Composites Communications 8 (2018) 24–30

Contents lists available at ScienceDirect

Composites Communications

journal homepage: www.elsevier.com/locate/coco

Effects of glass fiber reinforcement and thermoplastic elastomer blending on the mechanical performance of polylactide

S. Deniz Varsavas, Cevdet Kaynak*

Materials and Metallurgical Engineering Department, Middle East Technical University, Ankara, Turkey

ARTICLE INFO

Keywords:
Polylactide
Glass fiber
Thermoplastic polyurethane elastomer
Mechanical performance

ABSTRACT

The purpose of this study was to investigate how optimum mechanical properties (strength-modulus-toughness) of inherently very brittle polylactide (PLA) could be obtained by reinforcing with E-glass fibers (GF) and blending with thermoplastic polyurethane elastomer (TPU). Composites and blends were compounded by twin-screw extruder melt mixing, while specimens were shaped by injection molding. SEM analyses revealed that 15 wt% GF and 10 wt% TPU domains, alone and together, could be uniformly distributed in the PLA matrix leading to significant improvements in properties. Mechanical tests indicated that use of TPU blending alone resulted in enormous increases in the ductility and fracture toughness values, while GF reinforcements led to significant increases in strength and elastic modulus values. When GF and TPU were added together, it was observed that crack deflection, debonding and fiber pull-out toughening mechanisms of GF reinforcements were as effective as the rubber toughening mechanism of TPU blending.

1. Introduction

Engineering polymers both thermoplastics and thermosets have been taking place of many conventional metallic and ceramic materials day by day due to basically their lightness and ease of processing. Nonetheless, since many of these engineering polymers are petroleum-based, polymer industry has encountered some problems namely difficulty in access to petrochemical resources and rising costs [1]. This situation creates a need for development of bio-based polymers classified as biopolymers. Poly(L-lactic acid), also termed polylactide (PLA), is today one of the most significant thermoplastic biopolymer with aliphatic polyester structure. It can be synthesized from fully renewable resources like corn starch. Due to its high level of biocompatibility and certain biodegradability, PLA is today mostly used in biomedical, textile and food packaging applications. There has been an increasing demand for PLA, it is expected that its global production capacity will reach to 800,000 t/year by 2020 [2].

On the other hand, although compared to other biopolymers PLA has rather higher level of mechanical properties, this is not the case if compared to conventional engineering thermoplastics. Therefore, mechanical properties of PLA; not only strength and modulus, but due to its inherent brittleness, toughness should be also improved. It is known that strengthening of polymer matrices can be achieved by fiber reinforcements, while toughening can be achieved by elastomer blending. In this study, effects of E-glass fiber (GF) reinforcement and thermoplastic polyurethane elastomer (TPU) blending would be investigated.

In the literature, it was observed that majority of the studies [3–14] used not E-glass fibers; instead, they used phosphate glass fibers. Because, due to the compositional similarities of bone structure and phosphate glass fibers, the main purpose of these biomedical studies was to develop a biodegradable and biocompatible implant material via tissue engineering. They especially investigate bone fixations which would be bio-absorbable without any harmful or toxic effect; and having a degradation rate that would slowly transfer the load to the healing bone. These tissue engineering studies were focused on the quality of the interface between phosphate glass fibers and PLA matrix, cyto-compatibility and mechanical properties of the composites, and the levels of degradation and retention of these properties under *in vitro* conditions.

Literature on the use of E-glass fiber (GF) reinforcement of PLA seems to be very limited. In one of these studies, Lin et al. [15] used GF reinforcement not for neat PLA, but for a PLA/PC (70/30) blend. Compounding of PLA with 10, 20, 30 wt% GF was done by melt mixing via twin-screw extruder. Mechanical tests of the injection molded specimens indicated that 30 wt% GF reinforcement resulted in 84%, 73% and 200% increases in tensile strength, flexural strength and notched Izod impact strength, respectively; while ductility of the blend decreased by 71%. Similarly, Lu et al. [16] used 5, 10, 20, 30 wt% GF reinforcements for the blend of PLA/HDPE (60/40). It was found that

* Corresponding author.
E-mail address: ckaynak@metu.edu.tr (C. Kaynak).

https://doi.org/10.1016/j.coco.2018.03.003
Received 12 January 2018; Received in revised form 15 March 2018; Accepted 16 March 2018

addition of 30 wt% GF resulted in 75% increase in tensile strength of the blend, while its impact strength and ductility were decreased as 57% and 83%, respectively.

In the work of Huda *et al.* [17] use of 30 wt% GF in PLA matrix, again via twin-screw extruder compounding and injection molding shaping; tensile strength and flexural strength were increased by 28% and 10%, respectively. In addition, elastic modulus, flexural modulus and notched Izod impact strength values were also raised by 145%, 152% and 53%, respectively. In another similar study, Jaskiewicz et al. [18] found that tensile modulus and notched Charpy impact strength of PLA having 30 wt% GF were 188% and 531% higher than that of neat PLA, respectively.

Literature survey indicated that in order to overcome inherent brittleness of PLA, rubber toughening could be used. In this respect, researches especially focused on the blending of PLA with an elastomeric material such as natural and synthetic rubbers [19–22] and also thermoplastic polyurethane elastomer (TPU) [23–40]. These studies generally revealed that, due to the effective rubber toughening mechanisms, significant increases in toughness and ductility would be attained; of course with certain degree of losses in strength and modulus values of PLA.

In order to compare mechanical behavior of PLA with traditional engineering thermoplastics, it would be wise to consider effects of fiber strengthening and rubber toughening together. However, to the best of our knowledge, there is no study reported on the effects of both GF reinforcement and TPU blending, yet. Therefore, the purpose of this study was, as the first time, to investigate not only strengthening level of PLA with increasing GF reinforcement content but also toughening level of PLA by TPU blending with and without GF.

2. Experimental

2.1. Materials

PLA matrix material used was L-lactic acid type polylactide (NaturePlast, PLE 001). As it is indicated in its technical data sheet, it melts between 145°-155°C and degrades in the range of 240-250 °C; with a density of 1.25 g/cm^3. Furthermore, by using the static light scattering spectroscopy (SLS) (Malvern CGS-3) technique; number average molecular weight of this PLA was determined as 375,600 g/mol. GF reinforcement used was E-glass type chopped fibers (CamElyaf Glass Fiber, PBT2) with the average length and diameter of 4.5 mm and 10.5 μm, respectively. The producer indicates that fibers have silane sizing compatible with thermoplastic polyesters of PBT and PET. As the rubber toughening agent, polyurethane type thermoplastic elastomer was chosen. This TPU (Interplast, Epaflex EL 392A 25) has a density of 1.19 kg/dm^3, hardness of 93 Shore A, tensile strength of 40 MPa, and elongation at break of 550%.

2.2. Compounding and shaping of PLA with GF and TPU

Composites and blends of PLA with GF and TPU were all produced by two industrially compatible steps; i.e. “twin-screw extrusion melt-compounding” and “injection molding melt-shaping” with laboratory size equipment. First, PLA powders and TPU granules were pre-dried for 15 h and 4 h, respectively; in a vacuum oven at 60 °C. Then according to the formulation, PLA, GF and TPU particles were pre-mixed manually, and these mixtures were melt compounded via laboratory size twin-screw extruder (Rondol Microlab 300 with D = 10 and L/D = 20). The temperature profile chosen was 115-170-180-175-145 °C from feeder to die, with the screw speed of 75 rpm. Strands coming from the die were transformed into 2–3 mm pellets by a four-blade cutting mechanism.

Before shaping of the specimens required for the mechanical tests, these pellets were re-dried again in a vacuum oven at 60 °C for 15 h. In order to shape standard sized specimens, a laboratory size injection molder (DSM Xplore Micro) was used with the barrel and mold temperatures of 160 °C and 35 °C, respectively.

GF reinforced PLA matrix composites were produced with the loadings of 5, 10, 15 and 20 wt%. These composites were designated by using the format of “PLA/*x* GF”, where *x* denotes wt% of GF used. In the case of toughening with TPU, blending was applied only with 10 wt% TPU; because in the former study [40] of our group conducted for a different grade of PLA blended with 5, 10, 15, 20 wt% TPU, use of 10 wt % resulted in optimum toughness values almost without any decrease in the strength values. This specimen is designated as PLA/10 TPU. As would be discussed in the following results and discussion section, since use of 15 wt% GF revealed the optimum mechanical properties; use of TPU blending with GF reinforcement was applied only with this GF content. Thus, this specimen is designated as PLA/10 TPU/15 GF.

2.3. Mechanical testing and analysis

Strength and modulus values of the specimens were determined both with tension tests according to ISO 527-2 standard, and also with flexural tests in terms of three-point bending according to ISO 178 standard. Apart from tension and flexural tests; fracture toughness tests with single-edge-notched-bending specimens according to ISO 13586 standard were also conducted. All these mechanical tests were performed with a 5 kN universal testing system (Instron 5565 A). For each composition, tests were repeated 5 times, so that the mechanical properties were evaluated as the average values with standard deviations.

Furthermore, morphological analysis on the fracture surface of the fracture toughness test specimens were conducted by scanning electron microscope (SEM) (FEI Nova Nano 430) to investigate the distribution of GF and TPU domains in PLA matrix and also the interface between them.

3. Results and discussion

3.1. Distribution and morphology of GF and TPU in the PLA matrix

Even distribution of the fiber reinforcements is one of the key factor to obtain enhanced mechanical properties of polymer composites. Thus, SEM analysis on the fracture surfaces of fracture toughness test specimens were conducted first to observe effect of silane sized GF content in the neat PLA matrix, and then also in the matrix of PLA/TPU blend.

Lower magnification SEM images in Fig. 1 shows that 5, 10, 15 wt% GF reinforcements were rather uniformly distributed in the neat PLA matrix. On the other hand, use of 20 wt% GF content resulted in decreased uniformity of GF distribution; thus, as would be discussed in the next section, with this content, mechanical properties started to decrease. Fig. 1 also indicates that there was no uniformity problem of 15 wt% GF distribution in the matrix of PLA/10 TPU blend.

It is known that due to the immiscibility of TPU and PLA, when blended they lead to a two-phase structure, where round shaped TPU domains form in the matrix of PLA. Since these TPU domains are micron sized, it was possible to observe them only in the higher magnification SEM images of Fig. 2. Due to the certain degree of compatibility between PLA and TPU domains, Fig. 2 moreover shows that micron-sized TPU domains were also uniformly distributed in the PLA matrix. The reason of this partial compatibility is the certain interactions between the carboxyl, hydroxyl end groups and ester carbonyl groups of PLA and polar groups of the hard segments of TPU. Fig. 2 also shows that there were certain levels of “debonding” and “pull-out” of GF reinforcements in each matrix. As would be discussed later, these phenomena lead to additional toughening mechanisms.

3.2. Effects of GF and TPU on the strength and modulus of PLA

Tension tests and three-point bending tests were conducted to