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Synergetic effect of epoxy resin and maleic anhydride grafted polypropylene on improving mechanical properties of polypropylene/short carbon fiber composites

Minggang Li, Xin Wen *, Jie Liu, Tao Tang *

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

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ABSTRACT

The influence of epoxy resin (EP) and maleic anhydride grafted polypropylene (PPMA) on mechanical properties of polypropylene/short carbon fiber (PP/SCF) composites was studied. The combination between EP and PPMA showed a synergistic effect on improving the mechanical properties of PP/SCF composites, including tension, flexural and notched impact properties. The synergistic mechanism was studied by means of SEM observation, FTIR analysis, extraction test and rheological measurement. The results showed that the synergistic mechanism was attributed to the improved network structure of SCF in PP matrix assisted by EP and PPMA. EP adsorbed onto the surface of SCF reacted with PPMA to form an enhanced interfacial interaction between PP and SCF, meanwhile the crossover sites of adjacent SCFs were locked by the cured EP component to form a strong network.

1. Introduction

With the demand of high-performance polymeric materials, short fiber reinforced polymer composites (SFRP) have attracted increasing interest for researchers in the field of materials science from both academia and industry [1–3]. According to the source and chemical composition, the short fiber can be classified into glass fiber, carbon fiber, aramid fiber, Kevlar fiber and natural fiber. Among all of these fibers, short carbon fiber (SCF) was more attractive due to its advantages with light mass, high conductivity, and superior reinforce-effect for polymer matrices [4,5].

Polypropylene (PP) is one of the most widely used common plastics with widely applications in the field of packaging, textiles, automobiles, electric industry, etc. [6–8]. However, its application as engineering plastics is greatly restricted due to its low modulus and strength. Therefore, considering the advantages of SCF, a feasible way to improve the stiffness of PP is to prepare PP/SCF composites. Hitherto much excellent research work has been done in PP modification and novel material exploitation by incorporating SCF. For example, Fu et al. [9] investigated the effects of fiber content and length on tensile properties of PP/SCF composites. Rezaei et al. compared mechanical properties of PP/SCF composites with steel to choose for car bonnet application [10,11].

It is well known that the interfacial adhesion between fillers and polymer matrix was one of the key factors to determine the structure and properties of obtained polymer composites [12,13]. Maleic anhydride grafted polypropylene (PPMA) is generally employed as compatibilizer to improve the interfacial adhesion between PP and filler [14–16]. Karsli et al. used PPMA to enhance the interfacial adhesion between SCF and PP, and the ultimate tensile strength and modulus of modified PP composites were higher than those of SCF directly reinforced PP composites [17]. This may be ascribed to the reaction between PPMA and epoxy resin (EP) on the surface of SCF. As we know, EP is often used as an important component of sizing agent to improve surface properties of carbon fiber [18,19]. However, the incompatibility between PP and epoxy resin will damage the performance of the composite. Recently Ha et al. [20] have confirmed the generation of an ester linkage from the reaction between the anhydride group of anhydride grafted polyethylene and the hydroxyl group of epoxy resin by FTIR spectra. Jiang et al. [21] found that the addition of PPMA improved interfacial adhesion between PP and EP, therefore impact strength and tensile strength of PP/EP blends were increased.

Although the addition of PPMA can promote the mechanical properties of PP/SCF composites, the improvements are still not enough to meet the demand as engineering plastics. This might result from the characteristic of weak interaction between crossover sites of different SCFs in the matrix. As a result, the effective network structure of SCF for bearing load was not formed in the

* Corresponding authors. Tel.: +86 431 85262004; fax: +86 431 85262827.
E-mail addresses: wenxin@ciac.ac.cn (X. Wen), ttang@ciac.ac.cn (T. Tang).

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PP composites. We wonder whether the formation of network structure of SCF in PP matrix can further promote the mechanical properties of PP/SCF composites by adding PPMA and EP together. Here PPMA can improve the interfacial interaction between PP and SCF, and the added EP is expected to lock crossover sites of different SCFs in the matrix. In this work, EP was introduced into PP/PPMA/SCF system, and an *in-situ* cured technology of EP for locking crossover sites of different SCFs was developed during the melt compounding. Thus a strong network structure of SCF was formed in PP matrix. As a result, the mechanical properties of the resultant composites were much higher than those of PP/PPMA/SCF composites. The improved mechanical properties of PP/PPMA/EP/SCF composites were ascribed to the synergistic effect between PPMA and EP in the composites. The synergistic reinforcing mechanism was also discussed on the base of SEM observation, FTIR analysis, extraction test and rheological measurement. According to our best knowledge, there is no report in which both PPMA and EP were added together to modify PP/SCF composites.

2. Experimental sections

2.1. Materials

Polypropylene powder (PP, isotactic, T30s, $M_w = 2.89 \times 10^5$ gmol^{-1}, PDI = 3.45, melt flow index at 230 °C: 6.8 g/min) was purchased from Panjin Petrochemical Co. The maleic anhydride grafted polypropylene (PPMA, $M_n = 7.43 \times 10^4$ gmol^{-1}, PDI = 2.73, melt flow index at 230 °C: 32 g/min) with 0.8 wt% of MA group was supplied by Starbetter (Beijing) Chemical Materials Co. Short carbon fiber (SCF, 3 mm in average length, epoxy resin sizing agent of 2.8 wt%) was purchased from Shanghai Yingjia special fiber material Co.

Epoxy resin (EP, diglycidyl ether of bisphenol-A) with epoxy value of 0.51 was supplied by Bluestar New Chemical Materials Co. The curing agent imidazole was reagent-grade obtained from Tianjin Chemical Co. All the materials except for imidazole were dried in a vacuum oven at 80 °C for 12 h before using.

2.2. The preparation of PP composites

The composites were prepared in a Brabender mixer (Banbury mixer) by melt compounding. The temperature and the rotor speed were set at 180 °C and 50 rpm, respectively. In a typical experiment, PP or PP/PPMA was melted, and then EP at 4 min, SCF at 6 min and imidazole at 8 min was in turn added to the melt, respectively. The mixture was removed at 12 min and then cut into small pieces and cooled. The dosage of imidazole (as curing agent for EP) was 4 wt% of EP [21,22]. Table 1 shows the formulation of PP/SCF composites with various compositions.

The mixture was first dwelled at 190 °C for 2 min in a hot press, and then compressed at 15 MPa for 2 min. Two picture frames (1 mm and 4 mm thickness, with 15 × 15 cm^2 hole) were used to constrain the composite deformation. After that the frame was transferred to a cold press and compressed at 10 MPa until the sample reached room temperature. Finally composite sheets (15 × 15 cm^2) with 1 and 4 mm thickness were fabricated, respectively. Then the sheets were cut by mould into the provision shape for mechanical property testing. For FTIR characterization, the PP, PPMA and PP composites were pressed into film with a thickness less than 20 μm, and EP was directly tested by dropping the liquid onto a KBr sheet.

Table 1
The formulation of PP/SCF composites with various composition.

Sample	PP (wt%)	PPMA (wt%)	EP (wt%)	SCF (wt%)
PP	100	0	0	0
PP/SCF	73.6	0	0	26.4
PP/PPMA/SCF	66.1	7.5	0	26.4
PP/PPMA/EP/SCF	54.5	7.5	11.6	26.4
PP/EP/SCF	62.0	0	11.6	26.4

The dosage of imidazole (as curing agent for EP) was 4 wt% of EP.

2.3. Characterization

Uniaxial tensile tests were performed with an Instron 1121 testing machine (Canton, MA) according to ISO 527-2 standard. Specimens (10 × 2 × 1 mm^3) were cut from the previously compression-molded sheet into a dumbbell shape. The measurements were conducted at a crosshead speed of 1 mm/min at room temperature. The flexural properties were tested under three-point bending in a DXLL-5000 machine (Shanghai Jiedeng Instruments Ltd., China) in accordance with ISO 178:2003. The size of the flexural testing samples used was 80 × 10 × 4 mm^3. The machine was operated at a crosshead speed of 1 mm/min and a span length of 60 mm. The V-notched specimens (80 × 8 × 4 mm^3) were tested to measure the impact strength according to ISO 180 procedures with an impact testing machine (CEAST, Chengde, China). All tests were carried out at room temperature and 50% relative humidity. At least five runs for each sample were measured, and the results were averaged.

The tensile-test specimens fracture surface and residues of composite materials after solvent extraction with xylene were observed under XL30ESEM FEG field emission scanning electron microscope to study interfacial adhesion.

FTIR (Bio-RadFTS-135) was used to characterize composite samples, which were pressed into thin films at 185 °C. Rheological measurements were conducted in a Physcia MCR300 rotation rheometer under nitrogen atmosphere, Round samples (25 mm in diameter × 1 mm in thickness) were prepared for frequency scanning at 185 °C, with a gap of 0.8 mm and a frequency scope from 0.05 to 100 rad/s, and a strain of 1% was used, which was in the linear viscoelastic regime for all samples.

The composite was placed in a muffle furnace at 500 °C for 60 min. The matrix resin was decomposed under this temperature and the carbon fibers were remained. The length distributions of remaining carbon fibers were quantified using an image analysis technique. The fibers were dispersed in ethanol and then coated on the glass slide. Images of various fiber lengths were taken by a Panasonic WV-CP280 Closed-circuit surveillance camera equipped on Shanghai Jinke XTZ-E continuous variable times microscope. The images were then analyzed using Nano Measurer processing software. A series of 1000 samples were measured for remaining carbon fibers. The distribution and polydispersity of the fiber length were then calculated through the formula below:

$$\text{Number average length,} \quad L_N = \frac{\sum N_i L_i}{\sum L_i} \tag{1}$$

$$\text{Weight average length,} \quad L_W = \frac{\sum N_i L_i^2}{\sum N_i L_i} \tag{2}$$

$$\text{Polydispersity,} \quad d = \frac{L_W}{L_N} \tag{3}$$

3. Results and discussion

3.1. Effects of EP and PPMA on mechanical properties of PP/SCF composites

The tensile properties of neat PP and PP/SCF composites were initially investigated. As shown in Fig. 1a, it is apparent that the