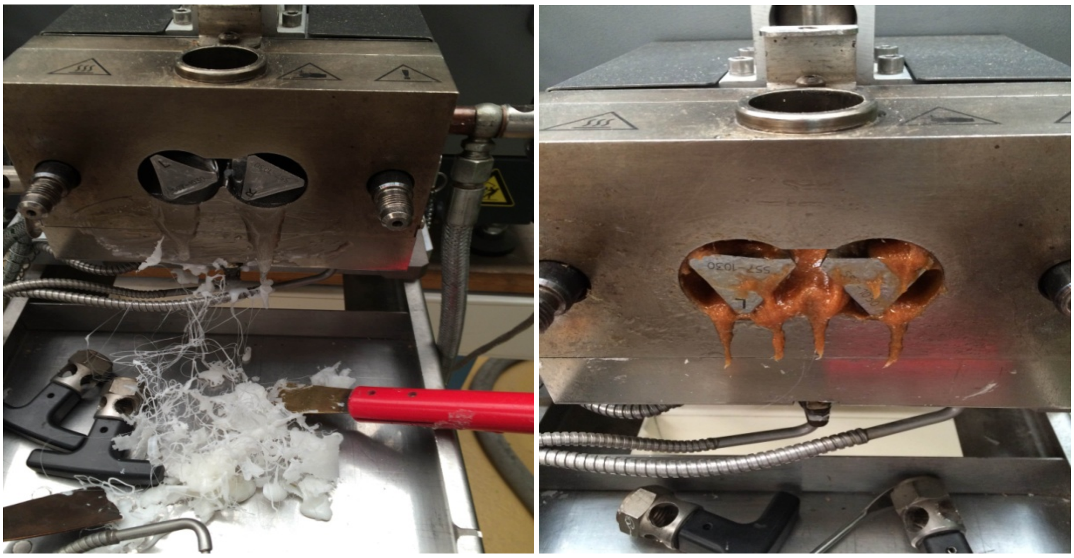


Figure 117: PBS and a mixer of PBS with fibers in the chamber of the batch mixer

II.2. Thermal properties of composite

II.2.1.DSC experiment

The crystallinity of the polymer component can be determined by:

$$X\text{c (\% crystallinity)} = \left(\frac{\Delta H_f}{\Delta H_f^0}\right).\frac{100}{w}$$

Where ΔH_f^0 is the enthalpy of 100% crystalline polymer in the composite. The crystallinity depends on the crystallization conditions of polymer matrix [102]. Moreover, in this case, the cold crystallization peak appeared slightly small and close to the melting point. The degree of crystallization is approximately calculated as follow:

$$X_c \approx \frac{\Delta H_c}{\Delta H_f^{\infty}.w}.100$$

Where ΔH_f^{∞} (110.3 J/g) is the fusion enthalpy of 100% crystalline polymer and w is the percentage of PBS [136].

As ΔH_f^{∞} is constant, the decrease or increase of ΔH_c proved that the crystallinity decreased or increased.

DSC curves of neat PBS and composites reinforced with 4 types of bamboo fibers are depicted in figure 118. As can be seen from the graph, PBS has the melting point of 116.8°C. Therefore, in the experiment, PBS was mixed with bamboo fibers at 130°C and then the mixture was pressed at 150°C to create composites. We examined the DSC behavior of these composites.

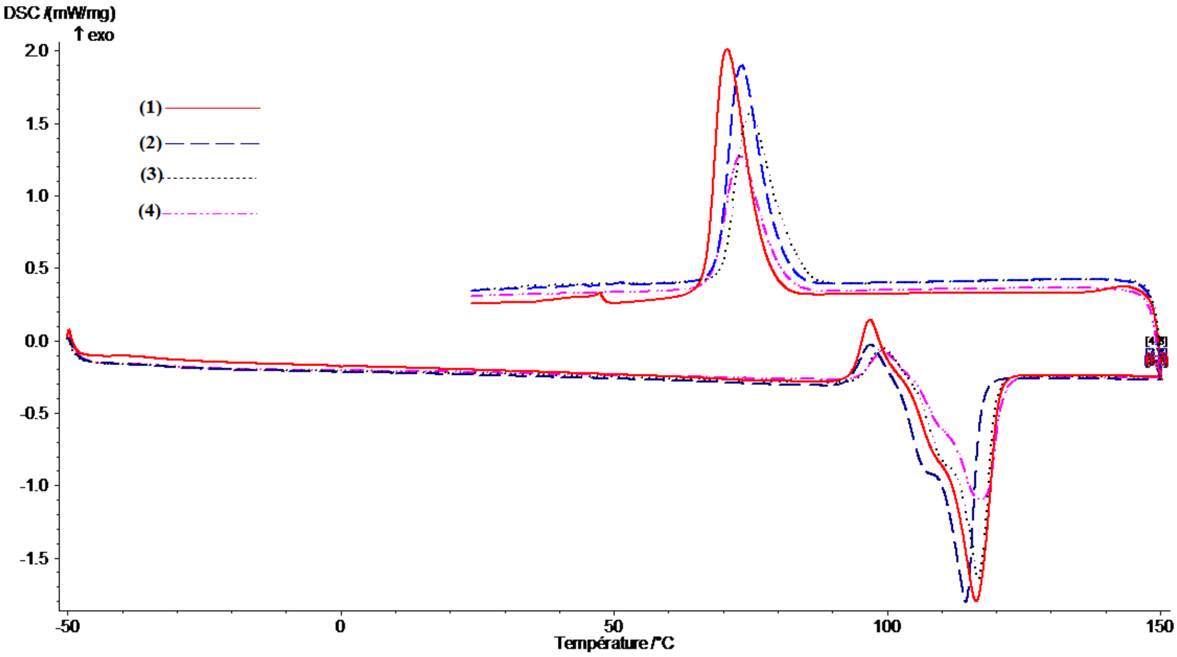


Figure 118: Dependence of DSC thermographs of composites (based from PBS) on fiber loading

Where (1): PBS neat; (2): PBS- acetic acid/silane treated fibers 10% (by weight); (3): PBS- acetic acid/silane treated fibers 20% (by weight); (4): PBS- acetic acid/silane treated fibers 30% (by weight).

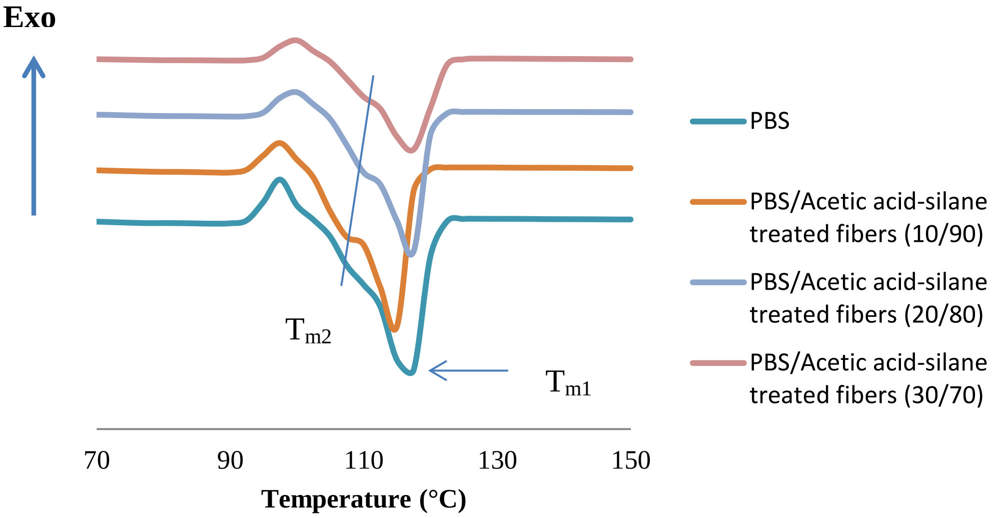


Figure 119: Dependence of DSC heating thermographs of composites (based from PBS) on fiber loading

Table 26: Detailed information obtained from DSC of PBS and its composites reinforced with acid acetic - silane treated bamboo fibers

Composition of fibers (% weight)	ΔH_f (J/g)	T_{m2}/ T_{m1} (°C)	ΔH_c (J/g)	Degree of Crystallinity (%)	T_c (°C) (Crystallization temperature)
0	102.7	116.4	70.56	63.97	71
10	79.56	107.5 /117.2	64.93	65.41	73.4
20	73.04	111.2 /117.0	57.78	65.48	74.5
30	60.45	111.2/117.3	41.93	54.31	73.2

In the preliminary experiment, acetic acid –silane treated fibers were used. As can be seen from the graph, the enthalpy decreased with the increase of fiber load. It is attributed to the reduction in the free volume of PBS caused by the amount of bamboo fibers [99] and reduced the polymer mobility [122]. In other words, the fibers acted as diluents in PBS matrix [102] The amount of fibers could lead to the limited growth of the PBS spherulite, hence causing a depression in the heat of fusion ΔH_f [99].

Also, according to the calculation, the degree of crystallinity increases when adding 10% and 20% of fibers, respectively. However, it decreases when the fiber content is 30%. The results suggest that fibers act as nucleation agent at low content (10% and 20%) and fibers play the role as diluents at high content (30%). In fact, there are 2 factors that control the crystallization of polymeric composite systems (1) the nucleation effect of fillers, which improves crystallization; and (2) the hindering effect of fillers on the movement of polymer molecular chains to the surface of the growing polymer crystal, which inhibits crystallization [105].

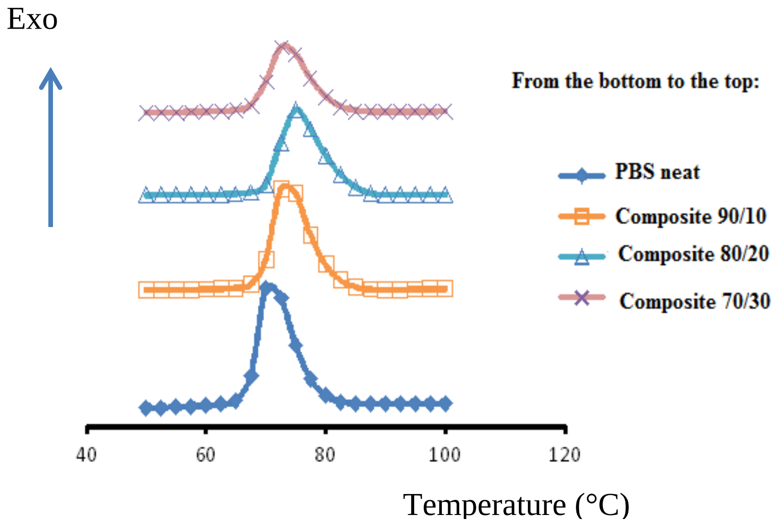


Figure 120: Dependence of crystallization temperature (Tc) on fiber content of composite reinforced with acetic acid –silane treated fibers.

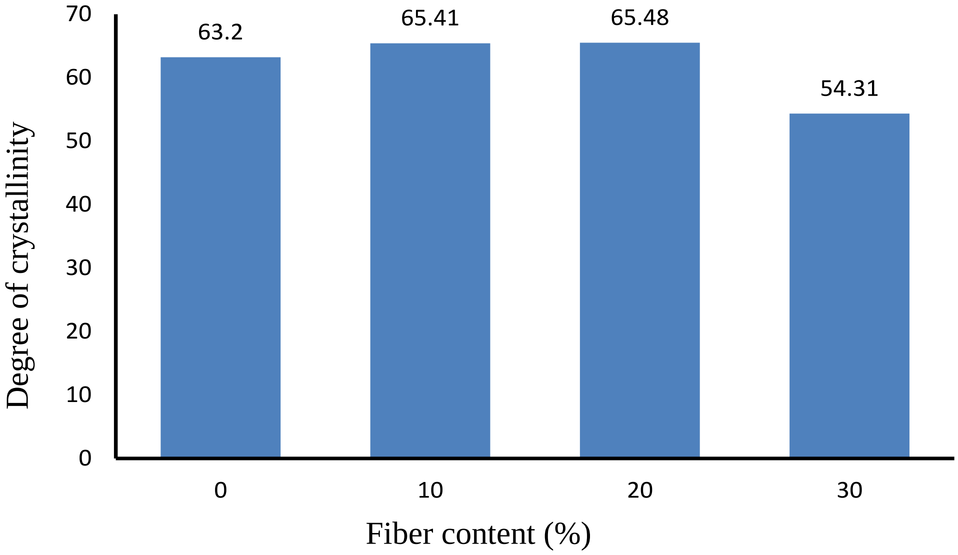


Figure 121: Dependence of degree of crystallinity on fiber content

Crystallization temperature of PBS and its composites were obtained from the cooling curve during DSC. The crystallization temperature of PBS was increased in the presence of bamboo fibers. In general, the increase in the crystallization temperature (*Tc*) was attributed to cellulose fibers which acted as an efficient nucleating agent for the crystallization of polymer [100],[101], [102], [103]. These higher T_c values of the composites compared with that of the pure polymers also indicates that the crystallization rates of the composites are more rapid and the crystallization process is easier than that of polymer [87]. In other words, bamboo fibers increase the crystallinity under these cooling conditions and shift the crystallization temperature to higher values and the degree of crystallinity (%) proved that [123]. In this study, the result of degree of crystallinity is consistent with the values of Tc. For example, the increase in degree of crystallinity at 10 and 20% fibers corresponds with the increase of Tc and the Tc at 30% fibers is minimum, corresponds with the lowest degree of crystallinity of the three fiber contents (10%, 20% and 30%). The bamboo fibers and its treatment, thus, have an influence on the crystallization behavior of the matrix.

Table 26 shows that with the addition of bamboo fibers, composites exhibited two melting points at T_{m1} and T_{m2}. For the pure PBS, the main melting point corresponds to T_{m1}=116.8°C of its α-crystalline phase [101]. The double melting peaks were probably due to the occurrence of the reorganization of crystal during the heating run [65, 123, 124]. Usually, the double melting behavior depends on crystallization temperature, time, heating rate and molecular weight [123]. The two melting peaks are very close and approximate to the melting peak of PBS neat (116.8°C). It can also be seen that 3 kinds of composites have $T_{m1}\approx117°C$. PBS may form small crystallites on the surface of bamboo fiber and form a large crystallite alone [65]. Moreover, a new endothermic peak T_{m2} appears at lower temperature for all the composites. These values of T_{m2} are 107.5; 111.2 and 111.2 corresponding to the melting of the β-crystalline forms of PBS reinforced with 10 ;20 and 30%wt bamboo fibers (treated with acetic acid and silane), respectively. The β phase structure was formed in all 3 kinds of fiber filled composites as mentioned above, and this result agrees with reference [101]. It was found that some inorganic filler might act as β- nucleators and formed larger amounts of the β-form and thus, it influenced a lot to the properties of the composites [101]. In other words, trancrystallinity develops at the fiber-matrix interface involve the formation of β crystals [104].

Composites from 4 types of fibers (untreated bamboo fiber, bamboo fibers treated with acetic, bamboo fibers treated with silane and bamboo fibers treated with both acetic and silane) were investigated (The compositions of fibers were 20% by weight). The DSC curves were obtained as shown in the following graph:

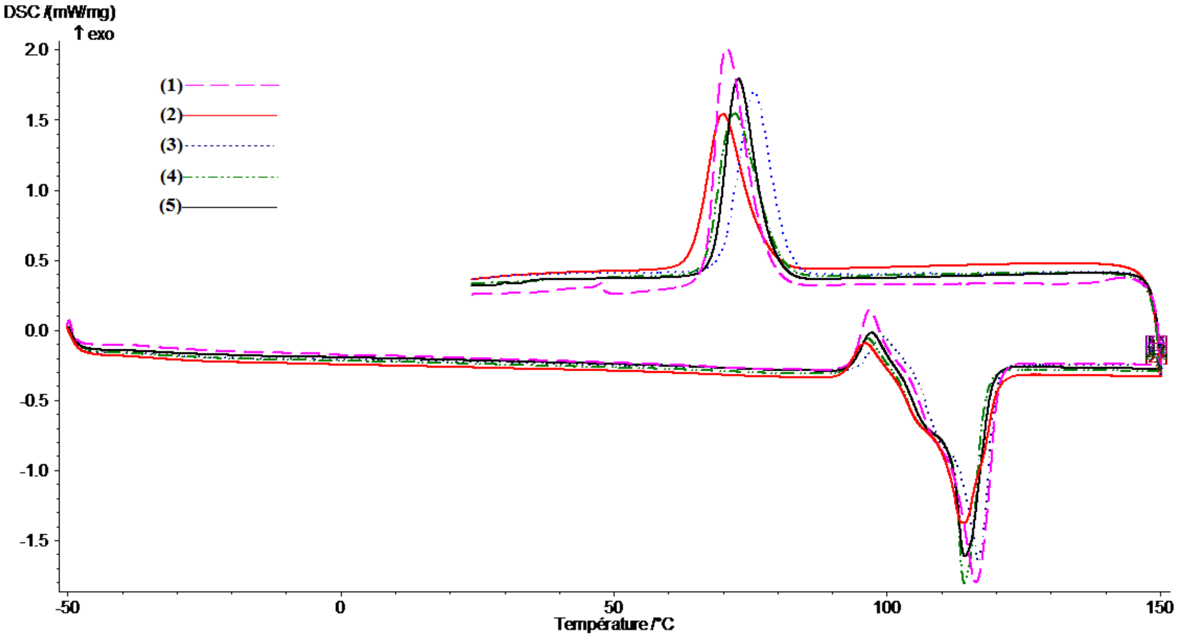


Figure 122: Dependence of DSC thermographs of composites (based from PBS) on types of fibers

Where (1): PBS neat; (2): composite from PBS and fibers treated with acetic acid ; (3) composite from PBS and fibers treated with acetic acid and silane; (4): composite from PBS and untreated fibers; (5): composite from PBS and fibers treated with silane.

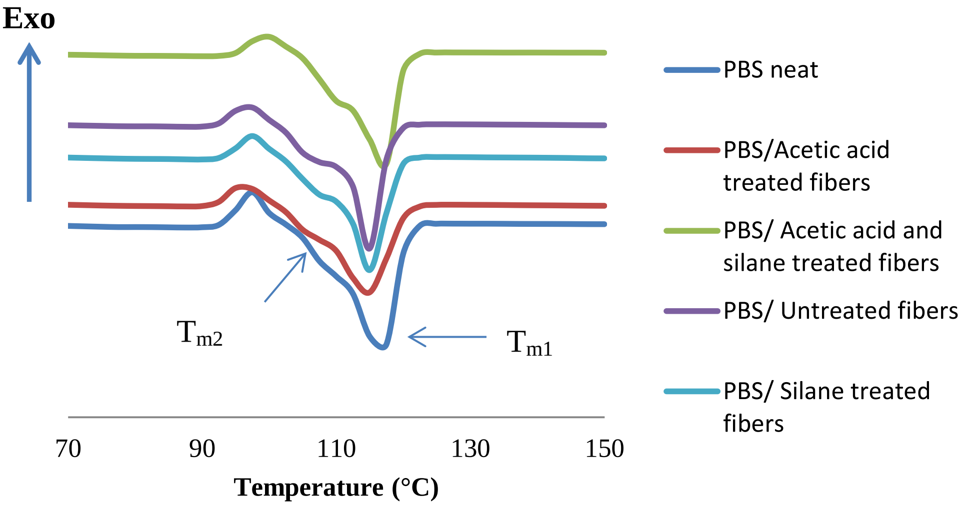


Figure 123: Dependence of DSC heating thermographs of composites (based from PBS) on types of fibers

Table 27: Detailed information obtained from DSC of PBS and its composites reinforced with different types of bamboo fibers

Composites (reinforced with)	Composition of fibers (% weight)	ΔH_f (J/g)	T_{m1}/ T_{m2} (°C)	ΔH_c(J/g)	Degree of crystallinity (%)	T_c (°C)
PBS neat	0	102.7	116.4	70.56	63.97	71
Untreated fibers	20	74.7	106.7/114.2	55.51	62.91	72.2
Silane treated fibers	20	76.728	107.5/114.4	57.77	65.47	72.9
Acetic acid treated fibers	20	74.46	106.4/113.9	53.98	61.17	70
Acetic acid – silane treated fibers	20	73.04	111.2 /117	57.78	65.48	75

Similarly, ΔH_f shows the decrease with the addition of fibers. As explained above, it is caused by the reduction in the free volume of PBS which is caused by the amount of bamboo fibers leading to the limited growth of PBS spherulite. Only composite reinforced with acetic acid -silane treated fibers exhibits T_{m1} slightly higher than that of neat PBS. Other composites show the lower T_{m1}, it is probably the fibers have less significant efficiency as a nucleating agent for the crystallization of polymer. Surface treatment is one of the important factors that affect to the melting point of composite. Moreover, T_{m2} corresponded to β-crystalline forms of PBS.

Besides, the crystallization temperatures in most cases were improved and higher than that of neat PBS. Composite based from acetyl – silane treated fibers also showed the highest value of degree of crystallinity and the maximum Tc, which reveals that the fibers act the role of nucleation agent. Only composite reinforced with untreated fibers showed the slightly smaller crystallization temperature (Tc) of 70°C and in this case, the fibers caused the slight confinement of the polymer chains [99]. The results can be seen in the two figures below.

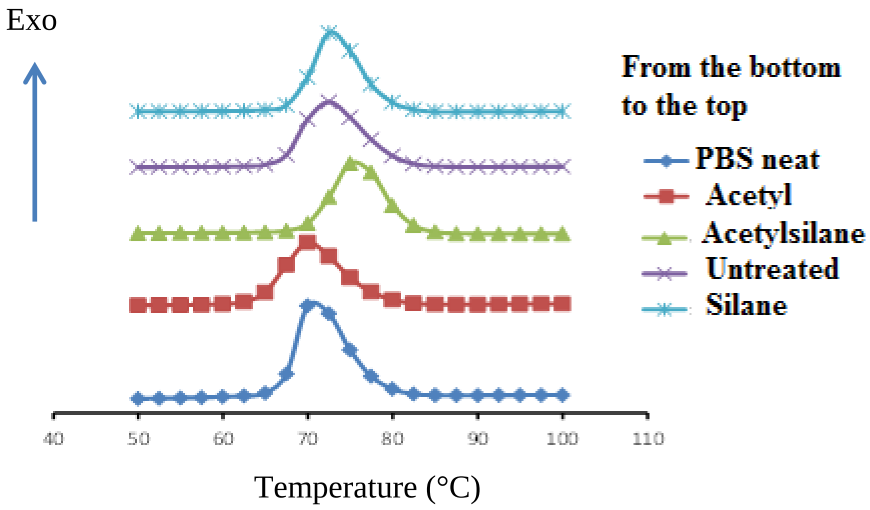


Figure 124: Dependence of crystallization temperature (Tc) on types of bamboo fibers reinforced the composites (with 20% fiber content)

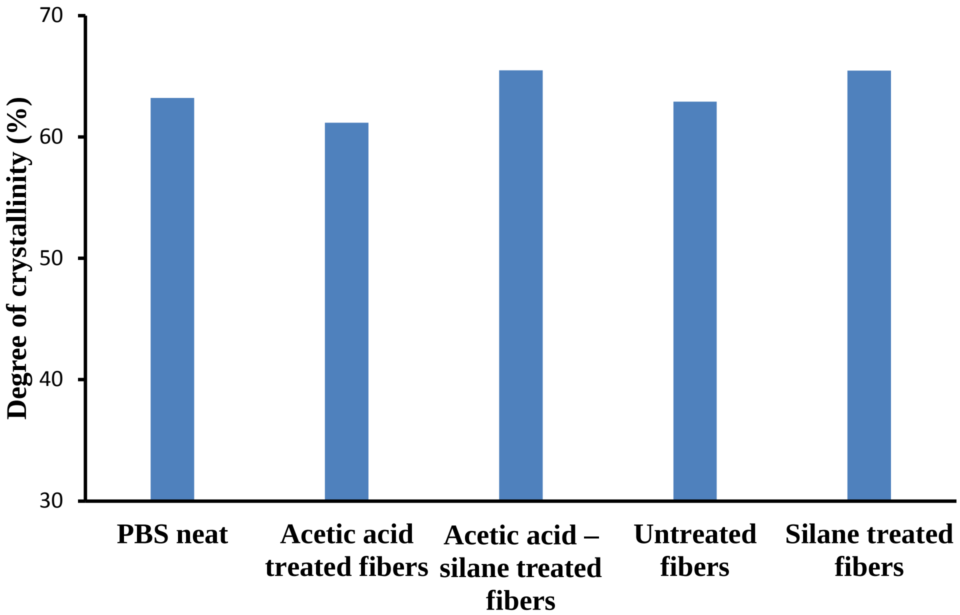


Figure 125: Dependence of degree of crystallinity on types of bamboo fibers reinforced the composites (with 20% fiber content)

II.2.2. TGA experiment

Thermogravimetric analysis (TGA) of PBS and its composites reinforced with bamboo fibers is shown in the Figure 126 below. In this case, bamboo fibers were treated by acetylation method followed by silane treatment. The temperature was increased from 25°C to 650°C with the speed of 10°K/min in the nitrogen atmosphere by machine NETZSCH, TG 209F3.

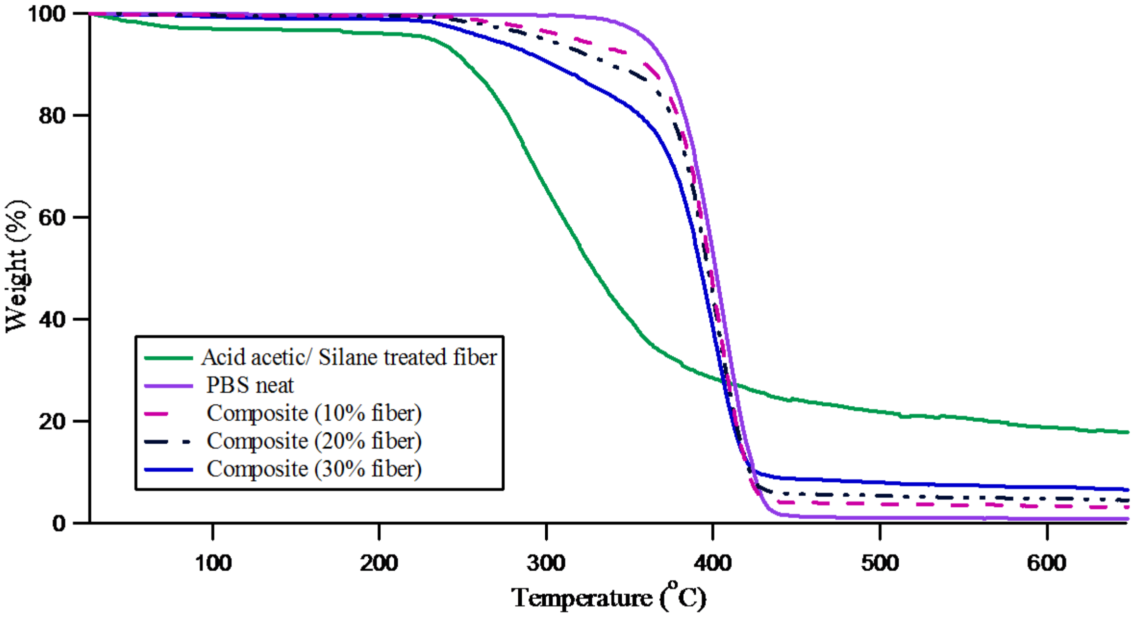


Figure 126: Dependence of thermogravimetric analysis (TGA) curves on fiber compositions of composite based from PBS matrix.

The behavior curves of composites are very similar to that of PBS because in all cases, PBS dominates the composition of composites. The TGA curve reveals that PBS undergoes thermal degradation above 340°C and quickly decreases nearly to 0% (almost degraded) at approximately 435°C. Above 435°C, PBS almost decomposed, thus, a plateau curve was obtained.

When the fibers were added in the matrix, the TGA curve shifted to the fibers neat curve and far away from PBS curve. It means that, the 10 % fiber composite curve is much more similar to the PBS neat curve than the curves of 20% fiber composite and 30% fiber composite. The curve of 20% fiber composite is in between the curves of 10% and 30% fiber composites and all these curves are between the curve of fiber and PBS neat. The composites reached the plateau of between 5 to 8% mass remain depending on the fiber contents. The more fibers were added, the less amount of composites decomposed. It matches with the degradation of fiber and PBS neat under temperature. PBS almost decomposed, while the thermal degradation of fibers was stable at around 20% mass remained. As referred, fibers underwent the process of degradation at around 280°C which is characteristic of low molecular weight components, such as hemicelluloses [87] (it is the thermal depolymerization of hemicelluloses and glycosidic linkages of celluloses) and 340°C corresponding to the cellulose decomposition. Composite is perhaps the combination of the thermal property of fiber and PBS neat. In the curves of composites, the degradation is quicker than that of the neat PBS. Also, the composite curves reveals humps caused by the addition of bamboo fibers [82], it was verified that the degradation temperature was shifted to a lower temperature of around 350°C showing that the presence of silane treated bamboo lowered the thermal stability of the polymer [108]. The composite curves showed the higher residue of composites at the end of process than the matrix and lower residue than fibers [82], [87]. In this case (composites reinforced with acetyl-silane treated fibers), the silane functionalization probably formed siloxane bridges between fibers and matrix during the degradation [107, 108]. And perhaps, these siloxane bridges enhanced the interfacial interaction which favored higher thermal stability [107]. It proves the effect of bamboo fibers to the thermal property of matrix.

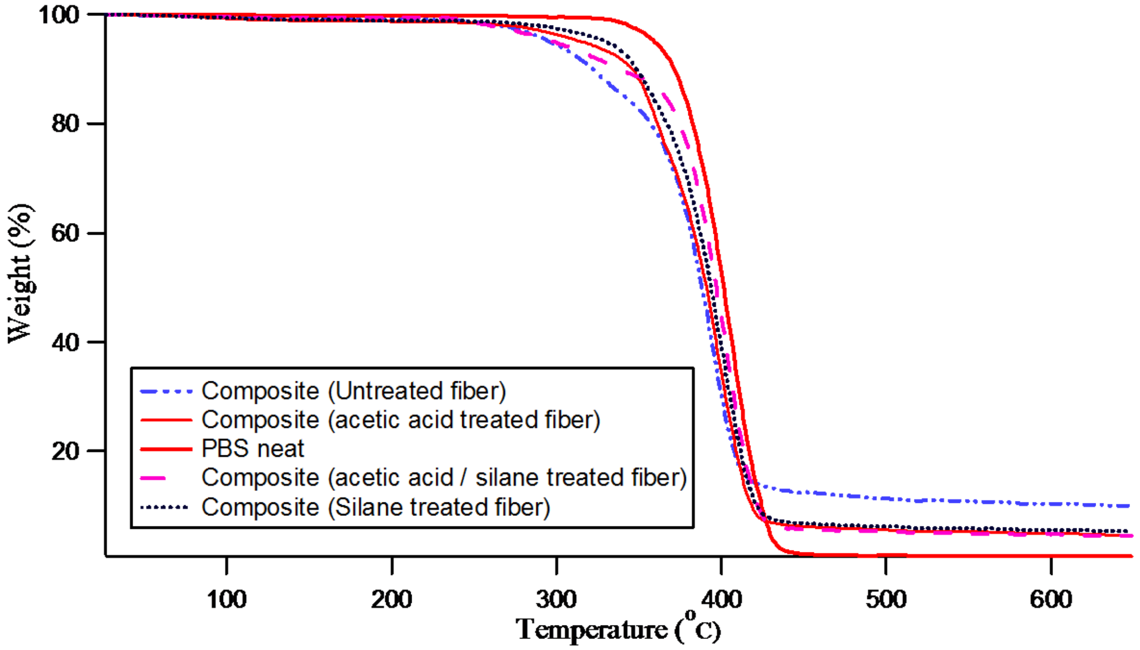


Figure 127: TGA curves of composite with fibers treated from different methods.

The TGA behavior curves for 4 kinds of composites showed consistently with the curves obtained from 4 kinds of fibers (with the same composition of fiber: 20% by weight), for example, the relative location of untreated fibers and treated fibers are the same with that of composite reinforced with untreated fibers and composites reinforced with treated fibers. As usual, the TGA curves showed that PBS based composites underwent quick thermal degradation above 340°C, similarly to the neat polymer because the matrix dominates in composites. The composite curves are always in between the curves of polymer neat and the corresponding bamboo fibers. Composites degraded less than the neat of PBS and after the process, there is still the residue of composites. The more fibers were added, the more composite curves shift to the curves of corresponding fibers. In the figure, the composites started to degrade at around 260°C.

II.3. Mechanical properties of composite

Tensile test

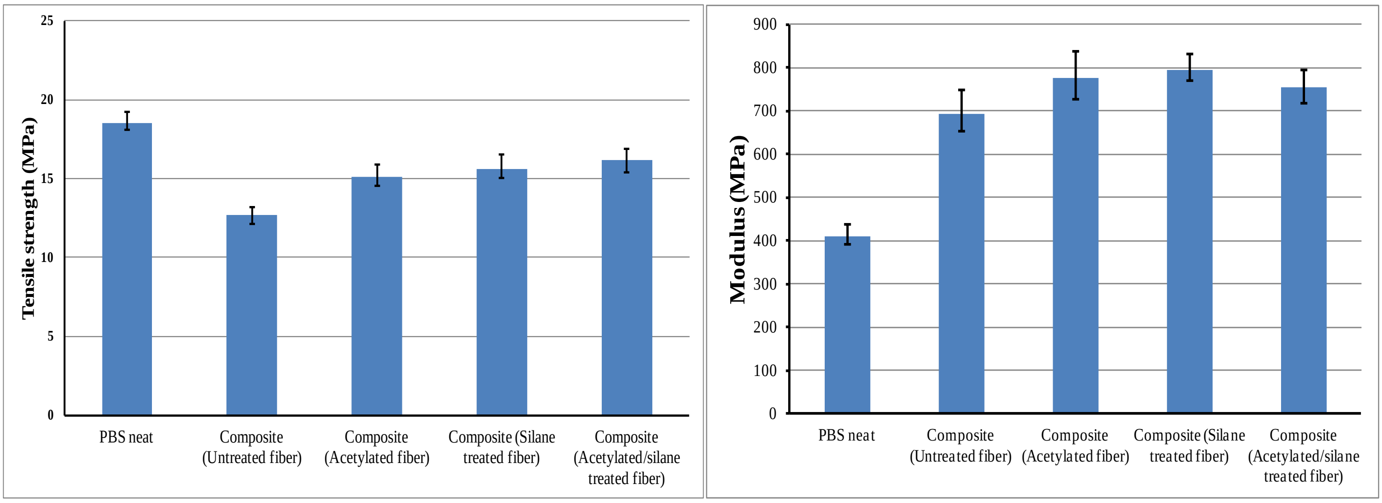
Similarly, tensile test was conducted to determine the mechanical property of PBS and its composites. For the mechanical properties, only tensile test was examined because we could only prepare the thin composite plates from PBS matrix.The tests were conducted using machine MTS Adamel Lhomargy –DY35XL and the load censor cell of 500N. The speed of crosshead was kept 10 mm/minute for all the tests. There are some decisive factors in determining this tensile property, including the fibers, preparation method, fiber orientation and interfacial adhesion. In this study, we focus on modifying the fibers, means that we improved the adhesion between fibers and matrix [70, 99]. Comparing to the untreated fibers, composites reinforced with treated fibers showed the better strength and modulus.

Fig.128 (b) showed that the modulus of composite (20% fibers by weight) reinforced with treated bamboo fibers were much better than composite reinforced with untreated fibers. For example, composite reinforced with silane was approximately 100 MPa more than the one reinforced with untreated fibers (20% fibers by weight). Similarly, the strength was significantly improved (Fig.128 a). However, the result showed that the addition of fiber caused the decrease of tensile strength. The strength declined of 2.3 MPa from 18.5 MPa of neat PBS to 16.2 MPa when adding 10% acetyl - silane treated fiber. At the same time, the modulus increased tremendously with the addition of fiber even the fibers are treated or not. Means that, even the fibers were modified with some method, it can help improve the modulus but not the strength [70].

These results proved that the modification of fibers play a role to improve the strength of composite compared to composite reinforced with untreated fiber. However, except for modulus, the strength was not improved by adding fibers. The strength was even worse when adding short bamboo fibers suggested that the adhesion needed to be further improved even that there is an interaction between fibers and matrix since they both have the polar groups [94].

The modulus increases tremendously due to the presence of fibers. The fibers have the much better modulus than the matrix. However, the interface region of fibers and matrix is weak, resulting to the debonding at the interface. Hence, the tensile strength decreases with the increase of loading fibers. The compatibility between matrix and fiber is the decisive factor to the tensile strength while the modulus depends mostly on the fiber aspect ratio [99].

In Figure 128a, composite reinforced with acetylated / silane treated fiber showed the slightly higher values than composite reinforced with silane treated fiber and acetylated fiber; however, its modulus showed the lowest value. It is supposed that a combination of acetylated method and silane treated method improve insignificantly the adhesion between the matrix and reinforcement, compared with separated method.



(a) (b)

Figure 128: Influence of fiber treatments to tensile strength and modulus of composites (20% fiber content)

However, all of the treatments exhibited that they have their own effects to the adhesion, the evidence is that the tensile property is improved, compared with the composite reinforced with untreated fiber. Fiber surface modification is particularly necessary to develop biocomposites with improved properties, it is because it can obviously decrease the moisture absorption and increase the wettability and interfacial bond strength with matrix polymer and also when the force is applied to the material, stress will be transferred from matrix to fibers [85]. For each system of composite, there is still the maximum amount of fiber load that can improve the property. In general, using too many fibers will cause the decrease in tensile strength [85].

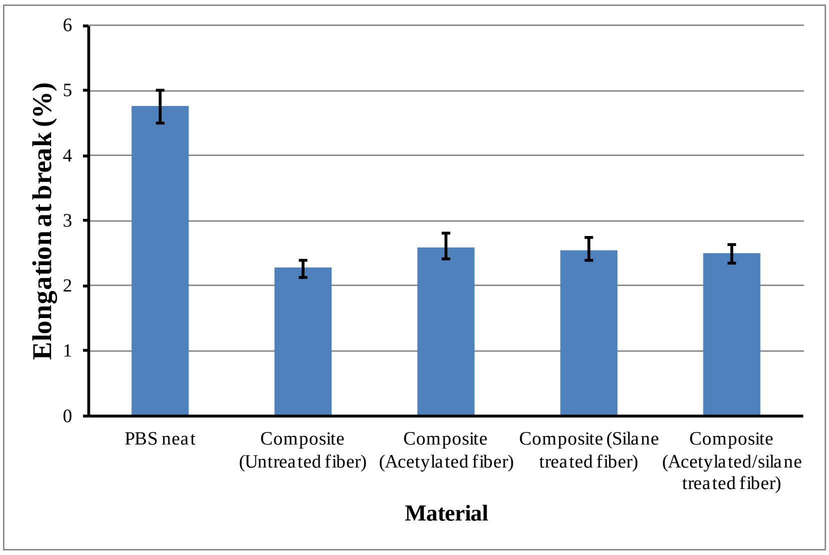
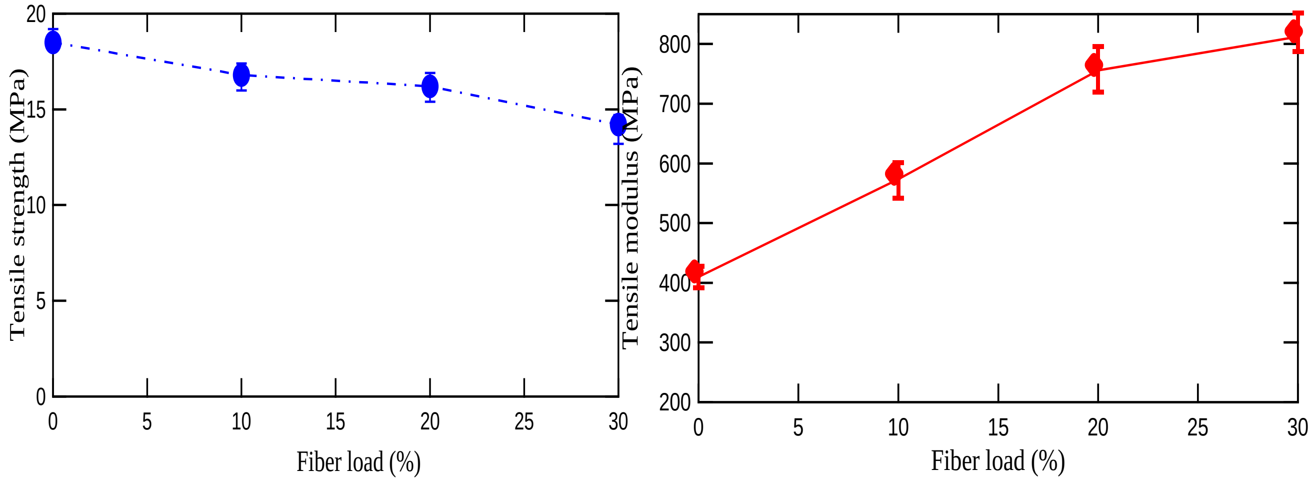


Figure 129: Influence of fiber treatments to the elongation at break of composites via tensile test

The elongation at break always showed the significant decrease in the presence of bamboo fibers. Firstly, it is because the PBS itself has a better strain than bamboo fibers (about 2.94 – 3.19%) and due to the poor adhesion between fibers and matrix, fibers are failed points that can generate a crack or there is a sliding of the fibers in relation to the matrix. It is also attributed to the structural integrity of PBS being destroyed by the loading of bamboo fiber [85]. The modification of fiber, however, improved the elongation at break a little as showed in figure 129.

Dependence of tensile test results on the composition of fibers



(a) *(b)*

Figure 130: Influence of fiber load to the tensile property

Figure 130 exhibited the tensile property of composites reinforced with bamboo fibers (treated with acetylated method and followed by silane treated method because this type of bamboo fiber reveals to be the best one to reinforce composites). Similarly to the results obtained from composite based from P34HB, composites from PBS revealed the same tendency. Figure 130 showed that, the addition of fibers increased the tensile modulus but lowered the tensile strength. Because the fibers have the much better modulus than the matrix, however, the adhesion in the interface between reinforcement and matrix was not good enough resulting to the decrease of tensile strength [70]. In order to improve the adhesion between fiber and matrix, using coupling agent is probably an effective method that can give the better compatibility [70, 13].

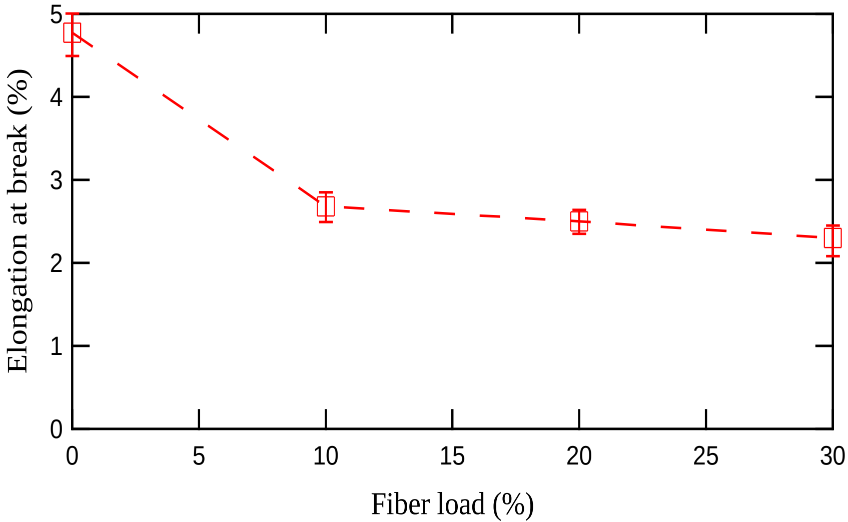


Figure 131: Influence of fiber load to the elongation at break of composites via tensile test

The elongation at break decreased when more fibers were added. This is attributed to the adhesion between the matrix and the fiber. As referred above, the decrease in elongation at break is mainly caused by the structural integrity of PBS being destroyed by the loading of bamboo fibers and the increase of fiber content means that the fiber/PBS adhesion becomes poorer that promotes microcrack formation at the interface, leading to the quicker fracture than pure PBS film [85].

III. Conclusions

In this part of the study, we aim to investigate the mechanical test of composite used PBS as the matrix. We expected that PBS can be well compatible with bamboo fibers. However, the modulus shows the significant improve while tensile strength does not reveal the improvement. It means that bamboo fiber can also contribute to the mechanical properties and shows its role in improving the modulus. To achieve the improvement upon overall mechanical properties, the adhesion of matrix and fiber has to be improved and coupling agent is likely a good candidate. In our study, we first tried to apply some treatments on fibers only to achieve the goal. Apparently, the treatments show their advantages and improvement by the comparison between untreated fibers and treated fibers. And of all those treatment, a combination method of acetylated method and silane treatment is the best one.

PBS has a low processing temperature and at the melting temperature, it flows. Therefore, to guarantee the dispersion of fibers in the matrix is more complicated. By compression molding method, it is also more difficult to adjust the thickness of composite plate as PBS is still at liquid state (at high temperature) or it quickly becomes brittle (at low temperature).

Conclusions and perspectives

In this study, the addition of bamboo fibers into polymeric materials reveals a promising way to create the material that is environmentally friendly. Three different ways of treatments were used to improve the adhesion between bamboo fibers and Polymer. In this study, two kinds of Polymers were used, they are P34HB (poly 3 hydroxy butyrate – co – 4 hydroxy butyrate) and PBS (poly butylene succinate).

The fiber were pretreated with alkali to remove waxes, pectins and volatile substances those are supposed to be not good for the adhesion with the matrix. The fibers were also modified by acetylation, silane and acetylation followed by silane treatments. The successes of all the treatments were verified by FTIR, TGA, water absorption test, SEM …

Influences of chemical treatments on fibers to composites were also investigated as we aimed to focus on the modification of fibers that can improve the compatibility between the matrix and fibers. The SEM results agreed with mechanical properties.

In all cases of fibers and matrix, with the addition of treated bamboo fibers the tensile strength or flexural strength decreased while the modulus was tremendously improved. In PBS case, the differences in tensile strength between the neat polymer and composites are insignificant. PBS has a lower melting temperature, however it is much more difficult for processing. For example, in this study, it is hard to control since PBS flows quickly at the melting temperature. Therefore it is hard to control the dispersion of fibers in the PBS matrix. Moreover, when the temperature gets cooler, the viscosity becomes very high and it is complicated to obtain composites plate.

The results also proved the effects of the fiber modification methods to the overall properties of composites, compared with the composites reinforced with untreated fibers. According to that, all the thermal properties, mechanical properties were improved and water uptake was decreased. Of all the treatment methods, a method that combines acetylation method and silane treatment method reveals as the optimal one. Composites reinforced with the fibers prepared by this method also show the increase in crystallinity with the increase of fiber content. The study may provide a good solution for fiber treatment that is not complicated but effective.

By using bamboo fibers, we can take advantage of the abundant amount of bamboo, make it a good reinforcement for polymer composite. It is an environmentally friendly material that is suitable for the purpose of using material with acceptable mechanical properties.

Moreover, it is possible to improve the strength by using coupling agent that we may continue to study. Coupling agent and compatibilizer are probably the good solutions to improve the adhesion, compatibility between fibers and matrix. Another kind of sample preparation methods should also be applied. Also, the effect of fiber size, the dispersion of fibers in the composite and the amount of silane used for the treatment should also be investigated. The compositions of P34HB should be understood because in this study we did not determine the percentages of P3HB and P4HB units in the copolymer. The influence of porosity should be concerned and the biodegradability should be investigated.

Besides, further properties can be investigated in order to improve our knowledge on the adhesion and compatibility between fibers and polymer matrix. Effectiveness of new treatment's methods and experimental condition could reveal new feature in structural modification.

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ETUDE DES MATÉRIAUX COMPOSITES DE MATRICES POLYMÈRES ISSUS DE RESSOURCES RENOUVELABLES ET DE FIBRES DE BAMBOU

Dans cette étude, les matériaux composites poly 3-hydroxybutyrate-co-4-hydroxybutyrate (P34HB) / fibres de bambou et polybutylène succinate (PBS) / fibres de bambou ont été préparés en utilisant le mélangeur interne et le moulage par compression. Les propriétés thermo-mécaniques de P34HB et de PBS ont été caractérisées.

Les fibres de bambou ont été modifiées par des traitements chimiques. Les propriétés mécaniques telles que la résistance à la traction, la résistance à la flexion, le module d'élasticité et les propriétés thermiques ont été étudiées. Pour les deux types de composites (P34HB et PBS), le module est significativement amélioré, cependant, la résistance du composite est légèrement diminuée. L'allongement à la rupture est plus faible que celui des polymères purs, ce qui indiquerait une bonne adhérence entre la matrice et les fibres. L'étude révèle que l'adhésion est améliorée avec les fibres modifiées avec le silane et l'acide acétique, ce qui entraîne une augmentation des propriétés mécaniques du matériau, par rapport à celles des composites renforcés avec des fibres non traitées. En outre, le taux de 20% de fibres est considéré comme la bonne composition de fibres pour garantir de bonnes propriétés thermo-mécaniques et une absorption d'eau faible.

En étudiant ces matériaux composites, nous visons à produire des matériaux respectueux de l'environnement. De plus, l'abondance des fibres de bambou permettra de réduire le coût de la matière première. Ce travail porte principalement sur la modification des fibres de bambou afin d'améliorer les propriétés globales des composites et sur la comparaison de ces propriétés par rapport à celles des fibres non traitées. Pour atteindre une meilleure adhérence matrice-fibre, un agent de couplage et/ou compatibilisant peuvent être étudiés et utilisés dans une future étude.

P34HB, PBS, fibres de bambou, composite.

ELABORATION AND CHARACTERIZATION OF BIOCOMPOSITE FROM RENEWABLE POLYMER MATRIX AND BAMBOO FIBERS

In this study, poly 3-hydroxybutyrate-co-4-hydroxybutyrate (P34HB)/bamboo fibers and polybutylene succinate (PBS)/bamboo fibers composites were prepared by internal mixer and compression molding. P34HB and PBSwere characterized with mechanical and thermal methods while bamboo fibers were modified with chemical treatments. Mechanical properties such as tensile strength, flexural strength, modulus and thermal properties were investigated.

For both 2 kinds of composites (from P34HB and PBS), it was found that the modulus was significantly improved, however, the strength of the composite was slightly decreased and the elongation at break was lower than the neat polymer suggesting that the adhesion between matrix and reinforcement should be improved more. The study reveals that modifying the fibers with both silane and acetic acid would improve the adhesion, resulting to the better mechanical properties of the material, compared with composites reinforced with untreated fiber or fiber treated with other methods. Also, 20 % of fiber content is regarded as the good composition of fiber to guarantee the good mechanical, water absorption and thermal properties.

By taking advantage of P34HB, PBS and bamboo fibers, we aim to produce the material which is environmental friendly. Moreover, the abundant bamboo fibers can be used and these bamboo fibers will reduce the cost of the material. Within this work, we focus on the modification of bamboo fibers to reach our goal of improving the overall properties of the composites, compared with composites reinforced with untreated fibers. To achieve the better adhesion between fibers and matrix, coupling agent and compatibilizer may be used and studied in our future study.

P34HB, PBS, Bamboo fiber, composite.

Discipline : CHIMIE

Spécialité : Chimie des matériaux

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