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Preparation and Properties of Unmodified Ramie Fiber Reinforced Polypropylene Composites

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Abstract: Ramie fiber (RF) was used to reinforce the polypropylene (PP). The composites were prepared with a melting hybrid technology. Tests had been performed on PP and composites with different RF contents (10 wt%, 20 wt%, and 30 wt%). By using SEM, DSC, TGA, electronic universal testing machine, HDT-VICAT tester and coefficient of linear expansion tester, the effects of the RF loading were assessed on the basis of morphologies, mechanical and thermal properties as well as vicat softening temperature and CTE of the resulting composites. The results show that the thermal degradation temperature of the PP/RF composites becomes lower with higher fiber content. The crystallization rate of the PP matrix is accelerated by the unmodified RF. Because of the inferior interfacial bonding strength between RF and PP, the tensile strength of composites decreases by the presence of RF. And the RF used is relatively long compared with the diameter, the impact strength of the composites is improved by the unmodified RF. The vicat softening temperature of composites can be increased by about 5 ℃ in the presence of RF compared with PP. The CTE is reduced significantly in the presence of RF. Generally speaking, impact strength, crystallization rate, vicat softening temperature and CTE of PP/RF composites could be improved in the presence of RF. The tensile strength is decreased and thermal degradation temperature of composites becomes lower, but these should not affect most subsequent normal uses of the composites. As the unmodified RF is used directly, no hazardous waste is produced during the fabrication process, combined with the low price, so, a facile and economic preparation pathway is given by using unmodified natural fiber to reinforce polymer and composites with good performance obtained.

Key words: ramie fiber; polypropylene; composites; characteristics; properties

1 Introduction

As a result of the desire to reduce the cost of conventional fibers (*i e*, glass and carbon) reinforced petroleum-based composites, and the increasing demands for sustainability and also reconsideration of renewable resources, natural fibers (NFs) used as reinforcements in composites have been found in an increasing number of applications in recent years[1-4]. Most of the NFs are hydrophilic in nature as they are mainly composed of lignocellulose, which contains strongly polarized hydroxyl groups. Sometimes, the hydrophilic nature of natural fibers affects negatively interfacial adhesion with hydrophobic polymeric matrices and finally influences the mechanical properties of composites, especially for the tensile strength. Currently, in order to improve the fiber-matrix adhesion, various treatments were used to decrease the polarity of the natural fibers' surface. Current available modification methods like plasma, mercerization, acetylation, coupling agents, polymer grafting, can be mainly grouped into physical and chemical treatments[5-8]. The results showed that the treated NFs reinforced composite offered superior mechanical properties compared to that of untreated NFs. However, potential problems are that most of the modification methods have the disadvantages of using polluting organic solvents, producing hazardous waste and posing a risk to the environment. It would

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be undesirable that these potential problems impaired the advantages of using NFs such as environmental friendliness and safety factors. The ideal situation is that good properties or acceptable performance were obtained by using the NFs directly as reinforcements in composites. NFs have different origins such as cotton, flax, jute, hemp, sisal, ramie, bark, wood, nut shells, bagasse, corncobs, bamboo and cereal straw. Compared with conventional fibers, NFs provide many advantages: good mechanical properties, low cost and abundance, biodegradability, low density, renewability, non-abrasiveness to processing equipment and that incorporating the tough and light-weight NFs into polymer (thermoplastic or thermoset) matrices produces composites with good properties[3].

Compared with the pure polymer, if the properties of the untreated natural fibers/polymer composites remain at the same level, even mechanical properties of composites are slightly decreased; the composites are economically feasible and still competitive in the market, such as plastics and packaging industries, for lower price and low density of NFs.

Lots of studies focused on the tensile/flexural and impact strength of the NFs/polymer composites[3,4,6,7,9]. So far, not much attention has been paid to the vicat softening temperature, dimensional stability and other properties of unmodified RF as reinforcement by melt processing with thermoplastics matrix. And these properties should also be considered for practical applications of composites.

In the present study, polypropylene (PP) was used as matrix for their good properties and relatively low processing temperature which was essential because of low thermal stability of natural fibers. Commonly known as China grass, ramie is widely planted in both southern and northern China, used without modified as reinforcement. The effects of RF loading on some physical and mechanical properties of PP/RF composites were evaluated. We tried to prepare the composites with high vicat softening temperature and good dimensional stability by using unmodified RF as reinforcements. The purpose of this work is to give a facile and economic preparation and give a new insight into unmodified natural fiber-reinforced PP composites with acceptable performance.

2 Experimental

2.1 Materials

The ramie fibers (RF) were provided by Lu'An Hualong Hemp Spinning Crafts Co. Ltd, China. RF was cut with an average length of 10 mm before use. The matrix PP (T30S) was provided by Daqing Petrochemical Company, China. All the materials were dried at 110 ℃ for more than 6 hours before use.

2.2 Composites preparation

The samples of PP/RF composites were prepared with a melting hybrid technology. Firstly, the RF and PP were mixed homogeneously with a double-roller blending rolls, and then the mixed material was hot pressed into board by a hot pressing machine. Finally, the standard samples for mechanical property test were prepared by sawing or milling from the board. A series of composites with different RF contents were prepared.

2.3 Characterization

2.3.1 Morphology

The surface morphology of RF and fractured surfaces of composites were observed by a Quanta 200 FEG Environmental Scanning Electron Microscopy (SEM) system. All samples were gold coated prior to being loaded into the SEM chamber.

2.3.2 Thermal behaviors

The thermal behaviors of the composites were investigated using differential scanning calorimetry (DSC) and Thermal gravimetric analysis (TGA). DSC studies were carried out using a Q100 instrument (TA instruments, USA) in a nitrogen atmosphere. All samples were heated to 190 ℃ and held for 5 min to eliminate the influence of thermal history. A scanning rate of 10 ℃/min was adopted. The weight of the samples was about 5-10 mg. TGA studies were carried out using a Q-5000 IR instrument (TA instruments, USA) in an nitrogen atmosphere at a heating rate of 10 ℃/min. The temperature range used for the analysis was 40-700 ℃.

2.3.3 Mechanical properties

Tensile strength was determined out with an electronic universal testing machine (CMT6101, Shenzhen Sans Testing Machine Co., Ltd., China) at a speed of 10 mm/min according to GB/T 1040.2-2006.

Charpy notched impact strength was measured by using a XCJ-4 Impact Tester, according to GB/T 1043.1-2008. More than five specimens were tested for each test and the average data have been reported.

2.3.4 Vicat softening temperature

The vicat softening temperature was determined with a HDT-VICAT tester (ZWK1302-B, Shenzhen SANS Testing Machine Co., Ltd., Shenzhen, China) based on GB/T 1633-2000. Tests were conducted at 10 N loads from room temperature up to 200 ℃ at a heating rate of 120 ℃/h.

2.3.5 Coefficient of thermal expansion

The coefficient of thermal expansion (CTE) of composites was measured by linear expansion coefficient tester (PCY- III, Xiangtan Huafeng Instrument Manufacturing Co., Ltd., China) at a heating rate of 1 ℃/min.

3 Results and discussion

3.1 Surface morphology of RF

The surface morphology of the RF was investigated by SEM, as shown in Fig.1. It can be observed that the surface of untreated RF is not very smooth with characteristic longitudinal striations and has some defects in the form of pits and corrugations.

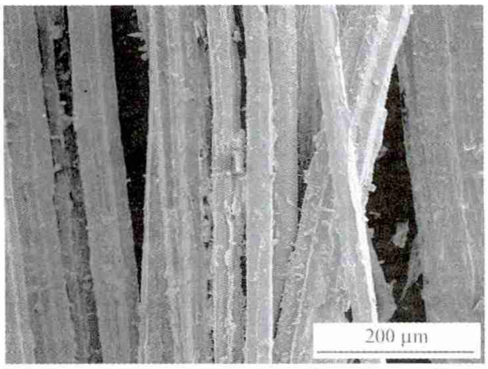

Fig.1 Morphology of the RF

3.2 Thermal analysis

As a basic measure of thermal stability, TGA analysis was performed on PP and the composites with different RF loadings. As shown in Fig.2(a), the pyrolysis of PP occurred at about 424 ℃. Thermal degradation temperature of the composites was decreased to 355, 341 and 327 ℃ for 10 wt%, 20 wt% and 30 wt% RF contents, respectively. In addition, it was found that the higher the fiber content, the lower the thermal degradation temperature of the PP/RF composites would become.

Fig.2(b) presents the peaks temperatures obtained from derivative thermograms of PP and composites. The degradation of PP was a one step process and the peak was observed around 471 ℃. In the composites two peaks were obtained; a minor peak at about 360 ℃ due to α-cellulose and hemicellulose degradation and the major peak at 470 ℃ indicating the degradation of PP. The addition of RF results in a decrease of degradation temperature. On comparing the stability of PP and composites, it was seen that thermal stability of composites containing unmodified RF decreased.

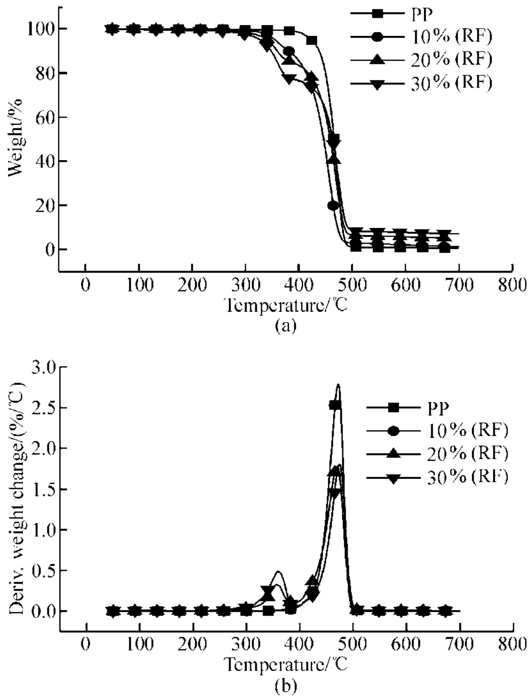

Fig.2 TGA (a) and DTG (b) results of PP and PP/RF composites

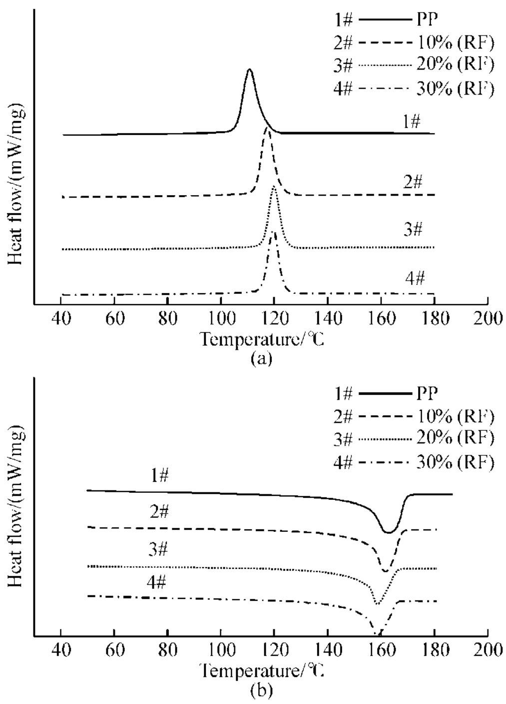

Fig.3 DSC cooling (a) and heating (b) curves of PP and PP/RF composites

The DSC heating and cooling thermograms for PP and composites are shown in Fig.3. The melting temperature (T_m), crystallization temperature (T_c), and heat of fusion ($\triangle H_m$) are listed in Table I. From Table 1, it is clearly observed that the T_m slightly decreased with increasing fiber loading, while the T_c increases obviously in the presence of RF. It is well known that the degree of supercooling, $\triangle T$ can be used to characterize the crystallization behavior of polymer. A decrease in △T generally indicates that the crystallization rate is accelerated. The △T values are given in Table 1. It is obvious that △T values were decreased with increasing RF content, which means that the crystallization rate of the PP matrix is accelerated by the unmodified RF.

Table 1 Melting and crystallization properties of PP and composites

Item	PP	10wt% RF	20wt% RF	30 wt % RF
T_m/℃	162.8	161.8	158.6	158.8
T_c/℃	110.6	117.3	120.0	119.6
△T/℃	52.2	44.5	38.6	39.2
△H_m(J/g)	108.1	91.3	80.5	78.2

3.3 Mechanical properties

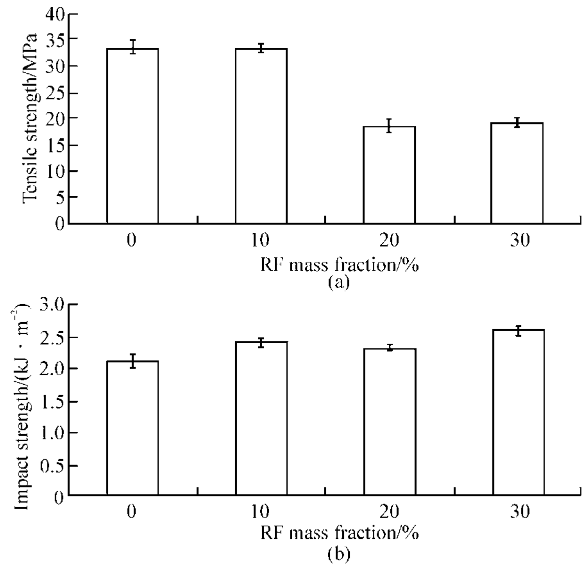

Fig.4 Effects of RF content on tensile strength (a) and charpy notched impact strength (b) of PP/RF composites

Fig.4 presents the variation in tensile strength and charpy notched impact strength with fiber weight fraction, respectively. As shown in Fig.4(a), when RF content is 10 wt%, the tensile strength is almost the same as PP. As fiber content increases, the tensile strength of composites decreases.

It is well known that no strong effect can be obtained unless the interfacial interaction between the PP matrix and the unmodified RF is sufficiently strong. This in turn could reduce adhesion at the interface, which causes inferior interfacial bonding strength as compared to the modified polymer/NF samples[10].

As shown in Fig.4(b), it is evident that moderate increase in impact strength occurred upon filling the PP matrix with the unmodified RF, as compared with pure PP. As for impact strength, the energy dissipation mechanisms operating during impact fracture include matrix and fiber fracture, fiber-matrix debonding and fiber pull out[11].

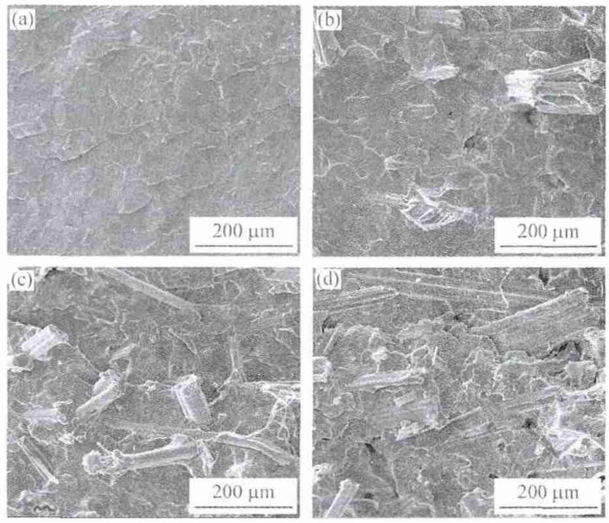

Fig.5 Fractured surface of PP/RF composites, (a)-(d) represent RF content at 0 wt%, 10 wt%, 20 wt%, 30 wt%, respectively

To further investigate the mechanism of the impact strength that was improved by the unmodified RF, the fractured surface was carefully analyzed by SEM, as shown in Fig.5. There were many fibers pulled out from the matrix. It can be seen that the surface of many pull-out RF was clean, and some evident gaps could be seen between the fibers and the matrix, indicating that the adhesion between matrix and fibers was weak. There was few fibers fractured that could be observed in Fig.5. Fiber fracture dissipates lesser energy compared to fiber pull out. The main failure mechanism in these composites is fiber pull out (as there is not significant interfacial adhesion), and the length of the RF used for this study was 10 mm, which was relatively long compared with the diameter. So impact strength of the composites was improved by the unmodified RF.

3.4 Vicat softening temperature

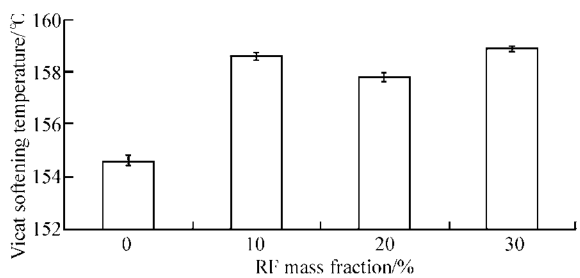

Fig.6 Effects of RF content on vicat softening temperature of PP/RF composites

The vicat softening temperature against PP and compositions is shown in Fig.6.

Vicat softening temperature test is a useful method for quantifying the effects of a solid additive or fiber in thermoplastic systems. If the fiber dissolves in the polymer by forming a solid solution, the softening temperature decreases. If the fiber is a second phase, the softening temperature increases[12] . From Fig.6, it can be seen that the vicat softening temperature of composites can be increased by about 5 ℃ in the presence of RF in comparison with PP.

3.5 Coefficient of thermal expansion

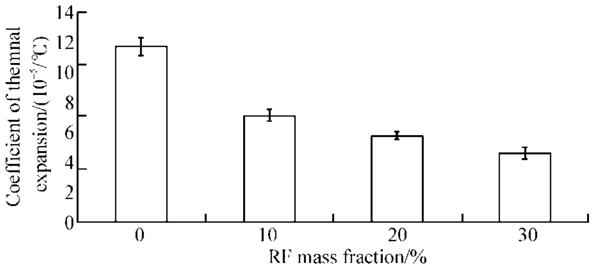

Fig.7 Effects of RF content on CTE of PP/RF composites

As shown in Fig.7, the CTE reduced significantly in the presence of RF. In addition, the CTE was found to decrease with increasing fiber loading. It is well-known that the difference of CTE between different composites for functional parts may cause deformation, cracking, and fracture during their application, resulting in the failure of the functional parts. As the polymer/NF composites are usually used in plastics and packaging industries, composites with a low CTE are becoming more and more important.

4 Conclusions

This study focused on the effects of using unmodified RF to obtain the composites with good properties. The impact strength, crystallization rate, vicat softening temperature and CTE of composites could be improved in the presence of unmodified RF. As the unmodified RF was used directly, fiber reinforcing efficiencies were not as high as the modified fiber or other fiber-reinforced system by using compatibilizers. The tensile strength was slightly decreased and the thermal degradation temperature of the composites became lower, but these should not affect most subsequent normal uses of the composites.

This study also provided evidence and gave a new insight to further understand the mechanism for the modified fiber-reinforced polymers. And no hazardous waste was produced during the fabrication process, combined with the low price, the introduction of unmodified RF into PP can further extend the use of natural fiber-reinforced PP composites in plastics, wood-plastic composites, board, packaging and other industries.

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