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An effective surface modification of carbon fiber for improving the interfacial adhesion of polypropylene composites

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ABSTRACT

A simple and effective modification for carbon fiber (CF) was presented in our work. CF was coated with ethylene–methyl acrylate–glycidyl methacrylate (E–MA–GMA) terpolymer through solution dipping. A uniform layer of 2.0 wt.% E–MA–GMA was confirmed on CF by IR, TGA and SEM. XPS showed that surface oxygen-containing functional groups were obviously increased after modification, which were advantageous to promote the reactivity of CFs. The treatment turned out to be helpful in enhancing the interfacial adhesion by micro-droplet experiment and the interfacial shear strength was 157% higher. The physical properties of PP/mCF composites were improved by static and dynamic mechanical analysis and the improvement was more noteworthy when maleic anhydride grafted PP (MAPP) was added to the matrix, which was consistent with the fracture morphology. The ultimate flexural strength, impact energy and tensile strength were increased by 139.3%, 233.9% and 126.1%. Besides, the mechanical performance of PP composites with 0–30 wt.% CFs were all significantly enhanced by CF surface treatment in combination with MAPP modification. We believed that the excellent performance was not caused by fiber length or crystallinity, it was mainly due to the superior interfacial interaction by intermolecular chain entanglement, as well as chemical reaction between E–MA–GMA and MAPP.

1. Introduction

Carbon fiber (CF), as a very important reinforcing fiber for thermoset and thermoplastic composite materials, has been widely used in aerospace, sports and automobile industries, owing to its high specific strength, specific modulus, lower density and outstanding thermophysical properties [1,2]. Thermoplastic composite materials have received increasing interest over the last few years, because of their shorter cycle times and greater potential recyclability compared to thermoset polymers [3,4]. Among the available thermoplastic polymers, polypropylene (PP) is one of the general plastics produced and consumed in large quantities, due to its good comprehensive performance and versatile applications in different fields [5–7].

However, the sizing agent on commercial CF surface is mainly designed for thermoset epoxy resin and not suitable for thermoplastic matrix. This usually results in poor compatibility and weak interaction between CF and low-polar PP. Thereby, excellent fiber–matrix properties could not be expected. Hence, how to improve the interfacial adhesion has been one of the most important topics of developing CF reinforced PP composites.

Several methods have been developed to modify the CF surface in order to better reinforce the PP matrix, including thermal treatment, wet chemical [8,9] or electrochemical oxidation [10], plasma treatment [11,12], gas-phase oxidation [13,14], coating treatment [15–18], irradiation treatment [19,20], and so on. The purpose of these surface treatments have been to increase the surface energy, induce chemically active functional groups, or change the microstructure of the CF surface. Solution dipping treatment is to form a ductile polymer layer on the fibers through soaking them in resin solutions. It has been particularly preferred for the advantages of easy operation, controllability and continuous production.

Ethylene–methyl acrylate–glycidyl methacrylate (E–MA–GMA) is commonly used as a toughener to improve the impact strength of engineering thermoplastics like PA, Polyesters (PBT, PET), PC/PBT and PC/ABS alloys [21,22]. It can also be used as a compatibilizer for Polyesters/Polyolefins blends and as an adhesive for some laminate structures. In these cases, E–MA–GMA was directly added into the matrix during processing. In this study, a novel method using E–MA–GMA solution impregnation was proposed to improve the interfacial characteristics between CF and PP matrix.

An alternative method to improve the interfacial adhesion of CF and matrix is to modify the polymeric matrix with strong-polar compatibilizer. Maleic anhydride grafted polypropylene (MAPP) proved to be an effective compatibilizer in fiber reinforced PP plastics [23–25]. Given this, we made use of the chemical reaction between E–MA–GMA on CF surface and MAPP in PP matrix to further improve the interface.

The effects of CF surface treatment in combination with MAPP modification on the mechanical and interfacial properties of PP composites

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were investigated. The influence of fiber weight fraction on the flexural and impact properties of PP composites were also discussed. Through making a comparative study, we proved that solution dipping using the novel E–MA–GMA modifier was an effective CF surface treatment so as to enhance the interfacial bonding with PP matrix. Besides, varying the matrix with MAPP also played a crucial role in improving the interfacial adhesion between fiber and resin, subsequently endowing them superior mechanical properties.

2. Experimental details

2.1. Materials

PP pellets (Y2600T, MFR = 26, Petroleum & Chemical, China) and CF bundles (T700SC 12K, Toray, Japan) were used as the polymer matrix and the reinforcing material. The modifier E–MA–GMA (Lotader AX8900, Arkema, France) was a random terpolymer with the MA and GMA contents of 24 wt.% and 8 wt.%, respectively. Maleic anhydride grafted PP (MAPP, SUNNY, Shanghai) with a MAH content of 1.0 wt.% was used as a compatibilizer.

2.2. Carbon fiber surface modification

4.42 g E–MA–GMA was firstly dissolved in 250 ml toluene at 70 °C to form a 2 wt.% solution. 40 g CF bundles were then soaked in the solution for 2 h. Besides, ultrasonic assistance was applied permanently during the impregnation process by a bath sonicator. The E–MA–GMA modified CF (mCF for short) were taken out and excess solution was carefully removed. Finally, the mCF were completely dried in a vacuum oven at 60 °C overnight.

2.3. Composites preparation

Prior to the preparation of composites, CF and mCF were chopped into an average length of 10 mm, and then dried in an oven at 70 °C for 12 h together with PP pellets. MAPP was used directly without drying. The melt blending of different loadings of CF or mCF (0–30 wt.%) with PP or PP/MAPP (20 wt.% MAPP in PP) were carried out for 10 min by an internal mixer (Thermo Haake PolyDrive, USA). The rotor speed and temperature were set at 50 rpm and 190 °C, respectively. The compounds were then placed in a mold of size 10 × 10 cm^2 with a thickness of 2 mm and compressed using Platen Press Machine (XLB-D, Labtech, Germany) at 200 °C under a pressure of 15 MPa. At last, the composite sheets were cut into rectangular specimens of 100 mm × 10 mm × 2 mm using Waterjet Cutting Machine (Flow, USA) for mechanical tests. The composites were defined as PP/CF, PP/mCF, PP/MAPP/CF or PP/MAPP/mCF.

2.4. Characterization and testing

2.4.1. FT-IR spectroscopy

Fourier transform infrared (FT-IR) spectra of fibers, E–MA–GMA, PP and its composites were recorded on a Paragon 1000 FT-IR spectrometer (Perkin Elmer, USA) equipped with an Attenuated total reflectance (ATR) accessory. The scan range was 4000–400 cm^{-1} and four scans were collected for each sample with a resolution of 2 cm^{-1}. E–MA–GMA film was prepared by hot pressing a few elastic pellets at 80 °C.

2.4.2. X-ray photoelectron spectroscopy (XPS)

The chemical composition and functional groups on CF and mCF surface were characterized by X-ray photoelectron spectrometer (AXIS Ultra DLD, Shimadzu, Japan) equipped with a monochromatic source of Al Kα (1486.6 eV), spot area of 700 μm × 300 μm, base pressure below 5 × 10^{-9} Torr, pass energy of 160 eV and 40 eV for survey scans and narrow scans, respectively. The binding energy peaks were calibrated with C1s at 284.8 eV as reference.

2.4.3. Thermogravimetric analysis (TGA)

To obtain the content of E–MA–GMA modifying agent on mCF surface. The thermal decomposition behaviors of CF, mCF and E–MA–GMA were investigated by Thermogravimetric Analyzer (Q5000IR, TA, USA) in the range of 40–600 °C at heating rate of 20 °C/min and N_2 flow rate of 40 ml/min.

2.4.4. Differential scanning calorimetry (DSC) analysis

The crystallization and melting behaviors of neat PP, PP/CF, PP/mCF, and PP/MAPP/mCF (containing 30 wt.% CF) were analyzed through DSC (Q2000, TA, USA). The temperature ranged from 40 °C to 200 °C and the samples were tested under N_2 atmosphere. The heating and cooling rates were both 10 °C/min.

2.4.5. Average fiber length and distribution measurement

Fiber length measurement was done on the molded specimens of PP/CF, PP/mCF, and PP/MAPP/mCF. Approximately 100 mg sample were taken from each specimen and placed in a crucible. The PP matrix was completely burned out in the muffle (SXL-1008, Jinghong, Shanghai) at a temperature of 600 °C for 10 min and CFs were recovered. Small parts of recovered fibers were then transferred to a glass slide and dispersed in glycerin for microscopic analysis. The images were captured by the polarized optical microscopy (DMLP, Leica, Germany) equipped with a CCD digital camera. In every sample, at least 500 fibers were measured using Winroof software.

2.4.6. Mechanical properties test

Flexural tests of neat PP and its composites were conducted by a Universal Testing Machine (Criterion 43, MTS, USA) with three-point bending (TPB) testing mode at a constant speed of 2.0 mm/min and a span length of 64 mm in accordance with ASTM D790. Tensile tests were

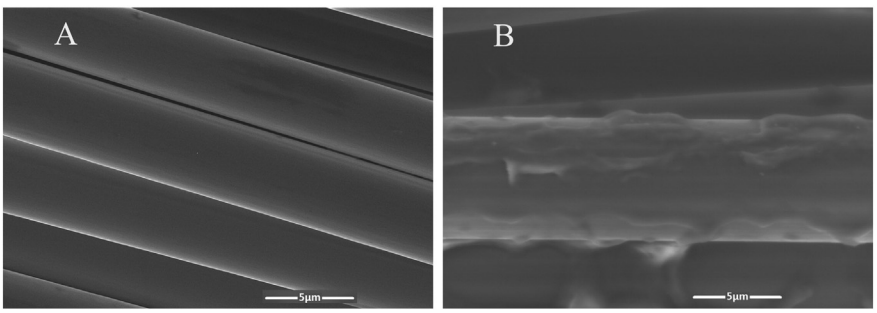

Fig. 1. SEM images of (A) untreated CF (B) mCF.