Study of the addition of the hybrid sisal fibers on the dynamic mechanical property of SFs reinforced polylactic acid (PLA) composites

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Abstract. When sisal fiber (SF) is added into polylactide (PLA) matrix, the storage modulus of PLA/SF composites increases greatly which indicate the rigidity of the composite material increases obviously. Comparing PLA composites with pure PLA, it can be found that the glass transition temperature (Tg) of PLA composites is significantly higher than that of PLA which showed the heat resistance of the PLA composites can be improved obviously because of the addition of SFs in PLA matrix. The energy storage modulus of PLA/HSFs is the highest of all PLA composites. HSFs could improve the dynamic mechanical properties of PLA composites more significantly than ASFs and USFs.

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. Experiment

2.1. Materials
PLA 3051D, Nature Works™, was purchased by Shenzhen Bright China Industrial Company (China). SF bundles (GB/T 15031-94) were provided by Guangxi Sisal Company of Guangxi Province, China. Other chemical reagents were commercial products.

2.2. Samples Preparation
SFs were submerged into 10% NaOH solution (mass concentration) for 3 h. Then, ASFs were washed with distilled water and dried in the open air for 48 h. USFs were mixed with ASFs to fabricate HSFs in a mass ratio of 1:1 and then PLA, ASFs, USFs and HSFs were dried at 100 degrees for 4 h. Then PLA was compounded with SFs with a mass ratio 4:1 using a two-roll plastic mill (SK-160B, Shanghai Rubber Machinery Factory, China) at 180 degrees. Four kinds of samples were made: pure PLA, PLA/USFs, PLA/ASFs, and PLA/HSFs. Then, they were compressed into sheets by a hot press (QBL-350, Wuxi No.1 Rubber Plastics Mechanical Co. Ltd, China). The compression molding temperature and pressure were 190 degrees and 10 MPa, respectively.

2.3. DMA test
Perkin-Elmer DMA-7 was used to test the DMA of PLA and PLA composites. The size of the sample is 60×10×4mm, three-point bending mode is adopted, the vibration frequency is set as 1 HZ, and the heating rate rises from 50 to 250 degrees.

2.4. Polarizing Microscope
Polarizing microscope (POM) investigation was performed with a POM (Axioskop 40 POL, ZEISS, Germany).

3. Results and discussion

3.1. DMA analysis
As one of the test methods to characterize the mechanical properties of materials, dynamic mechanical properties analysis (DMA) is used to measure the strain response of materials under alternating stress. The dynamic energy storage modulus (E) obtained from DMA reflects the rigidity of the material, and the loss factor (tan δ) reflects the micro motion and phase transformation of the polymer chain in the material.

Figure 1 shows the relationship between temperature and storage modulus of PLA and PLA composite. It can be observed that the storage modulus of both pure PLA and composite materials decreases slowly, then decreases sharply in the range of glass transition temperature (Tg), and finally tends to be stable as the temperature goes up.

Comparing pure PLA with PLA composite, it can be found that after sisal fiber is added into PLA matrix, the storage modulus of composite materials increases significantly, that is, the rigidity of composite materials is significantly improved. For example, the storage modulus of PLA is 3300 MPa, while the storage modulus of PLA composites is above 4500 MPa at 50 degrees. It is mainly because
that the motion of molecular chains of PLA matrix is restricted due to the addition of sisal fibers with high specific area. Moreover, the flexural modulus of sisal fiber is about 12GPa which is much higher than 3600MPa of PLA. is blocked because of the interaction force between fillers and matrix.

Comparing PLA/ASFs with PLA/USFs, it can be found that the storage modulus of PLA/ASFs is higher than that of PLA/USFs. It is partly due to the better compatibility of ASFs and PLA matrix. In addition, alkali treatment convert some flexible bonds (cellulose-hemicellulose) of SFs into rigid bonds (cellulose-cellulose) with higher rigidity and thus enhanced the crystallinity of cellulose and ASFs, which can also improve the rigidity of PLA composite.

![Figure 1](image_url)

**Figure. 1** Curves between storage modulus and temperature of PLA and PLA composites

It can also be observed that the storage modulus of PLA/HSFs is the highest of three composites. It is mainly because that USFs in HSFs have better tensile property and ASFs in HSFs have better interface bonding with PLA matrix. Therefore, they can play a synergistic role and improve the rigidity of PLA/HSFs.

\( \alpha \) is the mechanical loss angle, and its tangent is known as the mechanical loss factor, which is commonly used to characterize the magnitude of mechanical loss or internal friction. Figure 2 shows the relationship between temperature and the tan of PLA and PLA composite. The peaks in figure 2 correspond to the \( \alpha \) relaxation of the main chain, which are believed to be the glass transition temperature (Tg) of the polymers.

It can be seen from figure 2 that the mechanical loss Angle \( \alpha \) is very small when temperature is below Tg, which means the mechanical loss is very small. It is mainly because the rates of the deformation of polymers mainly caused by the deformation of bond lengths and bond angles are quickly under external force and almost completely keep up with the change of the stress.

With the temperature increasing, the polymers change from a glassy state to a highly elastic state. The chain segment starts to move while the viscosity of the system is still very high. Therefore, the friction resistance of the motion of the chain segment is relatively large, which result the high elastic deformation are far behind the change of stress and large internal friction. When tempering temperature further heightens, the deformation gets larger. The chain segment moves freely and thus \( \alpha \) and internal friction decreases.

It can also be observed that the \( \alpha \) of PLA is much larger than that of PLA composite which indicated...
that the internal mechanical loss of PLA is much greater than that of PLA composites in the process of deformation. It can be seen from figure 2 that the transition peak of the PLA composites moves to the direction of high temperature obviously. Compared with pure PLA (Tg = 63.0 degrees), Tg of PLA/USFs PLA/ASFs and PLA/HSFs is 64.2 degrees, 68.1 degrees and 67.0 degrees respectively, and the height of the transition peak was also reduced. SFs have high rigidity and low density and thus a volume with little mass is still large. In addition, SFs are easier to aggregate. When added SFs to PLA matrix, the homogeneity of the two phases will be worse and the whole molecular chain of the blend system lacks flexibility.

It can also be seen that Tg of PLA/ASFs and PLA/HSFs is obviously higher than PLA/USFs. It is mainly because the interface bonding of the PLA/ASFs and PLA/HSFs is better than the PLA/USFs, which result the chain motion of the matrix molecules of the former two more restricted. In addition, the rigidity of SFs is improved after alkali treatment, which is another reason for the higher glass transition temperatures of PLA/ASFs and PLA/HSFs. Tg is the minimum temperature for the movement of macromolecular segments, which is closely related to the properties of polymers, especially the mechanical properties. Plastics will lose the properties of plastic and translate into rubbers with apparently lower modulus than plastics when temperature is higher than Tg. Therefore, the heat resistance and the operating temperature will be dramatically improved by adding SFs into PLA.

![Curves between storage modulus and temperature of PLA and PLA composites](image)

**Figure 2** Curves between storage modulus and temperature of PLA and PLA composites

### 3.2. POM analysis

POM of PLA and PLA composites are presented in figure 3. It can be seen that the crystals of PLA are like branches. However, a layer of crystals perpendicular to the axial direction of sisal fibers appears around SFs which indicated that a new crystal morphology namely transcrystallization appeared because of the addition of SFs in PLA matrix.

The crystals are oriented around the fibers in the direction of the fiber axis in transcrystallization which is mainly because some factors make the fiber become the nucleating material that induces the crystallization of the polymer matrix and thus a large number of crystal nuclei and crystals produced on the fiber surface which squeeze against each other and grow in a directed way. The dynamic and young's
modulus of transverse crystal are obviously higher than those of spherulite [8-9], which may be one of the reasons why the rigidity of the PLA composite is higher than that of PLA.

4. Conclusion

The storage modulus and Tg of SFs reinforced PLA composite were higher than PLA, which showed good rigidity and heat resistance of PLA/SF composites. As reinforcement, HSFs can improve the dynamic mechanical properties of PLA composites more significantly than ASFs and USFs.

![Fig. 3 POM investigation of PLA and composites](image)

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