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Influence of silicone oil modification on properties of ramie fiber reinforced polypropylene composites

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ABSTRACT

This paper focused on the analyses of the composition, microstructure, thermal stability and mechanical behavior of modified ramie fiber and its reinforced polypropylene composites. Ramie fiber (RF) was treated with epoxy-silicone oil (ESO) at 160 °C in argon gas. The FTIR and XRD analyses indicated that some silicone molecular chains were bonded on the surface of modified RF, which decreased the crystallinity of the fiber without changing the crystalline type of cellulose. The SEM results of fracture surface showed that the modified RF/PP composite had better interfacial bonding between RF and PP. The mechanical tests showed that the impact strength and the elongation at break of RF/PP were increased by 17.0% and 196% after modification, respectively. The tensile strength of 30RF/PP was improved from 18.95 MPa to 25.96 MPa compared to pure PP. The results of TGA showed that fiber treatment could improve the degradation temperature of RF/PP composites.

1. Introduction

As a result of the increasing demand for environmentally friendly materials and the desire to reduce the cost of traditional fibers (i.e. carbon, glass and aramid) reinforced petroleum-based composites, natural fiber reinforced polymer composites have been found in an increasing number of applications in recent years (Alcock, Cabreta, Barkoula, & Peijs, 2006; Peijs, 2003). These fibers are high specific strength and modulus, low price, low weight, degradable, recyclable, etc. (Bullions, Hoffman, Gillespie, Price-O'Brien, & Loos, 2006; Soykeabkaew, Supaphol, & Rujiravanit, 2004). However, there are some disadvantages of natural fibers. One is the low processing temperature of natural fiber (NF), which makes that the NF/polymer composites are not easy to be processed. On the other hand, the hydrophilic natural fibers have a poor interfacial adhesion with the hydrophobic polymer matrices. This leads to poor adhesion at the interface of NF and polymers and finally influences the mechanical properties of composites. So it is necessary to modify the natural fibers and change their surface properties.

Currently, various treatments were used to improve the matrix-fiber adhesion (John, Francis, Varughese, & Thomas, 2008; Yu, Ren, Li, Yuan, & Li, 2010). This step is considered critical in the development of NF/polymer composites. Current available modification methods can be grouped into physical treatment and chemical treatment. The chemical graft is one of the mainly used chemical treatment method. Most researchers were interested in chemical modification. They tried to form chemical bonds between the cellulose in fiber and polymer matrix with a kind of chemicals, such as acetic anhydride, alkali, silane, and so on (Alix et al., 2009; Bessadok, Roudesli, Marais, Follain, & Lebrun, 2009; Han & Yan, 2010; Joseph, Joseph, & Thomas, 1999; Qin, Soykeabkaew, Xiuyuan, & Peijs, 2008). So far, most work has been done with low molecular weight agents. The coupling agents with higher molecular weight have the potential to achieve better modification effects on the interfacial adhesion between NF and polymer, mechanical properties, and heat resistance of NF/polymer composites than those with lower molecular weight.

Therefore, the epoxy-silicone oil (ESO) with a high weight-average molecular weight of 40,000 was applied to modify ramie fiber (RF) in this work. Then RF/PP composites were fabricated. The treatment caused a higher dispersion of ramie fibers in PP matrix and a richer adhesion between fibers and matrix. As a result, the mechanical properties of the composites were improved by the treatment.

2. Experimental

2.1. Materials

Ramie fiber and polypropylene (PP 1100, PetroChina Lanzhou Petrochemical Company, China) are commercial products.

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Epoxy-silicone oil (KHS-207) with viscosity of 3000 mPa s was from Jiaxing Kaihua Organic Silicon Materials Co., China.

2.2. Modification process of ramie fiber

The ramie fiber was treated with the home-made silicone oil emulsion in a high temperature reactor (GCF-2 autoclave). The treatment was conducted at 160 °C for 3 h with the atmosphere of argon. Then the treated ramie fiber was cleaned and dried.

The home-made silicone oil emulsion was composed of ESO, alkylphenols polyoxyethylene (OP-10) and cetyl alcohol. The three materials were mixed in a flask with distilled water, then stirred and ultrasonic-dispersed for 3 h at 50 °C.

2.3. Fabrication of composites

The samples of RF/PP composites were prepared with a hybrid technology of extrusion and injection. Firstly, the anhydrous ramie fiber and polypropylene were mixed homogeneously with a TE-35 double screw extruder, and then the mixed material was cut into particles. Finally, the particles were injected into samples for mechanical property test by an HD-1100 injection machine (Hangzhou Huada Plastics Machinery Co., Ltd., China). The 10RF/PP, 15RF/PP, 20RF/PP, 25RF/PP, and 30RF/PP composites with the modified ramie fiber and the unmodified ramie fiber were prepared. The 10RF/PP is namely as the ramie fiber/polypropylene composites with fiber content of 10 wt.%, and so forth.

2.4. Characterization

The composition, microstructure and thermal property of the fabricated composites were analyzed with FTIR, XRD, TGA and SEM technologies. The FTIR spectra were recorded with a Perkin Elmer 2000 FTIR instrument. The non-reacted epoxy-silicone oil (ESO) on the ramie fiber was removed by acetone for 48 h before FTIR test. The crystal changes of the fibers were evaluated by X-ray diffraction (XRD). The XRD patterns were obtained by using Siemens Diffractometer D5000 with radiation Cu K_α at a scanning rate of 6° min^{-1} from 4° to 70°. The thermogravimetric (TGA) curves were carried with NET ZSCH STA-449 PC/PG under continuous air flow at a heating rate of 10 °C min^{-1}. Fracture morphology was characterized with an environmental scanning electron microscope of FET QUANTA 200. Izod impact test was performed with a CBL-11J pendulum apparatus according to ASTMD 256. Tensile test was performed on a WDW3020 testing machine according to ASTMD 638.

3. Results and discussion

3.1. FTIR analysis

Infrared spectra of ESO, the modified ramie fiber and the unmodified fiber are displayed in Fig. 1. It was found that there were two new peaks presented in modified fiber at 1259 cm^{-1} and 804 cm^{-1}, respectively, which are the absorption peaks of $-CH_3$ and Si–C in Si–CH_3 (Feng, Zhang, Li, & Zhu, 2004). 2965 cm^{-1} is the C–H stretching vibration peak.

The peaks at 1030–1161 cm^{-1} are the absorption peaks of cellulose and Si–O–Si bond (Kim, Noh, Choi, Lee, & Jhon, 2000; Mulinari, Voorwald, Cioffi, da Silva, & Luz, 2009). The enhanced intensity of these absorption peaks at 1030–1161 cm^{-1} after modification proved the reaction between cellulose and ESO. The absorption peak of 901 cm^{-1}, which indicates the absorption peak of β-D-glucoside bond (Briner, Bernet, Maloisel, & Vasella, 1994) changed little after the modification, indicating the ESO did not damage the structure of the cellulose.

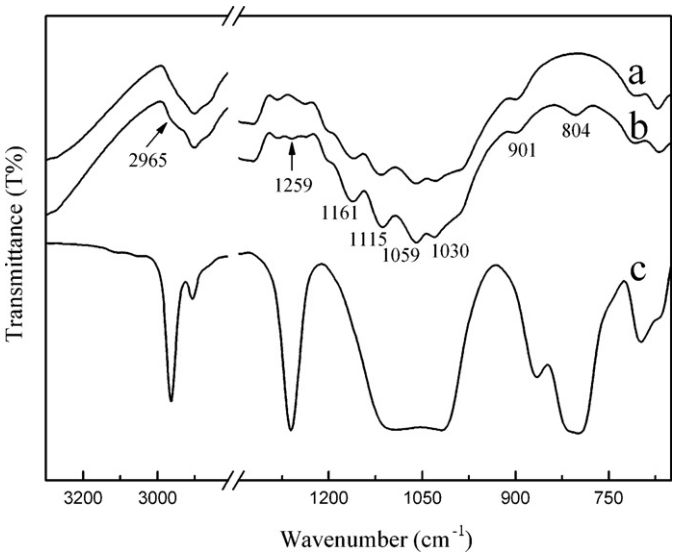

Fig. 1. FTIR spectra of ramie fibers (a) unmodified, (b) modified and (c) ESO.

3.2. X-ray diffraction analysis

The XRD patterns of the unmodified ramie fiber and the modified ramie fiber are shown in Fig. 2a and b, respectively. It was reported that the crystallinity index (CI) could be evaluated by using Segal empirical method according to the following Eq. (1) (Mulinari et al., 2009):

$$\mathrm{CI}(\%) = \frac{(I_{0\,0\,2} - I_{\mathrm{am}})}{I_{002}} \times 100 \quad (1)$$

where I_{002} is the maximum intensity of the [0 0 2] lattice reflection of the fiber and I_{am} is the maximum intensity of X-ray scattering broad band due to the amorphous part of the fiber.

According to the Eq. (1), the CI of the modified ramie (59.4%) was a little lower than 62.9% of the unmodified fiber. It could be explained that the increased disordered arrangement of cellulose decreased the crystallinity of the fiber. The CI of modified fiber and unmodified fiber nearly agreed with the theoretical value of ramie cellulose *I* as 64% according to the study of Ishikawa, Okano, & Sugiyama (1997). The spectrums also showed the X-ray diffraction spectrum of the modified ramie fiber was similar to that of the unmodified ramie fiber. This proved that the fiber treatment did not change the crystalline type of cellulose.

3.3. SEM analysis

The morphologies of the fractured surfaces of notched Izod specimens of the composites with untreated ramie fiber and treated ramie fiber were investigated by SEM. The results are shown in Fig. 3. Fig. 3a and c shows the fractured surface of the unmodified RF/PP composites, in which many fibers were pulled out from the matrix. It can be seen that the pull-out fiber surface was smooth and clean, and some evident gaps could be seen between the fiber and the matrix, which indicating the adhesion between matrix and fibers was weak. However, the fracture surface of modified RF/PP (in Fig. 3b and d) showed a small amount of matrix material (PP) attached on the surface of the pull-out ramie fibers, and the fibers were mostly embedded within the PP matrix. At the same time, there were a number of fiber filaments adhering to the surface of the matrix. These indicated that the fiber treatment resulted in better interface compatibility between natural fiber and PP, and hence improve the interfacial adhesion between NF and polymer.

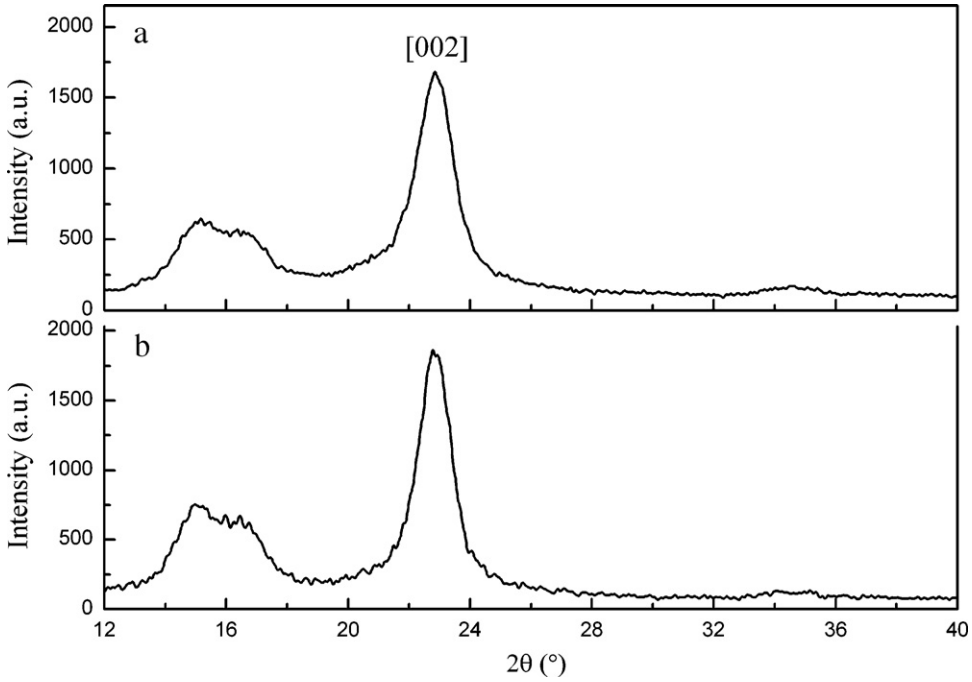

Fig. 2. X-ray patterns for ramie fibers (a) unmodified and (b) modified).

3.4. Mechanical properties of composites

The results of notched Izod impact strength of the tested composites are shown in Fig. 4. The impact resistance of the modified RF/PP composite was significantly higher than that of the unmodified composites. The ESO treatment improved the interfacial adhesion between ramie fiber and PP to resist crack propagation during impact test. Compared to the unmodified RF/PP composites, the higher the fiber content, the more increase of the impact strength of the modified RF/PP. It was improved by 17.0% with the addition of ramie fiber of 30 wt.%. In addition, the impact property of ramie fiber was lower than that of pure PP. This leaded to the decrease of impact strength of the RF/PP composites with the increase of the fiber content.

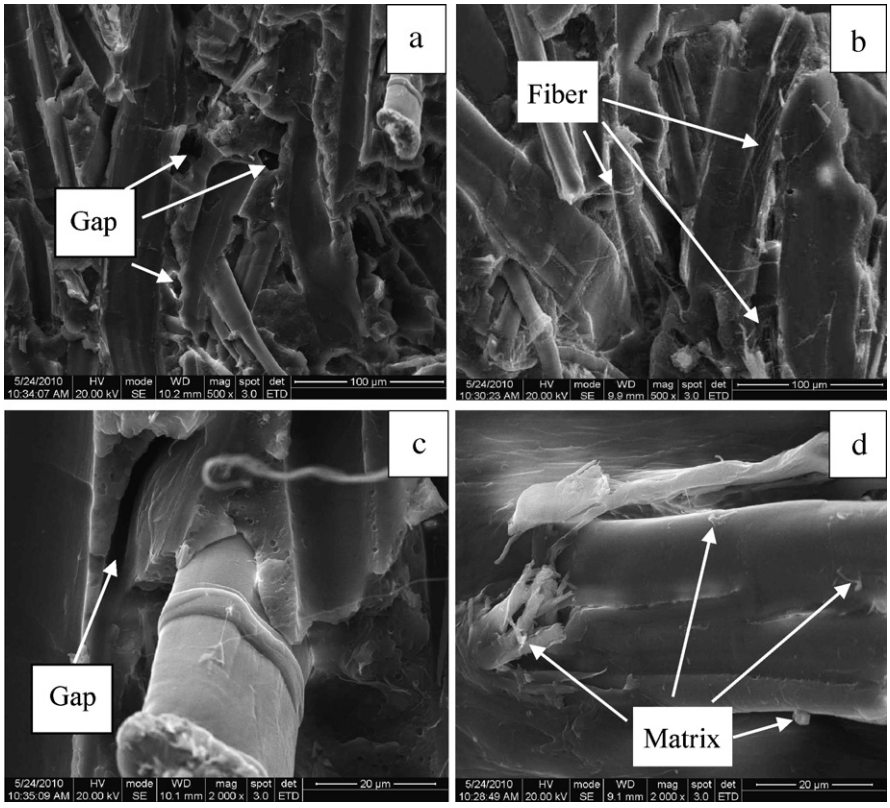

Fig. 3. SEM images of the unmodified RF/PP composites (a and c) and the modified RF/PP composites (b and d).

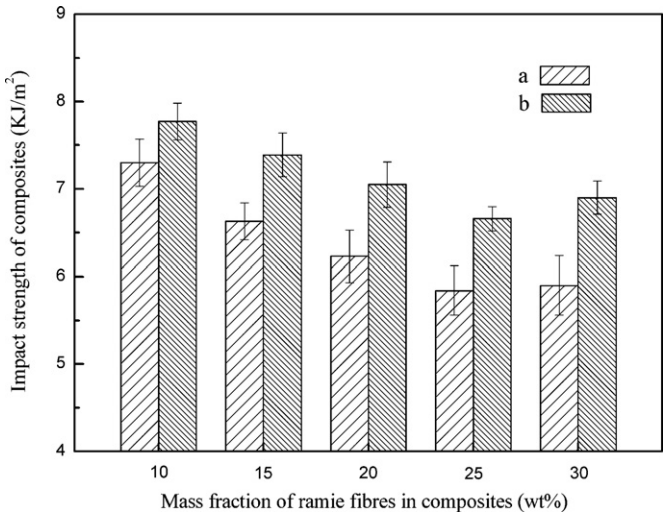

Fig. 4. Effect of ramie fiber content on impact strength of the RF/PP composites (a) unmodified, (b) modified.

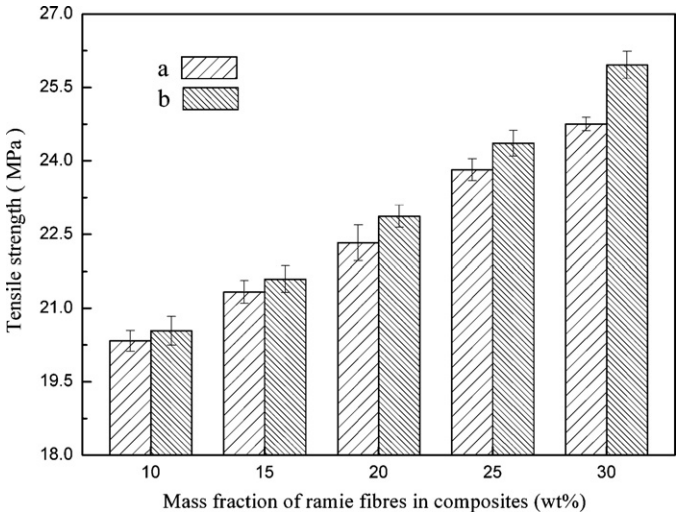

Fig. 6. Effect of ramie fiber content on tensile strength of the RF/PP composites (a) unmodified and (b) modified.

The typical stress–strain curves of the modified RF/PP composites were presented in Fig. 5. It was shown that the higher the fiber content, the stronger the tensile strength of the composites. The tensile strength of 30RF/PP composites was improved about 37% compared to that of the pure PP. With increasing of ramie fiber content, the fibers would distribute in the matrix continuously. At last the fiber and the matrix would have become interpenetrating network structure, inducing the stress of the matrix to be passed to the fiber, thereby enhancing the strength of the material.

In addition, the tensile strength and tensile modulus between the modified and the unmodified RF/PP composites were compared. Fig. 6 shows that the tensile strength of modified RF/PP composites have been somehow improved by 1–5% at different fiber contents, compared to those of unmodified RF/PP composites. And the comparison of tensile modulus between the two types of composites displayed the same trend like that of the tensile strength. It indicated that the fiber treatment with ESO played a little effect on improving the tensile properties of RF/PP composites.

Fiber treatment played an important role in the elongation at break of the RF/PP composites. Fig. 7 shows the elongation at break of the modified 10RF/PP composites increased by 196% compared to that of the unmodified composites. It also indicated that the higher the fiber content, the less improvement the elongation of the composites. The improvement of the elongation of 30RF/PP decreased to 25.3%. The elongation at break of the composites was mainly affected by the properties of the matrix. The treatment could improve the interface adhesion between the fiber and the matrix, which induced the stress of the matrix to be passed to the fiber and delayed the cracks propagation. Therefore, the modified composites presented a higher elongation.

3.5. Thermal analysis

TGA analysis was performed on the composites as a basic measure of their thermal stability. It could be seen that modification decreased the thermal decomposition rate of the 30RF/PP composites from Fig. 8. The pyrolysis of the main components in PP and the unmodified 30RF/PP composite occurred at about 324 °C, while thermal degradation temperature of the modified 30RF/PP composite was increased to 370 °C. In addition, it was found that the higher the fiber content, the better the heat resistance of the RF/PP composites. The reason was that the ESO treatment changed the surface features of the ramie fiber, and thus led to improve the heat

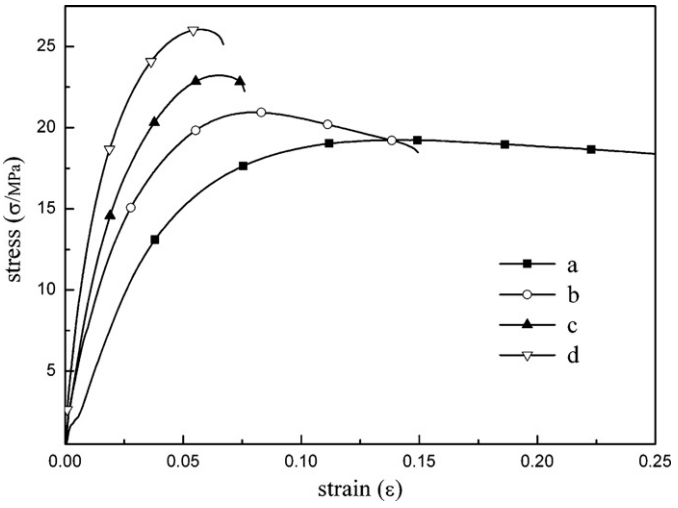

Fig. 5. Stress–strain curves of PP (a) and the modified 10RF/PP (b), 20RF/PP (c), and 30RF/PP (d) composites.

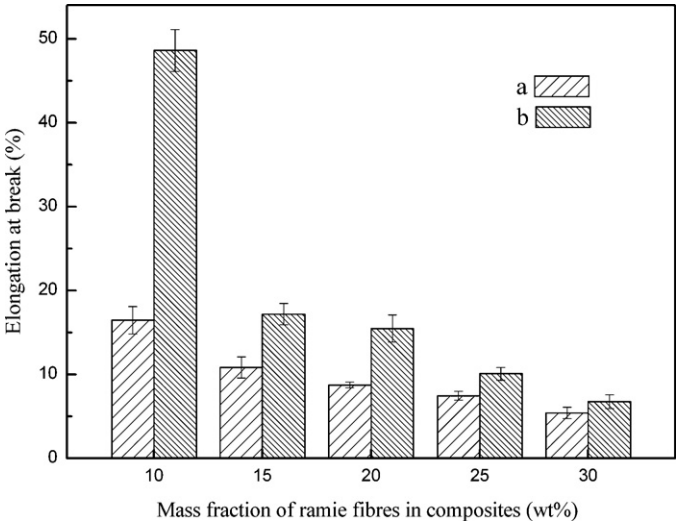

Fig. 7. Effect of ramie fiber content on the elongation at break of the RF/PP composites (a) unmodified and (b) modified.

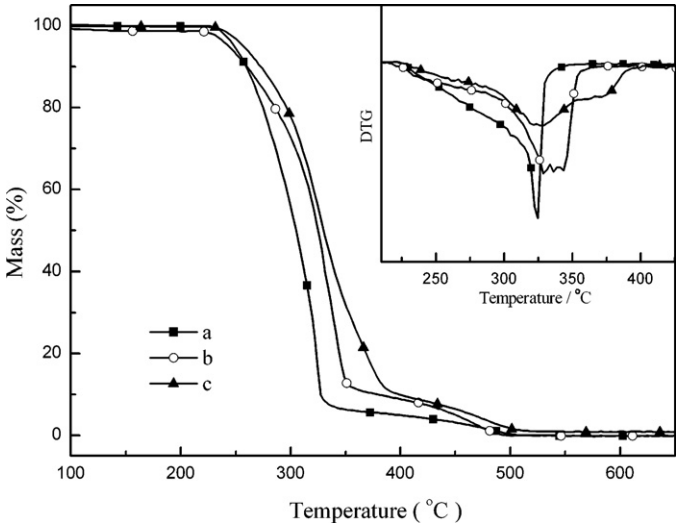

Fig. 8. TGA curves of PP (a) and the 30RF/PP composites (b) unmodified, and (c) modified).

resistance of the composites. It was also noticed that the modified RF/PP composite was in the color of white, and the unmodified RF/PP composites was in the color of shallow yellow. This suggested that the fibers in the unmodified RF/PP composites were oxidized by the air during extruding process due to its lower thermal resistance.

4. Conclusions

The epoxy-silicone oil was used to treat natural ramie fiber. The results showed that the surface treatment improved the compatibility between ramie fibers and PP matrix without changing the crystalline type of ramie fiber. The mechanical properties of the modified RF/PP were better than that of the unmodified composites and PP, due to the enhanced interfacial adhesion between the PP and the ramie fiber, especially the impact strength. The TGA results indicated that the modification improved the heat resistance of the composites, and the heat resistance also depended on the ramie fiber content. The results showed that the higher the fiber content, the stronger the heat resistance of the composites. Therefore, epoxy-silicone oil treatment could modify the surface features of natural fibers, and thus results in nature fiber/polymer composites with better thermal and mechanical properties.

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References

Alcock, B., Cabreta, N. O., Barkoula, N.-M. & Peijs, T. (2006). The mechanical properties of unidirectional all-polypropylene composites. *Composites: Part A*, *37*(5), 716–726.

Alix, S., Philippe, E., Bessadok, A., Lebrun, L., Morvan, C. & Marais, S. (2009). Effect of chemical treatments on water sorption and mechanical properties of flax fibres. *Bioresource Technology*, *10*, 4742–4749.

Bessadok, A., Roudesli, S., Marais, S., Follain, N. & Lebrun, L. (2009). Alfa fibres for unsaturated polyester composites reinforcement: Effects of chemical treatments on mechanical and permeation properties. *Composites: Part A*, *40*, 184–195.

Briner, K., Bernet, B., Maloisel, Jl. & Vasella. (1994). Glycosylidene carbenes. 19. Regioselective glycosidation of allyl 2-deoxy-2-phthalimido-D-allopyranosides. *Helvetica Chimica Acta*, *77*(7), 1969–1984.

Bullions, T. A., Hoffman, D., Gillespie, R. A., Price-O'Brien, J. & Loos, A. C. (2006). Contributions of feather fibers and various cellulose fibers to the mechanical properties of polypropylene matrix composites. *Composites Science and Technology*, *66*, 102–114.

Feng, S., Zhang, J., Li, M. & Zhu, Q. (2004). *Silicone polymer and its application* (1st ed.). Beijing: Chemical Industry Press., chapter 16.

Han, D. & Yan, L. (2010). Preparation of all-cellulose composites by selective dissolving of cellulose surface in PEG/NaOH aqueous solution. *Carbohydrate Polymers*, *79*, 614–619.

Ishikawa, A., Okano, T. & Sugiyama, J. (1997). Fine structure and tensile properties of ramie fibres in the crystalline form of cellulose I, II, III_1 and IV_1. *Polymer*, *38*(2), 463–468.

John, M. J., Francis, B., Varughese, K. T. & Thomas, S. (2008). Effect of chemical modification on properties of hybrid fiber biocomposites. *Composites: Part A*, *39*, 352–363.

Joseph, P. V., Joseph, K. & Thomas, S. (1999). Effect of processing variables on the mechanical properties of sisal-fiber-reinforced polypropylene composites. *Composites Science and Technology*, *59*, 1625–1640.

Kim, J. W., Noh, M. H., Choi, H. J., Lee, D. C. & Jhon, M. S. (2000). Synthesis and electrorheological characteristics of SAN–clay composite suspensions. *Polymer*, *41*(3), 1229–1231.

Mulinari, D. R., Voorwald, H. J. C., Cioffi, M. O. H., da Silva, M. L. C. P. & Luz, S. M. (2009). Preparation and properties of HDPE/sugarcane bagasse cellulose composites obtained for thermokinetic mixer. *Carbohydrate Polymers*, *75*(2), 317–321.

Peijs, T. (2003). Composites and recyclability. *Materials Today*, (April), 30–35.

Qin, C., Soykeabkaew, N., Xiuyuan, N. & Peijs, T. (2008). The effect of fibre volume fraction and mercerization on the properties of all-cellulose composites. *Carbohydrate Polymers*, *71*, 458–467.

Soykeabkaew, N., Supaphol, P. & Rujiravanit, R. (2004). Preparation and characterization of jute- and flax-reinforced starch-based composites foams. *Carbohydrate Polymers*, *58*, 53–63.

Yu, T., Ren, J., Li, S., Yuan, H. & Li, Y. (2010). Effect of fiber surface-treatments on the properties of poly(lactic acid)/ramie composites. *Composites: Part A*, *41*(4), 499–505.