

The Effect of Surface Modification on the Interfacial Feature of Polystyrene Composite Filled with Carbon Fiber

W.Z. Nie, X.Z. Li, and F.F. Sun

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The quality of interfacial interaction is dictated by the surface chemistry of the carbon fibers and the composition of the matrix. The composition of polystyrene was modified by the addition of maleic anhydride-grafted polystyrene (MAH-g-polystyrene). The surface properties of various matrix formulations were characterized by contact angle measurements. Carbon fibers were modified by nitric acid oxidation. The surface composition of the carbon fibers was characterized. The interaction between modified polystyrene and the carbon fibers was studied by single-fiber pull-out tests. The best adhesion behavior was achieved between polystyrene-containing grafted MAH and nitric acid-oxidized carbon fibers. The addition of MAH-g-polystyrene to the unmodified polystyrene caused the interfacial shear strength to increase. The apparent interfacial shear strength of this fiber-matrix combination allowed for the utilization of 100% of the yield tensile strength of polystyrene.

Keywords carbon fiber, contact angle, interfacial shear strength, single-fiber pull-out

1. Introduction

Carbon fibers are one of the most common reinforcements for polymer matrices; however, the nature of the carbon surface makes fiber-polymer compatibility the largest technical obstacle to widespread use of carbon fibers in thermoplastic matrices such as polystyrene (Ref 1). Polystyrene is used in applications where abrasion, chemical resistance as well as thermal stability are required (Ref 2). Carbon fiber-reinforced polystyrene represents a material that could be used in applications where chemical resistance and toughness are both required, such as in the oil and gas industry, where currently, conventional monolithic materials are used in deep-sea applications but will reach their limit if deeper reservoirs are to be exploited. The lack of compatibility between polystyrene and many reinforcing agents is due to the inert nature of the matrix and the lack of reactive groups, which limits the level of interaction between the reinforcement and the matrix. To date, there have been only a few studies that have investigated routes to improve the interaction between polystyrene and carbon fibers, and these studies have focused only on the effect of fiber surface treatments (Ref 3-7). Two alternative methods for improving the compatibility between carbon fibers and polystyrene matrices are the introduction of a miscible secondary polymer into the primary matrix and the modification of the homopolymer with moieties that promote adhesion.

This article focuses on the use of a modified polymer matrix to interact and/or react with surface functionalities of the carbon fibers, which are introduced by conventional nitric acid (HNO₃) oxidation treatments as a means to ensure adhesion.

Regardless of the route chosen to enhance adhesion, characterizing the surface of the individual components provides a better understanding of the mechanisms in play. Since the main factor dictating interfacial adhesion is the composition of the interface which is dependent on both the matrix and fiber surface composition (Ref 8), we studied the influence of a reactive compatibilizing agent for polystyrene as a means to improve adhesion to carbon fibers.

Grafted polymers possess a set of unique properties such as enhanced mechanical properties, thermal stability, good barrier and membrane properties, printability, and adherence properties (Ref 9, 10). The direct grafted method can be successfully applied to enhance adhesion properties and printability of high density polyester (HDPE), light density polyester (LDPE), polypropylene, ethylene-vinyl acetate copolymers, polyimides, polyethers, ethylene propylene copolymer, butadiene-styrene copolymers, etc. (Ref 11). In this article, we will concentrate on the effect of maleic anhydride-grafted polystyrene (MAH-g-polystyrene) on mechanical properties of the polystyrene composite.

The effect of the compatibilizing agent on the surface properties of polystyrene will be investigated by means of contact angle measurements. Polystyrene was blended with a reactive compatibilizer (MAH-g-polystyrene), and the adhesion between the matrix and various carbon fibers was quantified by single-fiber pull-out tests to determine the apparent interfacial shear strength (IFSS), as a practical measure of adhesion.

2. Experimental

2.1 Materials

Polystyrene and MAH-g-polystyrene were kindly supplied by Arkema (Serquigny, France). The polystyrene (homopolymer

W.Z. Nie, School of Mechanical and Automation Engineering, Shanghai Institute of Technology, Shanghai 200235, P.R. China; and X.Z. Li and F.F. Sun, English Group, Shouguang Experimental School, Shandong, Shouguang, P.R. China. Contact e-mail: lijian2004d@sina.com.

and modified) formulations were dissolved in dimethyl formamide (DMF, general purpose grade, VWR, Poole, UK) to make a 10 wt.% solution. A nonsolvent DMF/water (80/20, w/w) was added dropwise to induce precipitation. The precipitant was filtered, rinsed with ethanol, and then dried under vacuum at 100 °C. The product formed from solvent precipitation was a fine powder. Samples with the following compositions were prepared: pure polystyrene and polystyrene containing 1.25 ppm grafted MAH.

Untreated polyacrylonitrile (PAN)-based carbon fibers were kindly supplied by SGL Sigri Carbon (Meitingen, Germany). Severely oxidized carbon fibers were obtained by boiling carbon fiber for 5 h in HNO₃ under reflux ($T = 120$ °C). Afterward, the HNO₃-oxidized fibers were washed with distilled water in neutral pH.

2.2 Matrix Preparation

Polystyrene with MAH-g-polystyrene was prepared by hot pressing the powder formed after precipitation. The powders were placed directly between two 10 μm Upilex release films and pressed between two polished steel plates at 200 °C and at a pressure of 5 MPa (Moore Presses, Birmingham, UK).

2.3 Wetting Behavior of the Modified Matrix

Contact angles were measured using the drop shape analyzer (DSA, Hamburg, Germany) to determine the effect of the changing matrix composition on the wetting behavior of the polystyrene. Two types of contact angles were measured on the pressed films, sessile drop and captive bubble contact angles, to determine the influence of the surrounding environment on the surface properties of the matrix. Low-rate dynamic sessile drop contact angle measurements were performed by placing a droplet of roughly 10 μl of deionized water onto the surface followed by slowly increasing the droplet volume at a rate of 10 μl/min. To determine the low-rate dynamic captive bubble contact angles, the polymer films were equilibrated for 24 h in deionized water to allow polar functional groups to migrate to the surface (a phenomenon called hydrophobic recovery) (Ref 12, 13). The contact angles were measured by placing an air bubble of approximately 20 μl below the polymer surface. The bubble volume was increased at a rate of 10 μl/min and the receding contact angle (hr), i.e., that of displacing water from the surface, was measured.

2.4 Fiber Surface Composition

The fibers were characterized by x-ray photoelectron spectroscopy (XPS, ESCA 300, Scienta, Sweden) to determine the level of functionalization of the modified fibers. An initial survey scan was performed to determine the detectable elements, followed by high-resolution scans. The entire x-ray photoelectron spectrum was energy referenced to the C 1s peak of graphite (BE = 284.5 eV).

2.5 Single-Fiber Pull-Out Test

Single-fiber composites for the pull-out tests were prepared by a special embedding machine, which allows for the production of samples with the fibers orientated perfectly perpendicular to the surface of the matrix at a defined embedded length. A sample of the matrix was heated to the melt on an aluminum sample carrier. The fiber was embedded into the polymer melt droplet at a defined length varying

between 50 and 200 μm. The entire sample was allowed to cool to room temperature in air (approx. 2 min). The fiber diameters were measured using a laser diffraction method (Ref 14). Pull-out experiments were performed on a custom-made apparatus, which allowed for a short fiber-free length of 30 μm between the surface of the matrix and the fiber-clamping mechanism. The schematic of the experimental apparatus is shown in Fig. 1. The pull-out tests were performed at a rate of 0.2 μm/s while recording force and displacement. The maximum load is correlated to the full debonding along the embedded length from the matrix. The shape of the load–displacement curve itself reflects on the type failure occurring at the interface (Ref 15). The IFSS is determined by measuring the force required to debond the embedded fiber from the interface formed with the matrix.

The value of IFSS was calculated according to the following equation:

$$\text{IFSS} = F/\pi dl$$

where F is the maximum load, d is the diameter of the carbon fiber, and l is the length of the fiber embedded in the resin. The recorded value of IFSS was calculated from the normal distribution of more than 10 successful measurements.

3. Results and Discussion

3.1 Effect of Matrix Modification on Polystyrene Surface Properties

The effect of incorporating MAH into polystyrene on the wetting behavior of the matrix was characterized by sessile drop and captive bubble contact angle measurements. Sessile drop measurements probe the wetting behavior of dry surfaces. The polar, MAH, functional groups (or possibly maleic acid if ring opening occurs) can migrate to the surface under such conditions. Thus, the captive bubble contact angle decreases by 10° upon the addition of 1.25 ppm of grafted MAH to polystyrene. The measured captive bubble contact angles clearly show the increase in hydrophilicity of the matrix with the addition of MAH after the polymer surface was in contact with water. The lower the contact angle, the higher the adhesion between the matrix and the carbon fibers (Ref 16-18) (Fig. 2).

3.2 Surface Composition of Carbon Fibers

Tailoring the surface chemistry of carbon fibers allows for the improvement of adhesion with a matrix by providing sites for possible fiber-matrix interaction. The composition of the carbon fiber surfaces and the identification of the moieties that are generated by surface treatments were characterized by XPS.

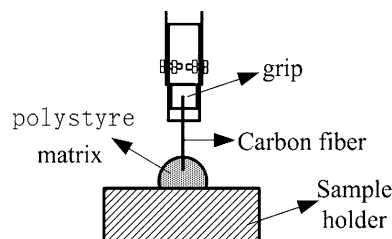


Fig. 1 The schematic of the experimental apparatus

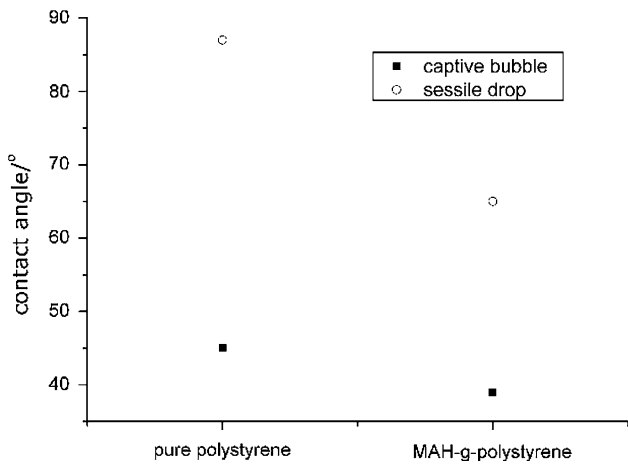


Fig. 2 Advancing sessile drop and receding captive bubble contact angles

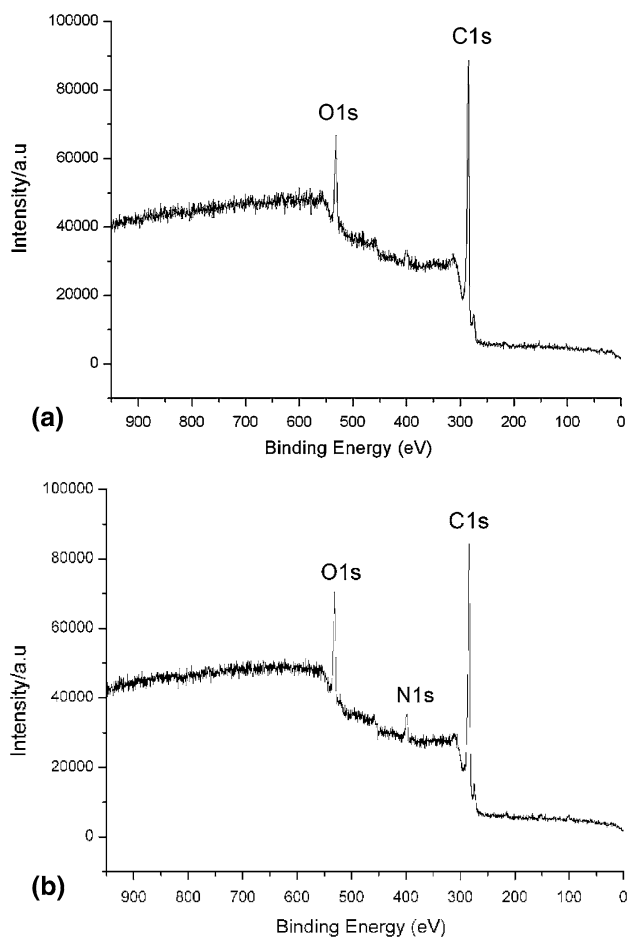


Fig. 3 (a) Wide-scan photoelectron spectra of untreated carbon fiber. (b) Wide-scan photoelectron spectra of HNO₃-treated carbon fiber

Figure 3 shows typical wide-scan photoelectron spectra of (a) untreated carbon fiber and (b) HNO₃-treated carbon fiber. Apart from strong C-signals (C 1s photoelectron), the spectrum of the untreated carbon fiber (Fig. 3a) shows relatively weak O-signals (O 1s) which is due to near-surface oxygen-containing functional groups of the fibers. After HNO₃ treatment (Fig. 3b),

Table 1 Surface elementary composition of carbon fibers

Surface treatment	Elementary composition, %			Atom ratio, % O/C
	C	O	N	
Untreated	90.87	9.13	...	10.05
HNO ₃ oxidation	72.63	25.02	2.35	15.31

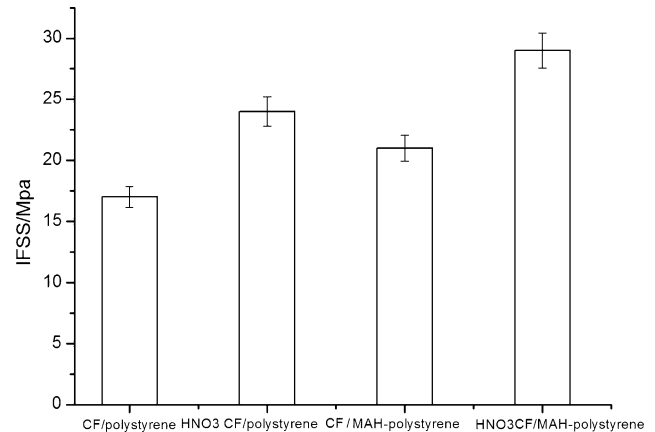


Fig. 4 IFSS of CF/polystyrene composites

these weak O-signals have been strengthened due to renewed oxidation. It is well known that the surface functional groups, especially oxygen-containing groups, of carbon fibers play an important role in improving the surface free energy and adhesion between the fiber and matrix (Ref 19).

Table 1 presents the surface composition of the carbon fibers used in this study. The results from the XPS analysis of the HNO₃-oxidized carbon fiber show an increase in both the oxygen and nitrogen content as compared to the untreated fiber. Nitric acid reflux caused a small but significant increase in the nitrogen-containing species on the surface of the carbon fibers. The introduction of polar oxygen groups onto the surface of the fibers leads to an increase of the fiber surface energy as well as changes to the surface energy components (Ref 20). These groups should lead to improved interaction between the fiber and the modified matrix. At the very least, the increase in the carbon fiber surface energy should lead to better wettability of the fibers by the nonpolar matrix and, therefore, to a more intimate contact between the phases.

3.3 Adhesion Behavior Between Carbon Fibers and Polystyrene

The assortment of functional groups on the surface of the carbon fibers is not expected to result in too much improved interaction with pure polystyrene (Ref 21), as shown in Fig. 4. However, some of the functional groups present on the carbon fibers should favorably interact with the MAH in MAH-g-polystyrene. With the exception of carboxyl groups, typical solid carbon oxides, such as carbonyl, phenol, lactol, and lactones, are not especially reactive. Since MAH opens to a dicarboxylic acid, hydrogen bonding may be an option for improved adhesion.

The IFSS performance is shown in Fig. 4. Figure 4 shows the distribution of the data between the maximum and

minimum IFSS for untreated carbon fiber in pure polystyrene, and the shear strength is 17 MPa. The single-fiber pull-out testing for HNO₃-oxidized carbon fiber in pure polystyrene was 24 MPa. Untreated carbon fiber does not show much improvement in interfacial adhesion with the increase of MAH-g-polystyrene. It is clear from these results that HNO₃-oxidized fiber surface treatments produce the appropriate surface groups to improve the interaction with the MAH moieties in the modified polystyrene matrices. The maximum possible IFSS is approximately the yield tensile strength of polystyrene; in this case, the manufacturer's claims 28 to 32 MPa. This fiber-matrix combination allows for almost full utilization of the intrinsic matrix properties, an unprecedented advancement in carbon fiber-reinforced polystyrene composites. The reasons attribute that the HNO₃ treatment was used as a method to bind oxygen functional groups on carbon fiber surfaces, which increase the interlock between the fiber and matrix, leading to the increase of the IFSS of composites, which can effectively transfer the stress from matrix to the fiber, so the fiber can bring more reinforcement. Therefore, the IFSS of the composite reinforced by HNO₃-treated carbon fibers are considerably improved.

4. Conclusions

Two methods of improving the interfacial interaction between carbon fibers and polystyrene were investigated: the modification of the matrix by adding the compatibilizing agent MAH-g-polystyrene and functionalization of the carbon fiber surfaces. Unlike the contact angle measured on dry polystyrene surfaces, sessile measurements, captive bubble contact angles decreased with addition of MAH polystyrene, highlighting the importance of the interface composition when analyzing interfacial interaction.

As expected with surface treatment of carbon fibers, the surface oxygen and nitrogen content increases, leading to an increase in overall surface energy of the fibers. Single-fiber pull-out testing provides a means of assessing likely performance in a potential composite, due to differences in surface chemistry and roughness of the fibers and compositional changes within the polystyrene matrix. Although, HNO₃ oxidation was effective in increasing the surface energy, MAH-g-polystyrene-modified polystyrene melts increased IFSS of the fibers obviously with HNO₃ treatment.

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