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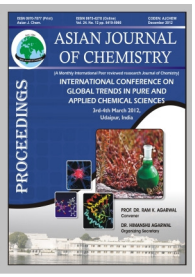

Synthesis of Composites with Microfibrillated Cellulose and Polylactic Acid†

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In this paper, we reported the synthesis of the composite prepared with microfibrillated cellulose and polylactic acid. The effects of various processing methods, the raw material of microfibrillated cellulose, processing temperature and the content of microfibrillated cellulose and the properties of the composite materials were discussed. The internal features of composites were characterized by scanning electron microscopy. The results showed that melt extrusion technique is better than physical mixture. Composite made of eucalyptus microfibrillated cellulose had a maximum tensile strength compared with that microfibrillated cellulose of bamboo and bagasse microfibrillated cellulose r, but the microfibrillated cellulose of bagasse has the best compatibility with polylactic acid. With the increase of processing temperature, the tensile properties of composite material were improved apparently, but the change of elongation at break is not obvious. With the addition of microfibrillated cellulose increased, the properties of composites decreased, when the content of microfibrillated cellulose was less than 20 %.

Key Words: Microfibrillated cellulose, Polylactic acid, Composite materials.

INTRODUCTION

More and more attentions have been paid on issue of environment and resources, studies on the composites of plant fiber and biodegradable plastic were increased. Many countries have begun to synthesize environmentally friendly biomass materials by using a new fully biodegradable materials. Plant fibers and polylactic acid composite involves a variety of plant fibers, such as kenaf, linen, bamboo, paper pulp, old newspapers, *etc*.[1-4]. The form of plant fiber filled in the polylactic acid was including fibrous, powdery and fabric-like[5-7]. The studies found that the properties of the composites were improved and the application were increased[8,9]. However, plant fiber is not easy dispersion and difficult to compatibility with polylactic acid. Where as the molecular diameter of microfibrillated cellulose is in the nanometer range and can be more compatibility with polylactic acid to become the wild phase of the composites. In this paper, the effects of various processing methods, the raw material of microfibrillated cellulose,processing temperature and the content of microfibrillated cellulose on the properties of the composites were discussed.

EXPERIMENTAL

After the slurry was eased by first PFI refiner pretreatment, the beating degree was increased, through catalysis oxidation

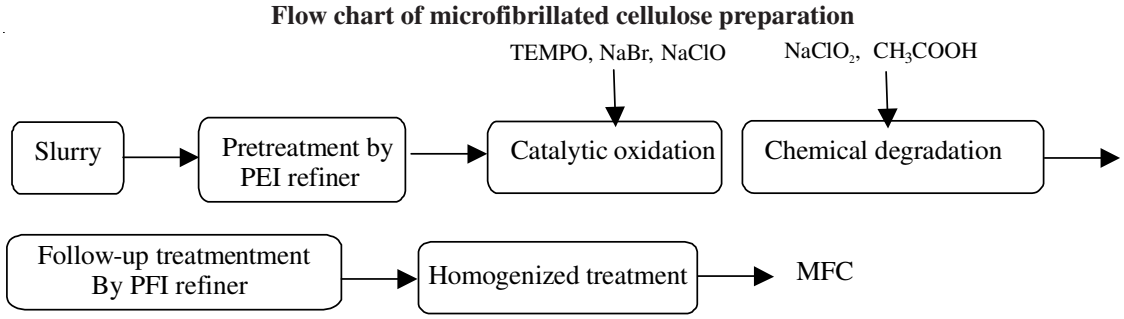

Fig. 1. Preparation route of microfibrillated cellulose

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degradation and chemical treatment, the length of fiber were reduced further and finally treated by using PFI to further improve the beating degree, so that fibers could become micronized and finally through high-pressure homogenizer for homogenization, the final products were obtained.

Preparation of composites: First, microfibrillated cellulose was mixed with polylactic acid powder. When the oven temperature reached 60 ºC, the mixed material was put into the oven and baked for 10 h, until the water in the materials evapourated. Mixtures of different ratio of microfibrillated cellulose and polylactic acid were added to the torque rheometer. The required temperature for the experiment was set and its speed was set to 60 r/min. The screw diameter was 20 mm, aspect ratio was 25 : 1. The mixed pellets were set into the tablet for press, tablet temperature was 180 ºC, time was 2 min.

Scanning electron microscope analysis: US EDAX's S-3400 scanning electron microscope was used to observe, the scanning voltage was 25.0 KV. Liquid nitrogen quenching method was used to analyze which ever section SEM.

Thermal gravimetric analysis: Test temperature range: room temperature to 450 ºC, heating rate 10 ºC/min; reference material: aluminum oxide; gases: nitrogen.

RESULTS AND DISCUSSION

Microfibrillated cellulose particle size analysis and morphological analysis: Microfibrillated cellulose size of eucalyptus microfibrillated cellulose, bamboo and bagasse microfibrillated cellulose after high-pressure homogenizer treated are shown in Table-1.

TABLE-1
PARTICLE SIZE OF MICROFIBRILLATED CELLULOSE (MFC)

Items	Bagasse MFC	Bamboo MFC	Eucalyptus MFC
Particle size (nm)	15.0	70.0	12.0

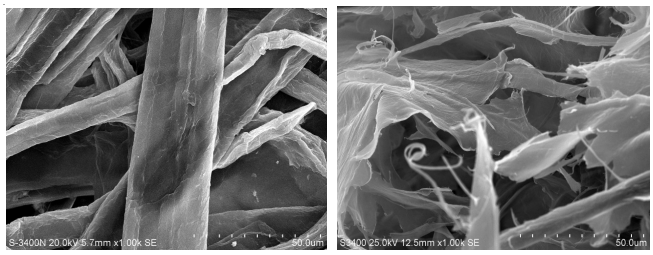
Table-1 shows that pulp samples of eucalyptus, bamboo and bagasse after the homogenization treatment have basically reached the nanometer particle size, surface area is relatively large, during the composite process, which can be mixed enough with the polylactic acid.

To investigate the effects of microfibrillation of pulp on the mechanical properties of polylactic acid composites, two types of fillers, eucalyptus raw fiber and eucalyptus microfibrillated cellulose, were mixed with polylactic acid by the solvent method. The filler content was 10 wt %.

Fig. 2 shows typical morphology of the fillers. As shown in Fig. 2, powdered fiber has a smooth surface and microfibrillated cellulose is completely disintegrated into nanoscale to submicron wide fibers, forming a network. Comparing Fig. 2 (a) and (b), it shows that, after microfibrillated cellulose wire broom within the fibers, fiber diameter becomes very small, fiber surface area is far greater than the untreated slurry-like fibers.

The SEM of composites prepared by powder fiber, microfibrillated cellulose and polylactic acid are shown in Fig. 3 and Fig. 4.

Fig. 3 is the SEM images of cross-section of the composite. It can be seen, wrapped in plant fibers are polylactic acid, but there are more obvious interface. Fig. 4 is the SEM images of composite material of polylactic acid and microfibrillated cellulose. Fig. 4 shows that, after treatment by high-pressure homogenization, the plant fiber become very short, in the composite mixture is relatively uniform, so the performance is better than the ones added with powder materials.



(a) Raw fiber (×1000) (b) MFC (×1000)

Fig. 2. SEM of raw fiber and microfibrillated cellulose

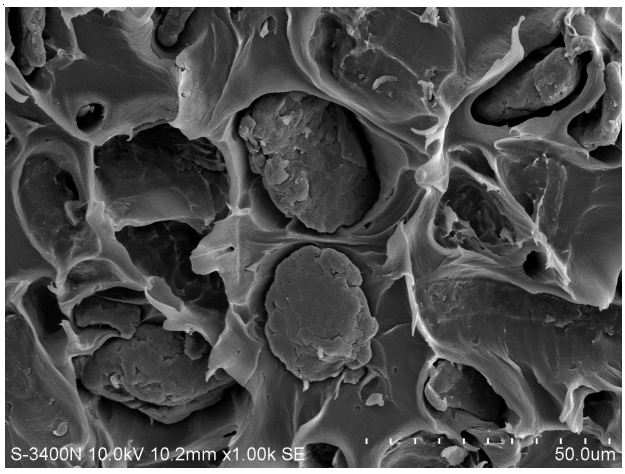


Fig. 3. SEM of the cross-section of composite material of polylactic acid and powder fiber (×1000)

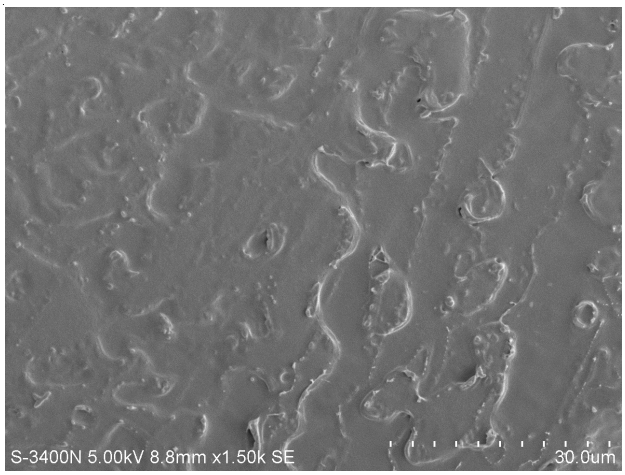


Fig. 4. SEM of section of composite material of polylactic acid and microfibrillated cellulose(×1000)

Effect of microfibrillated cellulose types on properties of composites:

(1) The effect of microfibrillated cellulose types on tensile properties of composite materials microfibrillated cellulose made of different fiber materials has different properties and

different influences on the composite properties. This paper compares the effects of microfibrillated cellulose types on tensile property of composite materials. In this paper, microfibrillated cellulose content is 10 % and processing temperature is 180 ºC. Table-2 shows the properties of the composites.

TABLE-2
FIBER TYPES *vs.* TENSILE PROPERTIES

Tensile strength (MPa)	12.09	11.26	12.43
Elongation at break (%)	1.97	2.60	1.95

Table-2 summarizes the composite materials used eucalyptus microfibrillated cellulose as the padding have the largest tensile strength, but the smallest elongation at break. This implies that the materials have better tensile property, but its ductility is worse than the other two materials. Composite materials made of bamboo microfibrillated cellulose have the smallest tensile strength and the largest elongation at break. This shows that the materials have better ductility, while its tensile property is worse. However, the overall performance of composite materials made of bagasse microfibrillated cellulose is situated between the other two kinds. From the point of whole, padding type doesn't affect the material properties much. This indicates that the three fibers' properties become similar when they were made into micro-fiber.

(2) The effect of microfibrillated cellulose type on water vapour permeability and water absorption of composite materials.

The water vapour permeability of materials determines the applications. Fig. 5 shows the effect of micro-fiber added in polylactic acid on properties of composite materials.

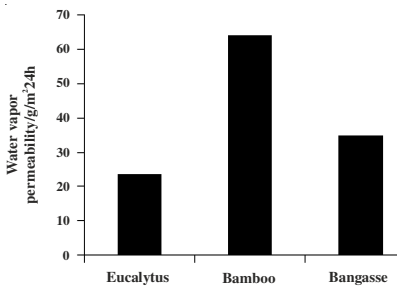


Fig. 5. Fiber type *vs.* water vapour permeability

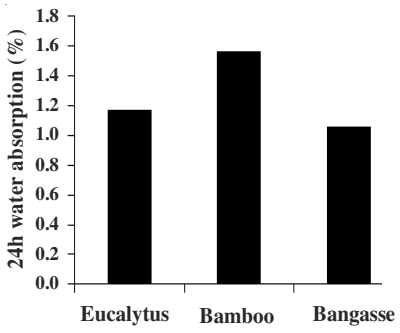


Fig. 6. Fiber type *vs.* 24 h water absorption

Water vapour permeability of materials added bamboo microfibrillated cellulose is larger, while materials added bagasse and eucalytus microfibrillated cellulose are decreased and lower than pure polylactic acid. This implies that the compatibility between the two micro-fibers and polylactic acid is better. Because of the smaller gaps of the two composite materials, water vapour permeability is smaller.

As can be seen in Fig. 6, 24 h water absorption of composite materials added the microfibrillated cellulose is arranged in order of bamboo microfibrillated cellulose > eucalyptus microfibrillated cellulose > bagasse microfibrillated cellulose. This is possibly because bamboo fiber in the microfibrillar processing has relatively high level of sub-wire broom, making a large number of hydroxyl and carboxyl groups exposed to fiber surface compared with bagasse microfibrillated cellulose and eucalyptus microfibrillated cellulose, so bamboo microfibrillated cellulose has a maximum water absorption.

(3) The effect of microfibrillated cellulose type on thermal properties of composite materials.

Microfibrillated cellulose made of different fiber materials has different properties and has different influences on properties of the composite materials. This paper compares the effect of microfibrillated cellulose type on DSC curve of composite materials (Fig. 7).

It can be seen from Fig. 7 that the polylactic acid in the composite materials added the eucalyptus microfibrillated cellulose has a higher glass transition temperature and cold crystallization temperature, with the smaller melting peak area. However, glass transition temperature of polylactic acid with bagasse microfibrillated cellulose is lower than eucalyptus microfibrillated cellulose but higher than that with bamboo microfibrillated cellulose. At the same time polylactic acid with bagasse microfibrillated cellulose has a minimum cold crystallization temperature and a maximum melting peak area. Polylactic acid with bamboo microfibrillated cellulose has a maximum cold crystallization temperature and its other thermal properties are situated between the other two materials. This indicates that the microfibrillated cellulose of bagasse and eucalyptus has the better compatibility with polylactic acid. In summary, composite materials with the addition of eucalyptus wood fiber microfibrillated cellulose added in polylactic acid have a better overall performance.

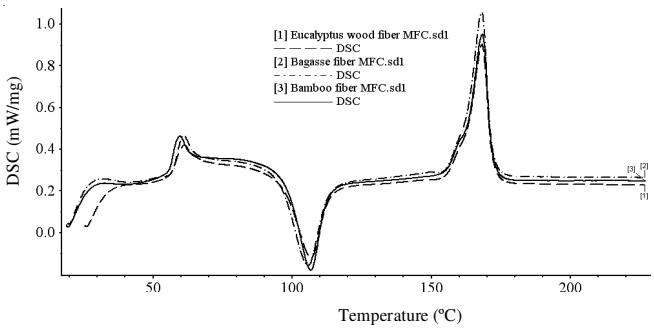


Fig. 7. Fiber types *vs.* DSC

Effect of processing temperature on properties of composite materials

(1) Figs. 8 and 9 show the effect of processing temperature on tensile property of composites. As can be seen in Fig. 8, with the increase of temperature, the tensile strength increases. And especially when the temperature is from 180 to 190 ºC, the tensile strength has been considerably improved, but the elongation at break has no obvious change, only rises

at 180 ºC. Polylactic acid is a kind of thermoplastic material and microfibrillated cellulose is smaller particle diameter. Therefore the increase of temperature results in the increase of the mobility of polylactic acid which is helpful for the compatibility of microfibrillated cellulose and polylactic acid, making a corresponding rise of the tensile properties.

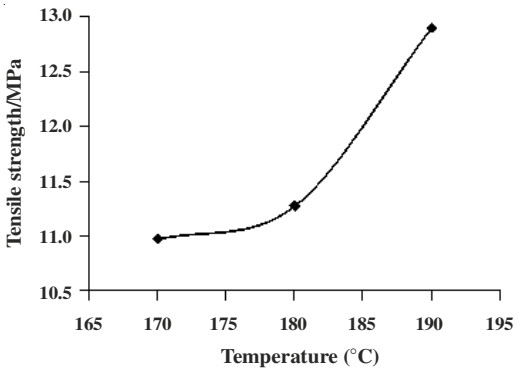


Fig. 8. Temperature *vs.* tensile strength

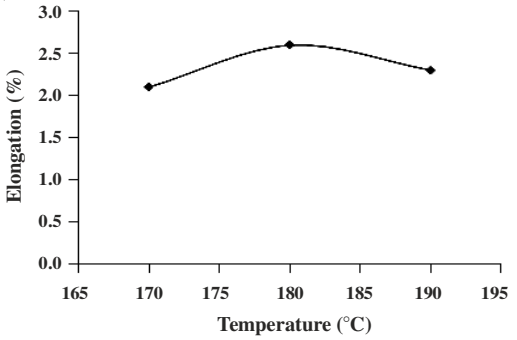


Fig. 9. Temperature *vs.* elongation

However, it can be seen that elongation doesn't change significantly in Fig. 9. This means that although the tensile properties of composite materials has increased, the ductility has not changed much.

(2) Figs. 10 and 11 show the effect of processing temperature on water vapour permeability and water absorption of composite materials. Different processing temperatures have different influence on water vapour permeability and water absorption of composite materials (Figs. 10 and 11).

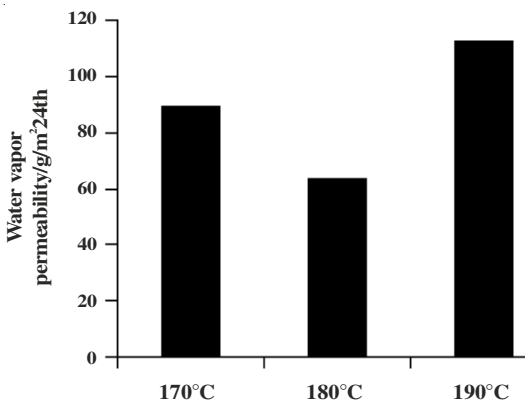


Fig. 10. Temperature *vs.* water vapour permeability

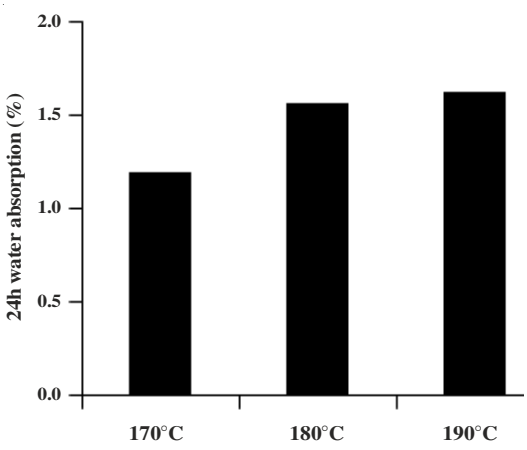


Fig. 11. Temperature *vs.* 24 h water absorption

For the composite materials with the addition of microfibrillated cellulose, performance changes with no fixed rules. Water vapour permeability of composite materials is arranged in order of 190 ºC > 170 ºC > 180 ºC, which is consistent with the change of the composites density. Material density and water vapour permeability are in inverse proportion relation. This rule is only for mixed materials of microfibrillated cellulose and polylactic acid, but materials mixed with the fiber powder and polylactic acid do not show the same pattern. While the water absorption is gradually increasing, this may be due to water molecules originally adsorbed in microfibrillated cellulose evapourate out with the increasing temperature. And the higher the temperature the more the amount of evapouration. When the materials were cool and forming, then encounter water molecules again, microfibrillated cellulose will adsorb water molecules. Considering all the performances of composite materials, the processing temperature of 180 ºC is preferred.

Influence of microfibrillated cellulose content on properties of composite materials: The effect of filler morphology indicated the importance of network formation in improving mechanical properties. Hence, the reinforcement effect of microfibrillated cellulose on the mechanical and thermomechanical properties of polylactic acid composites was studied as a function of microfibrillated cellulose content.

During the preparation process microfibrillated cellulose adsorb a large number of water molecules, within high water retention, which bring some problems to the preparation of composites. microfibrillated cellulose is more stable as the presence in solution. But once remove water molecules, those micro-fiber fiber originally present in the solution is easy to get together. So adding too much microfibrillated cellulose in the process will bring the difficulty of pre-treatment and poor dispersion, meanwhile fiber reunion can not be controlled, that is an uneven mixed results. Hence, control microfibrillated cellulose content below 15 %. Select five points 1, 3, 5, 10 and 15 % as test points for research. In this research, microfibrillated cellulose of eucalyptus fiber as the filler, the processing temperature is 180 ºC.

(1) The influence of microfibrillated cellulose content on tensile properties of composite materials.

Microfibrillated cellulose's smaller particle size, will have some impact on the tensile properties of composite materials,

the specific results are shown in Figs. 12 and 13. Figs. 12 and 13 shows that with the increase of microfibrillated cellulose, the tensile strength is gradually increased and arrive maximum when the amount of microfibrillated cellulose was up to 10 %. However,the elongation at break of composite materials decrease, but to flatten when the amount of microfibrillated cellulose went up to 5 %. It can be determined that 10 % of the microfibrillated cellulose dosage is the best content for the tensile properties.

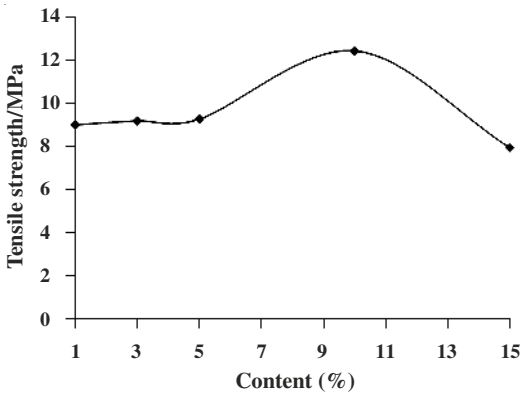


Fig. 12. Microfibrillated cellulose content *vs*. tensile strength

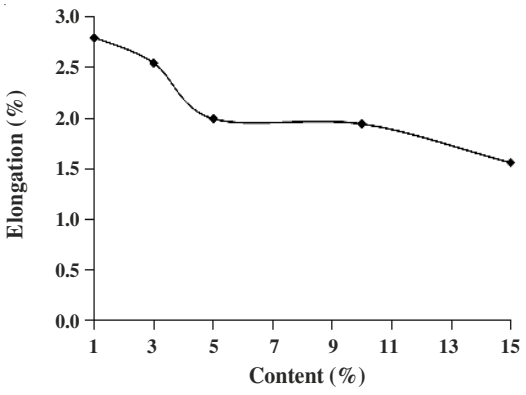


Fig. 13. Microfibrillated cellulose content *vs.* elongation

(2) The influence of microfibrillated cellulose content on water vapour permeability and water absorption of composite materials.

Better retention of microfibrillated cellulose have a greater impact on the water vapour permeability and water absorption of composite materials, the experimental results are shown in Figs. 14 and 15.

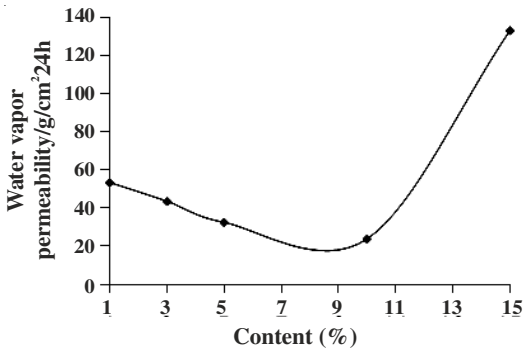


Fig. 14. Microfibrillated cellulose content *vs*. water vapour permeability

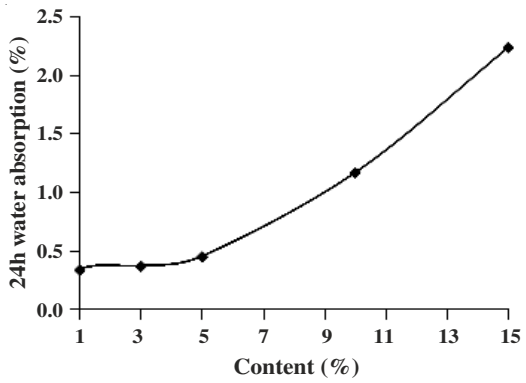


Fig. 15. Microfibrillated cellulose content *vs.* 24h water absorption

We can see from Figs. 14 and 15 that with the adding of microfibrillated cellulose, water vapour permeability and 24 h water absorption of composite materials have different trends. Water vapour permeability has shown a downward trend before 10 % addition level. However, according to trends in its adding 8 % to 9 %, there will be a minimum, after which will soon become larger. This indicates that in these five points designed in the test, the water vapour barrier of composite material arrive the top when 10 % of microfibrillated cellulose was added. This may be because polylactic acid can be well mixed with microfibrillated cellulose when the adding amount is 10 %, microfibrillated cellulose can fill most gap of polylactic acid, so that water vapour through become difficult. From the overall trend, when microfibrillated cellulose dosage is from 1 to 9 %, the composite material has a downward trend, but the relative change of overall water vapour permeability is not large, but after adding in microfibrillated cellulose 9 % of the amount, water vapour permeability have a greater increase. This may be due to microfibrillated cellulose to fill the gap between the polylactic acid molecules, with the added volume increasing, more and more gaps are filled, slowly the water vapour through from easy to difficult, causing the composite vapour transmittance decreased. However, to add greater than 10 %, due to higher water content of microfibrillated cellulose in the drying process, the role of prone reunion appears, the composites is mixed not very uniform and with the increase of microfibrillated cellulose, polylactic acid can not fully wrap fiber, so there will be some fibers left exposed, hence, the water vapour permeability of composite materials will dramatically increase. Fig. 15 shows that the 24 h water absorption of composite materials has an upward trend, especially after adding 5 % amount, the water absorption sharply increases. This is because in the process, the impact of processing temperature makes the water molecules adopted by microfibrillated cellulose in the preparation stage evapourate, when the composite re-exposed to water molecules, a large number of exposed hydroxyl and carboxyl groups will re-play role and absorb water molecules once again. The more microfibrillated cellulose contained,the more hydroxyl and carboxyl groups and water absorption there will be.

(3) The influence of microfibrillated cellulose content on thermal properties of composite materials.

Different microfibrillated cellulose content on the thermal properties of composite materials, different effects, the study

compare different microfibrillated cellulose contents DSC curves of the composites, the results are shown in Fig. 16.

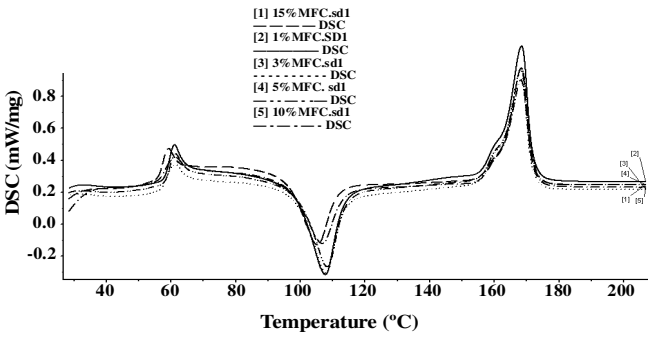


Fig. 16. Content *vs*. DSC

It can be seen from Fig. 16, with the content of microfibrillated cellulose increasing, the glass transition temperature and cold crystallization temperature of polylactic acid in composites decreases. microfibrillated cellulose is a greater retender of the material, even in the dry case, there will be some combination of water and polylactic acid is easily hydrolyzed macromolecules, when the both in high temperature mixed, the microfibrillated cellulose will evapourate water molecules, resulting in lower molecular content after hydrolysis of polylactic acid. The more of microfibrillated cellulose added, the more obvious this phenomenon will be, as a result the glass transition temperature of polylactic acid forward. And because of steric effects of microfibrillated cellulose,the cold crystallization temperature and peak area are smaller. Crystallization temperature of the polymer has a significant effect on molten, the lower the crystallization temperature is, the lower the melting point will be. Because molecular weight declines,higher levels of polylactic acid composite materials were added,the melting point will be lower, melting peak area will be smaller. But 10 % content polylactic acid relative to the glass transition temperature and cold crystallization temperature are higher than that of the other types of dosage, however, the melting peak area, or show a downward trend, which indicates that when the amount of microfibrillated cellulose added was 10 %, the two have a better compatibility. This is consistent with the change in tensile strength and elongation at break of composite.

Conclusion

Composite materials filled in eucalyptus microfibrillated cellulose have the maximum tensile strength, but the minimum rate in elongation at break. The one filled in bamboo microfibrillated cellulose fiber has the opposite results to the former.

As the processing temperature increases, the tensile properties of composite materials is rising, while the changes in elongation at break is not obvious, indicating not much change in the material ductility. Shrinkage, water absorption increase with increasing temperature, but changes are not so obvious. Considering each performance of composite materials, the best processing temperature is 180 ºC.

Microfibrillated cellulose filler increases the tensile properties, but not shown as an upward trend, which can be determined that for the tensile properties ,the dosage of 10 % is the best content.

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