Characterization of poly(butylene terephthalate) composites prepared by using various types of sized carbon fibers

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ABSTRACT

This paper aims to study the effects of sizing on properties of differently sized carbon fiber (CF) reinforced poly(butylene terephthalate) (PBT) composites by comparing them to unsized CF reinforced composites. Contact angle analysis was used to evaluate the wettability of CFs and the work of adhesion between the sizing agent and PBT matrix. It was found that wettability of PU sizing material by PBT matrix was better than that of other sizing materials by PBT matrix. Tensile and dynamic mechanical analysis (DMA) tests were performed to investigate the effect of sizing agent type on mechanical and thermomechanical properties. According to tensile test results PHE and PU sized CF reinforced PBT composites gave higher tensile strength and modulus values than the others. DMA revealed that PU sizing material gave better adhesion strength than other sizing materials. It was found that electrical conductivity values of all composites are about 10^{-2} S/cm. SEM analysis showed that PU sized CF surface covered a layer of PBT matrix in accordance with other test results. As a conclusion of all results, it can be suggested that PU is a proper sizing material to be used for CF surface for PBT matrix.

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1. Introduction

Thermoplastic polymers exhibit good properties such as high impact strength, and fracture resistance. Because of this reason, they are widely used in polymer engineering industry [1]. Poly(butylene terephthalate) (PBT) is one of these thermoplastic polymers and it has been mostly used in automotive, electrical, and electronic industries for many years due to its exceptional electrical insulation properties [1–3]. PBT is considered as the main competitor for polyamides, but it has the advantage over polyamides due to its much lower moisture uptake and better dimensional stability properties under wet conditions [4]. Moreover, PBT has been widely used in fiber-reinforced composites because of its good mechanical properties and properties of easy molding and fast crystallization [5]. When compared to glass fiber reinforced PBT composites; carbon-fiber-reinforced PBT composites exhibit higher tensile strength and modulus due to exceptional mechanical effects of carbon fibers [5]. On the other hand, mechanical properties of fiber reinforced composites not only depend on the intrinsic characteristics of the matrix and fiber, but also on the fiber/matrix interface adhesion. Since the stress transfer phenomena from the matrix to the fiber during deformation is affecting mechanical resistance of composites, better interfacial adhesion militates in favor of better stress transfer and

mechanical properties. Therefore, it is crucial to control the interfacial adhesion to get better mechanical properties [6,7].

The interfacial adhesion becomes more important when using thermoplastic matrix because of the poor chemical functionality of this matrix type [8]. Besides, carbon fibers contain very few reactive groups due to their carbonization process which occurs at elevated temperatures, since these functional groups on the fiber surface are eliminated at elevated temperatures [9]. The lack of reactive groups on the fiber surface and thermoplastic matrix leads to weak adhesion between carbon fiber and thermoplastic matrix. In the case of weak adhesion, the matrix cannot transfer the stress to fiber efficiently and fiber cannot perform its duty of carrying the applied load [8]. Two methods are generally used for obtaining better adhesion and stress transfer. These methods are matrix modification and fiber surface modification. One of the fiber surface modification methods is sizing and in this method, carbon fibers are usually coated with a sizing material which consists of a proper polymer or resin [7,10,11]. The sizing material includes functional groups and these groups change the surface free energy and wettability of carbon fiber surfaces [12]. Also they can react to or interact with the polymer matrix. This reaction or interaction enhances the fiber–matrix adhesion and correspondingly the ultimate properties of composites [13].

In the literature, a few studies about carbon fiber-reinforced PBT composites have been undertaken. One of these studies was reported by Ng et al. [14]. They added boron nitride (BN) and carbon fiber (CF) into PBT matrix and investigated the hybrid filler effect on the properties of PBT composites. They found that, while the combination of BN and CF in PBT significantly reduced electrical conductivity of the

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composites, the usage of mixed fillers did not lead to an improvement in thermal conductivity with respect to PBT/BN composites. They also observed that hybrid composites exhibited better tensile properties and processability than PBT/BN composites at the same total filler content. Another study was performed by Wiedmer et al. [15]. They studied the effect of electron beam radiation on carbon fiber reinforced PBT, PPS and PA composites. They prepared composites with and without the presence of crosslinking agent to clarify whether crosslinking could occur. They examined the thermal and mechanical properties of the composites before and after exposure to irradiation. Consequently, they observed that properties of PBT, PPS and PA46 composites did not change significantly in the presence of crosslinking agent after irradiation. On the other hand, CF/PA66 composites exhibited changes in some of their properties in the presence of a crosslinking agent after irradiation. Chen et al. [16] investigated the properties of recycled carbon fiber (RCF) reinforced PBT matrix composites. They also treated RCF surfaces with the solution of diglycidyl ether of bisphenol A in order to improve the interfacial adhesion between the RCF and PBT matrix. Their results showed that, surface treated RCF significantly improved the mechanical properties, heat distortion temperature, and thermal stability of the composites. The morphology studies of fracture surfaces also indicated that the RCF homogeneously dispersed in the PBT matrix. Although there are a few studies in the literature which were focused on the effects of sizing agent type, molecular weight and concentration on the properties of some of polymeric matrix based composites [17–19], there has been no study about the effects of sizing agent type on the properties of carbon fiber reinforced PBT composites to the best of authors' knowledge.

This study focuses on the effects of sizing material types on the properties of CF reinforced PBT matrix composites. For this work, CFs which were unsized and which were sized with five different types of sizing agent were used as reinforcement material. The properties of composites were analyzed by mechanical, thermomechanical, electrical, morphological tests and contact angle measurements.

2. Materials and methods

Matrix material PBT (Tecodur®) was supplied by Interplast (Turkey). Unsized CF and CFs sized with polyurethane (PU), polyamide (PA), polyimide (PI), phenoxy (PHE) and epoxy/phenoxy (EPO_PHE) were supplied by Akkök Group (Turkey) and used as reinforcement. PBT was dried in a vacuum oven at 120 °C for 8 h before the compounding process. PBT granules and 30 wt.% of 6 mm chopped carbon fibers were compounded in a laboratory scale co-rotating twin-screw mini extruder at 255 °C, 100 rpm. All the compounds were subsequently injection molded using a laboratory scale injection molding machine with a barrel temperature of 255 °C, mold temperature of 130 °C and injection pressure of 10 bars.

Contact angles of test liquids against the sizing materials and PBT matrix material were measured by the sessile drop method with Attention Theta Lite contact angle tensiometer. The used test liquids were ethylene glycol, diiodomethane and deionized water. Surface tension of test liquids was given in Table 1 [20]. Standard test specimen of neat PBT was produced for contact angle analysis using a twin-screw mini extruder and laboratory scale injection molding machine. In addition, thin films of each sizing material were cast onto clean microscope slides for contact angle analysis of sizing materials. Ten measurements were conducted to obtain average contact angle values.

Tensile tests were performed using Instron 4411 universal testing machine. The dimension of the test samples was 4 mm width, 2 mm thickness and 30 mm length. Average tensile strength and modulus values of composites were determined using 5 dumbbell-shaped samples for each composition at a constant crosshead speed of 5 mm/min. DMA was performed in tension mode by using Metravib DMA50 analyzer. Composites were tested under the condition of 1.5×10^{-5} m dynamic displacement and 1 Hz frequency. The scanning was carried out from 25 °C to 200 °C at 1 °C/min heating rate. Specimen dimensions were 10 mm height, 2 mm thickness and 4 mm width.

Electrical resistivity values of composites were measured with 2-point-probe test by using Haoyue M890G Digital Multi Meter. For obtaining good electrical contact in this technique, copper wires were attached to both ends of test sample with silver paste. After the hardening of silver paste, resistivity measurements were performed by contacting probes with these copper wires. After that, electrical conductivity values of composites were calculated using obtained resistance values of composites as in the following formula [21,22]:

$$\frac{\text{Sample Thickness (cm)}}{\text{Electrode Area (cm}^2\text{)} \ \times \ \text{Resistance (}\Omega\text{)}}. \tag{1}$$

Morphologies of the tensile fractured surfaces of composites were examined using a scanning electron microscope (JEOL JSM-6335F). Before the examinations, tensile fracture surfaces of composites were sputter coated with gold and palladium.

3. Results and discussion

3.1. Surface energy analysis

Sizing process which was applied to carbon fiber surface changes the surface energy and wettability of the surface and affects the fiber matrix adhesion performance. One of the methods to be used for analyzing adhesion performance of fiber surfaces is the contact angle measurement.

Contact angle concept which was first developed and formulized by Young, became the main concept for the development of later approaches. One of these approaches was developed by Van Oss, Good and Chaudhury, which aimed at estimating the surface energy values of solids [23,24]. According to their approach, a solid surface consists of two terms: one of them is the Lifshitz–van der Waals interactions, γ^{LW}, which includes dispersion, dipolar and induction interactions, and the other one is the acid–base interaction term, γ^{AB}, which includes all the electron donor (γ_S^-) and electron acceptor (γ_S^+) interactions. By combining this approach with the Young–Dupré equation, the general contact angle equation is obtained:

$$\gamma_L(1 + \cos\theta) = 2\left(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^+\gamma_L^-} + \sqrt{\gamma_S^-\gamma_L^+}\right). \tag{2}$$

The value of γ_S^{LW} is determined from the contact angle of an apolar liquid on the solid in which case Eq. (2) reduces to:

$$\gamma_L(1 + \cos\theta) = 2\left(\sqrt{\gamma_S^{LW}\gamma_L^{LW}}\right) \tag{3}$$

when γ_S^{LW} is known and the contact angles are obtained using different liquids on the solid, one can get two equations similar to Eq. (2), and these equations can be solved simultaneously for γ_S^+ and γ_S^-.

In addition to this, by writing Eq. (2) as below, work of adhesion between solid and liquid can be calculated:

$$W^a = \gamma_L(1 + \cos\theta) = 2\left(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^+\gamma_L^-} + \sqrt{\gamma_S^-\gamma_L^+}\right). \tag{4}$$

Table 1
Surface tension values of test liquids.

Surface tension	Diiodomethane	Ethylene glycol	Deionized water
γ_L^{TOT}	50.8	48	72.8
γ_L^{LW}	50.8	29	21.8
γ_L^{AB}	–	19	51.0
γ_L^-	–	47	25.5
γ_L^+	–	1.92	25.5