Interfacial Interaction in Stainless Steel Fiber-Filled Polypropylene Composites

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ABSTRACT: Surface treatment proves to be an effective way to enhance the mechanical properties of stainless steel fiber (SSF)-filled polymer composites, a candidate for shielding electromagnetic interference applications. To reveal the details of interfacial interaction in polypropylene (PP)-based composites, micro- and macromechanical performance of the materials as well as surface chemical features of the fibers extracted from composites were characterized. The results suggest that a chemical bond was formed between the SSF surface and modified PP (i.e., PP grafted maleic anhydride copolymer, PP-*g*-MAH) in addition to van der Waals forces, which accounts for the improved interfacial adhesion in the SSF/PP-*g*-MAH/PP system. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 2174–2179, 2000

Key words: stainless steel fiber; polypropylene; conductive polymer composites; interface; electromagnetic interference shielding

INTRODUCTION

Electromagnetic interference (EMI) emitted by electronic appliances is nothing but electronic pollution or noise. One of the most effective ways to prevent EMI lies in the use of EMI shielding materials as housings and enclosures of the devices that obstruct both external radiation and internal emission. Because shielding function arises from the combined action of absorption and reflection, and the resultant signal attenuation is proportional to the material's electrical conductivity and magnetic permeability, conductive polymer composites, composed of conductive fillers and insulating polymer matrix, have found applications where EMI shielding is needed.[1]

In general, physical properties of the composite are dominated by the nature of fillers. As a result, stainless steel fiber (SSF) serves as an important conductive filler material for EMI shielding composites because of its perfect ductility that minimizes fiber breakup during compounding and ensures sufficient electrical conductivity at low-fiber concentration. However, it should be noted that the incorporation of SSF into polymers usually leads to reduced mechanical performance and impact resistance in particular.[2,3] Considering an improved fiber/matrix adhesion is beneficial to

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strength and impact toughness enhancement in fiber composites, interfacial compatibilizers were adopted in SSF-filled polypropylene (PP) systems.[4] The results indicate that a balanced performance profile (i.e., increased flexural strength and impact strength associated with acceptable electrical resistivity) can be achieved by adding PP-grafted maleic anhydride copolymer (PP-*g*-MAH).

In the present work, a more careful investigation on the interfacial interaction in SSF/PP composites is performed with the help of micromechanics and surface characterization techniques so as to understand the nature of the metal fiber/polymer interface and provide knowledge for tailoring properties of the composites, which are less documented up to now.

EXPERIMENTAL

A commercial SSF (average diameter, 8 μm; axial tensile strength, 1.2 GPa) produced by a wire-drawing process without surface treatment was used as filler. PP (melt flow index, 2.3 g/10 min) was supplied by the Petroleum Chemistry Company of Guangzhou (P. R. China) and PP-*g*-MAH (melt flow index, 46.0 g/10 min) was kindly offered by the Chemistry Institute of Guangzhou. For the convenience of discussion, no additive was incorporated into either PP or PP-*g*-MAH. The coupling agent was silane A-174 supplied by the OSI Company (USA).

The microcomposite specimens for fragmentation tests were prepared as follows. A single SSF 10-cm long was immersed in water solution containing 1 vol % coupling agent for half an hour (except those untreated) and then the fibers were dried. The fiber was placed between two pieces of PP or PP-*g*-MAH sheets ($10 \times 2 \times 0.05$ cm^3) and the composite was then transferred to a press, while the fiber ends were fixed to keep the alignment. Then the fiber was connected with a power transformer for a certain time and thus adhered to the resin sheets because of electrothermal effect. Fragmentation tests were performed on a special mini tester at a tensile rate of 0.35 mm/min with the final tension strain of ~8%. The fragment lengths were measured through a video-equipped Olympus-BX60 microscope. When the critical fragment length, l_c, was determined, interfacial shear strength, τ, was evaluated by: $\tau = \sigma_f d/2l_c$, where σ_f and d denote tensile strength and diameter of fiber, respectively.

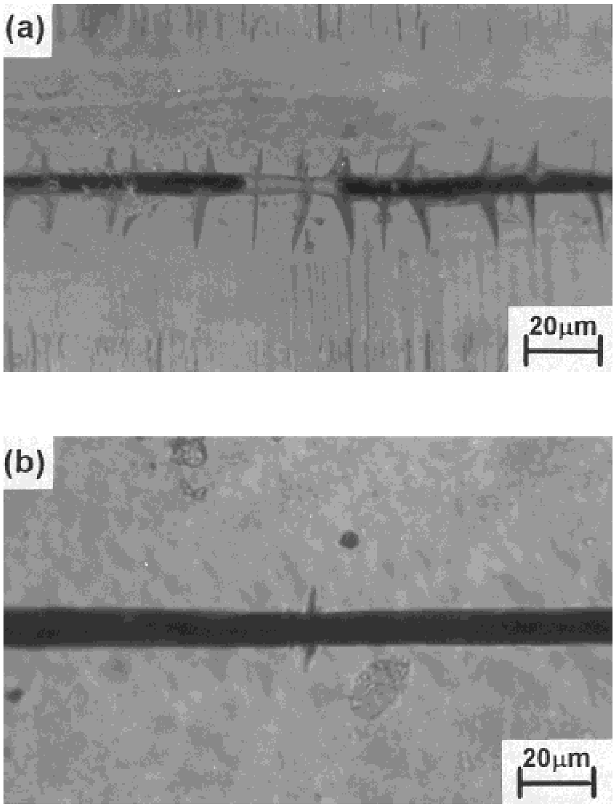


Figure 1 Microfailure modes in SSF/PP composites: (a) SSF (A-174-treated)/PP, (b) SSF/PP-*g*-MAH.

To prepare composite specimens for conventional mechanical tests, the fibers were chopped into lengths of ~5-mm and melt mixed with polymer (PP and/or PP-*g*-MAH) using a Brabender-like apparatus at 190–200°C and 32 rpm for 10 min. The mixture was then compression molded into sheets at 200°C. Flexural strength and modulus were determined by three-point bending tests with a loading speed of 5 mm/min at room temperature. Charpy unnotched impact strength measurements were performed with a test span of 40 mm. Five samples were tested for each case.

Besides the SSF as-received, other SSF for surface analysis were obtained by extracting either

Table I Characterization of SSF/PP Microcomposites in Terms of Fragmentation Tests

Microcomposites	l_c (mm)	τ (MPa)
SSF/PP	1.47	4.7
SSF (A-174-treated)/PP	0.90	7.8
SSF/PP-*g*-MAH	0.23	30.5

Table II Mechanical Properties of SSF-Filled PP Composites[a]

Materials	Impact Strength (kJ/m^2)	Flexural Strength (MPa)	Flexural Modulus (GPa)
Neat PP	11.8	37.8	1.35
SSF/PP	5.6	40.6	1.44
SSF/PP-*g*-MAH/PP (PP-*g*-MAH/PP = 20:80)[b]	10.1	50.7	1.76
SSF/PP-*g*-MAH	14.0	55.8	2.38

[a] SSF content is 2 vol % for each composite.
[b] The composition ratio of PP-*g*-MAH/PP is expressed in terms of weight percent.

the SSF as-received or the above composite using xylene. X-ray photoelectron spectra (XPS) of the fibers were recorded by means of a Vacuum Generators Escalb MK II X-ray photoelectron spectrometer with a resolution of 0.8 eV at 240 W (Mg Kα, 12 kV). For purposes of correction of specimen charging, the C1s bands were calibrated by assuming the binding energy of benzene peak as 284.6 eV. The Fourier transform infrared (FTIR) spectra of the fibers were collected by a Nicolet-250 spectrometer.

RESULTS AND DISCUSSION

Effect of Interfacial Bonding on the Mechanical Properties of SSF/PP Composites

To obtain information about interfacial bonding performance, fragmentation tests, which provide not only interfacial shear strength but also interfacial microfailure information that is not available in the case of microdroplet measurement,[5] were conducted prior to the surface analysis of the fibers.

From the measuring data listed in Table I, it is seen that the value of τ of the microcomposite with coupling agent A-174-treated SSF is slightly higher than that of untreated SSF-filled PP. That means that the coupling agent conventionally used in glass fiber reinforced composites could not result in higher interfacial adhesion in the current SSF/PP system. In the case of SSF/PP-*g*-MAH, however, the critical fragment length becomes rather short and the corresponding interfacial shear strength is seven times the value of SSF/PP, implying a strong interfacial interaction between maleic anhydride groups.

The micrographs in Figure 1 further evidence the above statement. For the SSF (A-174-treated)/PP microcomposite, debonding can be clearly observed at the broken ends of the single fiber and extensive microcracks presented themselves prior to fiber breakage [Fig. 1(a)]. This is indicative of poor interfacial adhesion and the brittle nature of the interlayer as well. In contrast with it, microcracks perpendicular to the fiber axis were formed after fiber breakage in SSF/PP-*g*-MAH [Fig. 1(b)] and propagated into the matrix with increasing tensile strain. Because no microcracks along the fiber/matrix interface were seen during the measurements, it can be concluded that interfacial adhesion between SSF and PP-*g*-MAH is much stronger.

Table III Surface Composition of SSF Expressed in Terms of Atomic Ratio

Fibers	C/Fe	O/Fe	O/C
SSF as-received	14.72	7.65	0.52
SSF extracted with xylene for 12 h	7.04	6.37	0.90
SSF extracted from SSF/PP with xylene for 48 h	16.41	9.16	0.55
SSF extracted from SSF/PP-*g*-MAH/PP (PP-*g*-MAH/PP = 20:80) with xylene for 48 h	54.33	12.23	0.22
SSF extracted from SSF/PP-*g*-MAH with xylene for 48 h	73.71	25.08	0.34

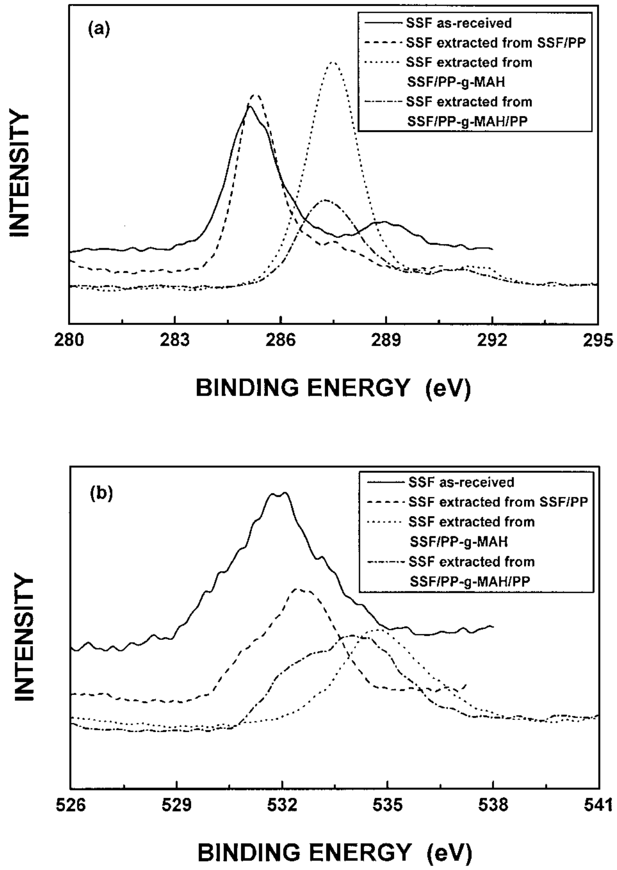


Figure 2 XPS spectra of SSF as-received and the extracted versions: (a) C1s, (b) O1s.

Actually, microfailure behavior at interface is closely related to macroscopic failure of composite materials.[6] The data in Table II agree well with the results of Table I and Figure 1. In consideration of the fact that the good affinity of PP-*g*-MAH for SSF leads to the formation of an insulating shield around the fibers detrimental to electrical conduction of the composites, PP-*g*-MAH should be used as an additive incorporated into SSF/PP composites. As reflected by Table II, the overall mechanical properties of the SSF/PP composite could be improved significantly even if only 20 wt % PP-*g*-MAH was added.

Chemical Characteristics of Fiber Surface

To understand the mechanism of interfacial bonding between SSF and modified PP, SSF as-received as well as SSF extracted from composites were examined by XPS, a tool successfully used in interfacial characterization of fiber glass composites.[7]

According to the calculated surface composition of the fibers (Table III), it can be seen that the C/Fe ratio decreases but the O/C ratio increases when the SSF as-received were extracted with xylene, suggesting alkane-like contaminants on the fiber surface were cleaned out except some oxygen-containing groups. In the case of SSF obtained from the SSF/PP composite, the ratios of C/Fe, O/Fe, and C/O are almost identical with those of SSF as-received. This means that the PP matrix was completely dissolved in the solvent and no specific interlayer structure was formed during compounding. In comparison with that, C/Fe and O/Fe ratios of SSF extracted from SSF/PP-*g*-MAH/PP and SSF/PP-g-MAH were rather high. The results strongly recommended the appearance of a strong interaction between SSF and PP-*g*-MAH, which resulted in an interphase unable to be dissolved in xylene.

The C1s and O1s spectra of the fibers are illustrated in Figure 2. The C1s peaks of SSF as-received and of that extracted from the SSF/PP composite center at 285 eV, whereas those of the fibers from composites with the incorporation of

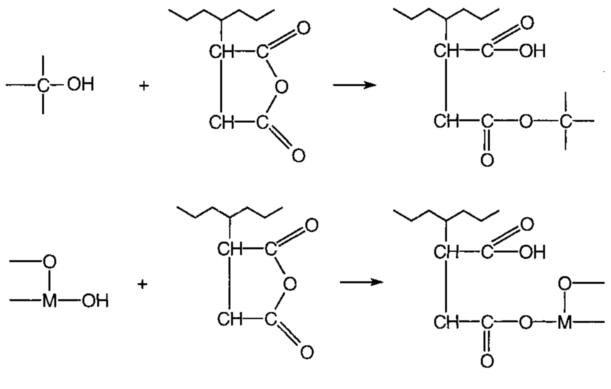
Table IV Percentage Fraction of Surface Groups of SSF

Fibers	[C—H]	[CH═CH, C—OH]	[COOH]
SSF as-received	67.21	17.25	15.53
SSF extracted with xylene for 12 h	55.47	22.87	21.38
SSF extracted from SSF/PP with xylene for 48 h	89.53	3.49	6.98
SSF extracted from SSF/PP-*g*-MAH/PP (PP-*g*-MAH/PP = 20:80) with xylene for 48 h	15.06	55.41	29.53
SSF extracted from SSF/PP-*g*-MAH with xylene for 48 h	28.01	46.13	25.86

PP-*g*-MAH center at 286–289 eV. It reveals that the surface chemical groups exist mainly in the form of C—H on the former two fibers, and in the form of —C—O— and —COO— on the latter. Similar results can also be perceived in the O1s spectra.

Table IV gives the fraction of surface groups of various fibers estimated through C1s deconvolution, which provides a quantitative support for the above discussion. By taking the peaks at 284.5 ~ 285 eV as the binding energy of graphite carbon and C—H, those at 286.2 ~ 286.5 eV as the binding energy of —CH=CH— and C—OH, and those at 288.5 ~ 289 eV as the binding energy of —COOH,[8] it is known that the fibers extracted from the SSF/PP composite consist of 89.53% C—H, 3.49% —CH=CH—, and C—OH, and 6.98% —COOH groups on the surface. For the fibers from SSF/PP-*g*-MAH, however, the corresponding surface group fractions are 15.06, 55.41, and 29.53%, respectively.

FTIR spectra of the fibers are presented in Figure 3. The spectrum profile of the fibers extracted from SSF/PP is similar to that of SSF as-received. In the case of the fibers from SSF/PP-*g*-MAH, two peaks at 1700 cm^{-1} and 1743 cm^{-1} appear, while the distinctive absorption of the anhydride group at 1785cm^{-1} cannot be observed. This suggests that maleic anhydride likely reacted with C—OH and M—OH on the SSF surface (M denotes metal atom), and the anhydride groups were transformed into acid as shown in Scheme 1.



Scheme 1

According to the mechanical testing and fiber surface analysis, it is evident that interfacial bonding between SSF and PP resin is governed by van der Waals forces (dipole-induced force and dispersion force). As a result, interfacial adhesion in the SSF/PP composite is poor because of the lower bond energy of these secondary bonds. When PP-*g*-MAH is compounded with SSF, chemisorption might well occur. The higher bond energy of the primary bond between SSF and MAH accounts for the strong interfacial interaction in SSF/PP-*g*-MAH.

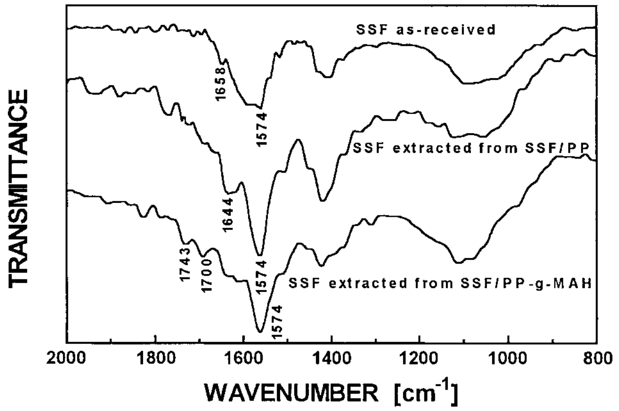


Figure 3 FTIR spectra of SSF as-received and the extracted versions.

CONCLUSIONS

The following statements can be made from the present investigation:

1. Both interfacial shear strength and microfailure characteristics of SSF/PP are quite different from those of SSF/PP-*g*-MAH, indicating the effect of strong interfacial interaction due to the presence of modified PP.
2. Interfacial adhesion greatly affects the macroscopic mechanical properties of SSF-filled polymer composites, including flexural strength, flexural modulus, and impact strength.
3. In comparison with the SSF/PP system, the amount and species of surface chemical groups of SSF are changed remarkably when PP-*g*-MAH is used to mix with SSF. The formation of a chemical bond is responsible for the strong interfacial adhesion between SSF and PP-*g*-MAH.

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