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Effect of aminated polyphenylene sulfide on the mechanical properties of short carbon fiber reinforced polyphenylene sulfide composites

Kun Zhang [a], Gang Zhang [b], Baoying Liu [a], Xiaojun Wang [b], Shengru Long [b,*], Jie Yang [b,c,*]

[a] College of Polymer Science and Engineering, Sichuan University, Chengdu 610065, China
[b] Institute of Materials Science and Technology, Sichuan University, Chengdu 610064, China
[c] State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, China

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ABSTRACT

The aim of this study was to investigate the effect of the aminated polyphenylene sulfide (PPS-NH_2) used as compatibilizer on the mechanical properties of carbon fiber (CF) reinforced polyphenylene sulfide (PPS) composites. The compatibilizers PPS-NH_2 which were synthesized by the condensation polymerization of sodium sulfide (Na_2S), p-dichlorobenzene (DCB), and the third active monomer 2,5-dichloroaniline (DCA). Composites with 20 wt% CF, 75 wt% PPS and 5 wt% PPS-NH_2 which were synthesized by different mole ratios of Na_2S/DCB/DCA were prepared by melt blending and injection molding. According to the results of mechanical properties tests, dynamic mechanical analysis (DMA), microbond test (apparent interfacial shear strength, τ_{app}) and scanning electron microscopy (SEM), the compatibilizers PPS-NH_2 could improve the macro-mechanical properties and interfacial bonding between CF and PPS matrix.

1. Introduction

Poly (phenylene sulfide) (PPS) is an attractive engineering thermoplastic which is widely used due to its good dimensional stability, outstanding high-temperature stability, flame retardant and resistant to chemicals, as well as having good processing properties [1,2]. Owing to the relative low mechanical properties of pure PPS, the applications of pure PPS have been somewhat limited. To improve the mechanical properties, composites formed using polymer blending, fiber reinforcing and/or particle fills are usually used in industry [3]. Consequently great attention has been given to the fibrous fillers because of the easy processing and the significant improvement in mechanical and other properties [4,5]. Among the group of advanced fibers, carbon fibers (CF) are widely used as advanced reinforcing fiber materials in polymer–matrix composites, due to their good mechanical and thermal properties [6]. Therefore, CF reinforced PPS composite is thought to be an outstanding composite in high performance engineering plastic [7–10]. However, the mechanical properties of CF reinforced PPS composites are not excellent. It is well known that, the properties of fibers reinforced composites depend on several factors such as the characteristics of matrix and fillers, form and volume fraction of fibers, chemical and physical interaction between fibers and polymer, and processing conditions. One of the main problem is the compatibility between fibers and the matrix [11]. Good interfacial adhesion between fiber and matrix is necessary for obtaining composites with excellent mechanical properties. However, on the one hand, PPS has some drawbacks such as brittleness and poor adhesion of hydrophilic reactive group in PPS chains. On the other hand, the virgin carbon fibers have poor interaction with most of the polymers due to it is non-polar surface and compound of highly crystallized graphitic basal planes with inert structures [12]. Therefore, the interfacial bonding between CF and PPS is poor, so that the interfacial adhesion and mechanical properties need to be improved.

The common methods for improving the interfacial adhesion between carbon fiber and matrix include fiber chemically functionalization [13,14], plasma treatment [15,16], coupling agent treatment [17], and adding compatibilizers [18,19], and so on. There into, the compatibilizers can improve the interfacial adhesion between the fiber and matrix by the "bridging" effect. The compatibilizers could either interact chemically or physically with the fiber surface or has excellent compatibility with the polymer matrix. And this method is low cost, simple and reliable. In the former research papers, the maleic anhydride graft polypropylene (PP) and polystyrene (PS) were used as the compatibilizers in PP/CF and PS/CF composites system, respectively. The results showed

* Corresponding authors. Address: Institute of Materials Science and Technology, Sichuan University, Chengdu 610064, China (J. Yang and S. Long). Fax: +86 28 85412866.

E-mail addresses: lsrhome@163.com (S. Long), ppsf@scu.edu.cn (J. Yang).

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that the maleic anhydride graft resin could significantly increase the mechanical properties and interfacial adhesion of corresponding composites [12,19]. However, very little work has been reported on the interfacial modification by adding compatibilizers in CF reinforced PPS composites.

The aim of this study was to improve of adhesion between PPS matrix and CF through adding compatibilizers which were synthesized in our laboratory. Usually, the compatibilizers prepared by graft modification of matrix resin would be easy. However, PPS is insoluble in common organic solvents and difficult to grafting. In the former studies of modified PPS, many of them are reported in the patents, such as CN1910045 A and CN1061667 C [20,21]. However, the study on grafting modification of PPS which can be used as compatibilizers is few. In the Díez–Pascual's studies, an aminated poly (phenylene sulfide) derivative was synthesized through addition of a nitric/sulphuric acid mixture followed by reduction of the nitro group to its respective amine [22]. And it also was used as the compatibilizer to covalently anchored to the surface of functionalized carbon nanotubes [23,24]. To our knowledge, the effect of modified PPS compatibilizers on the CF reinforced PPS composites have not been reported. In this study, an aminated PPS (PPS-NH_2) was prepared by the condensation polymerization of sodium sulfide (Na_2S), p-dichlorobenzene (DCB), and the third active monomer 2,5-dichloroaniline (DCA). And then these aminated PPS which contain different content of DCA were used as compatibilizers in CF reinforced PPS composites. The mechanical properties, fracture morphology and dynamic mechanical properties of CF reinforced PPS composites with or without PPS-NH_2 were discussed. The apparent interfacial shear strength (τ_{app}) obtained from microbond test was also used as microscopic and direct prove of improvement interfacial bonding.

2. Experimental

2.1. Materials

Poly (phenylene sulfide) (PPS) resin (M_w = 48,000, M_n = 21,000, melting temperature is about 285 °C) was supplied by Deyang Chemical Co., Ltd., Sichuan, China. Density and melting temperature were 1.36 g/cm^3 and 280 °C, respectively. Commercially available short carbon fiber with approximately 3 mm length and 7 μm diameter (T700SC-12K) purchased from Japan Toray. Commercially available sodium sulfide ($Na_2S \cdot xH_2O$, $Na_2S\% \approx 60\%$) (Nafine Chemical Industry Group Co., Ltd.), N-methyl-2-pyrrolidone (NMP) (JiangSu Nanjing JinLong Chemical Industry Company), 2,5-dichloroaniline (DCA) (99%, Chengdu AiKeDa Chemical Industry Company), p-dichlorobenzene (DCB) (99%, Quzhou, Rainful Chemical Industry Company) and other reagents and solvents were commercially obtained. The catalyst used in the synthesis was prepared according to the patent [25].

2.2. Synthesis of the aminated polyphenylene sulfide (PPS-NH_2)

A typical polymerization was performed as shown in Fig. 1. In a 1000 ml high pressure reactor, the $Na_2S \cdot xH_2O$, NMP and catalyst were added. Firstly, the mixture was stirred at 180 °C for 1 h to remove water. Secondly, the DCB and DCA were added into the reactor, stirred at 230 °C for 8 h to yield PPS-NH_2 granules. Next, the product was washed with water and ethanol; then dried under vacuum. After drying under vacuum at 100 °C for 12 h, the PPS-NH_2 was obtained.

The compatibilizer PPS-NH_2 (0.6), PPS-NH_2 (0.7), PPS-NH_2 (0.8), PPS-NH_2 (0.9), PPS-NH_2 (1.0) and PPS-NH_2 (1.2) represent the compatibilizers with different DCA molar fractions (0.6%, 0.7%, 0.8%, 0.9%, 1.0% and 1.2%, respectively) in DCB/DCA. The ratio of DCA/DCB in different compatibilizers is showed in Table 1. The weight average molecular weight of compatibilizers PPS-NH_2 (0.6)–(1.2) range from 40,000 to 60,000. All of materials were vacuum dried at 100 °C for 12 h prior to use.

2.3. Preparation of composites

In this work, the CF/PPS composites with PPS-NH_2 (CF/PPS/PPS-NH_2 = 20/75/5) and PPS compounds with 5% PPS-NH_2 were blended using a co-rotating twin-screws extruder (CTE-35, Nanjing Coperion Keya Machinery Limited Company, China). And the processing temperatures of the 9 zones and die of twin-screw extrusion were 260 °C, 280 °C, 300 °C, 310 °C, 310 °C, 310 °C, 310 °C, 310 °C, 310 °C and 305 °C. After blending, the pellets were injection molded through an injection-molding machine (CJ150NC, Zhengxiong Corporation, China) at the melt temperatures of 330 °C and mold temperature of 70 °C [26].

2.4. Characterization

2.4.1. Fourier transform infrared analysis

Fourier transform infrared (FTIR) spectra were studied by a FTIR spectrometer (Nexus 670, Nicolet Instrument Co., USA) in reflection mode. The spectral resolution was 4 cm^{-1}, ranging from 4000 to 400 cm^{-1}.

2.4.2. Mechanical testing

Tensile properties and flexural properties of PPS/CF composite and PPS/PPS-NH_2/CF composites were performed using Universal Testing Machine (Instron 5567, USA) at room temperature according to ISO 527 and ISO 178, respectively. Unnotched Izod impact strength tests for type 1A specimens were carried out using a Chengde Testing Machine (XJU-275) according to ISO 180 at room temperature. Each value obtained represented the average of five samples.

2.4.3. Dynamic mechanical analysis

Dynamic mechanical properties of the composites were studied using a dynamic mechanical analyzer (DMA Q800, TA Instruments). The samples were analyzed with three-point bending mode, from 40 °C to 200 °C under a heating rate of 5 °C/min and at a frequency of 1 Hz. The dimensions of each sample were 30 mm × 10 mm × 4 mm (length × width × thickness).

2.4.4. Scanning electron microscopy

Tensile fracture surface morphology of the composites were examined by scanning electron microscopy (SEM; JSM-5900LV, JEOL, Japan) at an acceleration voltage of 20 kV. All specimens were sputtered with 10 nm layer of gold prior to SEM observations.

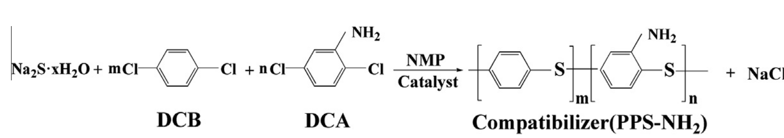

Fig. 1. Synthesis routes of compatibilizers PPS-NH_2 prepared by Na_2S, DCB and DCA.