Review of the Surface Treatments of Plant Fibers as Reinforcements in Polymer Composites

Z H Zhu 1, Y Zhang1, N Zhang 1, T Wang 1 and M Y Hao 2
1 School of advanced manufacturing technology, Guangdong Mechanical & Electrical Polytechnic, Guangzhou, China;
2 The Key Laboratory of Polymer Processing Engineering, Ministry of Education, South China University of Technology, Guangzhou, China
Email: 184823174@qq.com

Abstract. The poor compatibility between plant fiber and polymer matrix leads to many defects and deficiencies in plant fiber reinforced polymer composites. Various common physical or chemical treatments of plant fibers are listed in this paper. Surface treatments can improve the interface bonding of fibers and matrix, whereas the mechanical properties of plant fibers will be greatly reduced after treatments. How to retain the properties of plant fibers to the greatest extent and improve the comprehensive properties of plant fibers reinforced polymer composites is a problem that needs attention and urgent solution when treating plant fibers by various treatments.

1. Introduction
The research of natural fiber reinforced PLA composites has been a hot spot in the field of polymer composites in recent decades. Compared with traditional composites, natural fiber reinforced PLA composites have advantages of environmental friendliness and reproducibility. [1-2] The greatest challenge in preparing natural fibers reinforced PLA composites is their large variation in properties and characteristics. [3] Various kinds of methods for pretreating of fibers had been used to improve the interface bonding of matrix and fibers in the previous research. [4-7] Though these methods improved the interfacial adhesion of fibers and matrix, they eliminated some components and destroyed the construction of fibers, which declined the fiber strength and the mechanical properties of composites couldn’t be enhanced as expected. In our previous work, we compounded alkali-treated SFs (ASFs) with untreated SF (USFs) to prepare hybrid SFs (HSFs) which were then filled into PLA matrix to prepare PLA/HSF composites. It was found that HSFs could improve mechanical properties of PLA composites more significantly than ASFs and USFs. In this work, we give a further study of the dynamic mechanical properties analysis (DMA) of the PLA, PLA/ASF and PLA/HSF composite.
2. Treatments of plant fibers

The essential problem of the treatments of plant fiber is how to reduce the hydrophilicity of plant fiber and thus improve the interface property of the composites. [2] At present, the commonly used method of surface treatments of plant fibers mainly includes physical treatments and chemical treatments.

2.1 Physical treatments

Physical treatments improve the structure and surface morphology of plant fibers, which doesn't change the chemical composition of the plant fibers. After physical treatments, the surface roughness of plant fiber increases, the contact area between plant fiber and polymer matrix increases, and the physical adhesion between plant fiber and polymer matrix is effectively improved. [3] Common physical treatments mainly include heat treatment, discharge treatment, steam explosion treatment and so on.

2.1.1 Heat treatment

The presence of a large number of hydroxyl groups (\(-\text{oh}\)) makes the plant fiber have a strong water absorption and a high water content, so that the polymer matrix and the plant fiber cannot combine well. Heat treatment is the most direct method to reduce the moisture content of plant fiber. Etrissans et al. [4] studied the water absorption of wood fiber after heat treatment, and found that the contact angle of wood fiber changed after heat treatment, resulting in decreased water absorption and increased hydrophobicity, which could increase the interfacial compatibility between wood fiber and polymer matrix. Giebeler studied the influence of heat treatment on the mechanical properties and morphology of wood fiber, and found that the bending strength and tensile strength of wood fiber significantly decreased during the heat treatment of 180-200°C. Heat treatment reduced the moisture content of wood fiber, increased the insulation of wood fiber, and deepened the color of wood fiber. [5] Pétrissans et al. studied the water absorption of wood fiber after heat treatment, and found that the change of contact angle of wood fiber after heat treatment resulted in the decrease of water absorption and increase of hydrophobicity, which could increase the interfacial compatibility between wood fiber and polymer matrix. [6] Ayadi studied the resistance to ultraviolet light of wood fiber after heat treatment, and found that heat treatment could improve the resistance to ultraviolet light of wood fiber and increase the stability of wood fiber. [7]

2.1.2 Discharge technology treatment

Discharge technology treatment refers to the use of electron beam to treat plant fiber to improve the surface morphology and structure of the treatment. Among these treatments, surface corona treatment is commonly used, which is one of the effective methods to change the surface characteristics and improve the surface morphology and structure of plant fibers. Kan et al. treated the natural fiber with low-temperature plasma and studied the change of fiber surface morphology before and after treatment with scanning electron microscope. It was found that the surface roughness of natural fibers increased after low-temperature plasma treatment, and the degree of fiber orientation along the axis increased with the treatment time increasing. [8] Khan et al. studied the influence of ultraviolet irradiation on the mechanical properties of sisal fibers and found that the tensile strength and elongation at break of sisal fibers increased after ultraviolet irradiation. [9] Li et al. studied the effect of electron beam irradiation on mechanical properties of sisal fiber reinforced polycaprolactone (PCL) composites with different contents, and found that the mechanical properties of composites were the best when the SF content of sisal fiber (SF) was 45% and the irradiation dose was 150 kGy. [10]

2.1.3 Steam blasting treatment
Steam blasting treatment refers to the process of cooling plant fibers after being treated under high temperature and pressure for a certain period of time under the action of steam. After steam explosion treatment, the cell walls of plant fibers are broken, lignin and hemicellulose structures are destroyed and removed, and thus increasing the solvent accessibility of cellulose. The contact area between plant fiber and polymer matrix also increases at the same time. [11] Qu prepared the composite materials with Cotton bast fiber and LDPE with steam blasting and studied the mechanical properties of the composites. It was found that the mechanical properties of the composites were better than those of the untreated Cotton bast fiber and pure LDPE. Qu pointed out that the surface roughness of the cotton-skin fiber increased after steam explosion treatment, which increased the contact area between the fiber and LDPE matrix and thus improved the mechanical properties of the composites. [12] Kaushik et al. prepared biodegradable composites by blending Wheat straw fiber treated by steam blasting and Starch plastics, and found that the crystallinity of the fibers after steam blasting was 46.8% higher than that before treatment. [13]

2.2 Chemical treatment
Chemical treatment is the improvement the properties or structure of plant fibers, so as to improve the interfacial compatibility of plant fiber and polymer matrix, and make plant fiber distributed more evenly in the composites, eventually make plant fiber reinforced polymer composites effectively. The common chemical include alkali treatment, surface grafting, interfacial coupling and acetylation.

2.2.1 Alkali treatment
Alkali treatment is a commonly used treatment for chemical treatments of plant fibers, and also used for other pre. After alkali treatment, most of the lignin hemicellulose and pectin were effectively removed, the length-diameter ratio of the fiber was improved, and the surface roughness of the fiber was increased. The concentration, temperature, treatment time and the additives in the treatment solution or process can all affect the effect of alkali treatment. Xia et al. studied the changes in the microstructure, thermal properties and tensile properties of cotton fibers treated with alkali, and found that the tensile strength, tensile modulus and crystallinity of fibers treated with alkali improved. [14] Kabir et al. found that the tensile strength and tensile modulus of Kenaf fiber after alkali treatment were significantly improved. [15] Iannace et al. compared the changes of sisal fibers before and after alkali treatment in the mixing process, and found that the degree of fibrillation of sisal fibers with alkali treatment increased, and the length of sisal fibers with alkali treatment decreased, and the ratio of length to diameter increased. [16] Mishra et al. treated sisal fiber with a lower concentration (mass fraction 5%) NaOH solution for 1 h, and found that the surface roughness of sisal fiber increased, the tensile strength and tensile modulus decreased, while the elongation at break did not change significantly. [17]

2.2.2 Surface grafting
Surface grafting is a very effective treatments technology to change the surface properties of plant fibers, which introduces alkyl, acetyl, benzyol, and other groups on the surface of plant fibers to improve the hydrophilic and hydrophobic surface properties of plant fibers. The surface grafting can be carried out not only before the compounding, but also during the blending process. Acrylonitrile (AN), maleic anhydride (MAH) and polylactic acid (PLA) are commonly used graft reaction monomers. Mishra et al. studied the mechanical properties of cyanoethylated sisal fiber reinforced polyethylene terephthalate (PET) composites and found that the tensile properties, bending properties and impact properties of cyanoethylated composites were improved compared with alkali treatment. [18] Chuai et al. grafted onto the surface of wood fiber with
maleic anhydride (MAH) to improve the interfacial compatibility between wood fiber and polypropylene (PP) matrix. It was found that the machinability and mechanical properties of the composites were all improved. [19]

2.2.3 Interfacial conjugation

Interfacial conjugation is the process of treating plant fibers with coupling agent and thus change their surface properties and improve their interfacial compatibility with polymer matrix.

The commonly used coupling agents include silane coupling agent, titanate coupling agent, etc. Before the coupling agent treatment, alkali solution is generally used to pretreat plant fibers to increase the accessibility of cellulose. Liu et al. modified wood fiber with silane coupling agent and then mixed it with PVC to prepare composites. Study found that silane coupling agent enhanced the interaction between wood fiber and PVC matrix, and the interface strength were improved obviously. [20] Liao et al. found that titanate coupling agent could improve the interfacial bounding between wood fiber and Linear Low Density Polyethylene (LLDPE) [21]. Huda et al. prepared the PLA/KF compositeS and studied their mechanical properties. It was found that the hemp fiber treated with alkali solution and coupling agent had the best interfacial compatibility with the PLA matrix, and the corresponding composite had the best performance. [22]

2.2.4 Acetylation

Hydroxyl group (-oh) can react with acetic anhydride (ch3-co-o-co-ch3) or enone (-c =C=O)

\[
R \text{OH} + CH_3 \text{CO} - O - CO - CH_3 \rightarrow R - O - CO - CH_3 + CH_3\text{COOH}
\] (1)

Chen et al. [18] pointed out that acetylation treatment can reduce the hydrophilicity of plant fibers effectively, and thus improve the interfacial compatibility of fibers and matrix. Wei et al. treated poplar fiber with Acetic acid, Benzoic acid and Propionic acid respectively and blended them with high-density polyethylene. It was found that the thermal stability and tensile strength of the composites reinforced with acetylated poplar fiber were improved, and the tensile strength of the composites treated with benzoic acid acetylated was higher than the other two composites, among which the tensile strength of the composites treated with acetic acid increased the least. [23]

Due to the complexity of plant fiber, the single physical or chemical treatment of plant fiber is often unable to achieve a better treatment effect. At present, processing technologies are often combined with various physical or chemical processing technologies to modify plant fibers to achieve ideal treatment effect. For example, the alkali treatment process is often used for the pretreatment of other processes to increase the accessibility of cellulose in plant fibers. Heat treatment is often used as the final treatment process before blending plant fibers with polymer matrix to remove moisture from plant fibers.

3. Conclusion

From the above physical or chemical treatment, it can be found that these surface can improve the surface characteristics of plant fibers and improve the interface performance between plant fibers and polymer matrix. However, the mechanical properties of plant fibers will be greatly reduced after treatments, which will be induced which will affect the comprehensive properties of the composites.

Therefore, the treatments of plant fiber becomes valuable only when the improvement of interface property is greater than the decrease of the property of plant fibers. In the following studies, how to retain the properties of plant fibers to the greatest extent and improve the comprehensive properties of plant fibers reinforced polymer composites is a problem that needs attention and urgent solution when treating plant fibers by
various.

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