

HOMOCOMPOSITES OF POLY(ETHYLENE TEREPHTHALATE)

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Abstract

While the advantages of homocomposites over heterogeneous composites are obvious, the fabrication of homocomposites for fast crystallizing polymers is challenging because the melting temperatures of the fiber and the matrix are very close. In the present study, an approach of using poly(ethylene terephthalate) (PET), a slowly crystallizing polymer, to form homocomposites was investigated. Because PET experiences slow crystallization during typical polymer processing, distinct physical forms with a large difference in crystallinity and thus in melting temperature can be readily obtained. In the experiment, highly crystalline PET fibers laid between two amorphous PET films were compressed between heated platens at 180°C, a much lower temperature than the melting temperature of the fiber, and rapidly cooled after a holding stage of 90 seconds. The resulting homocomposites have a tensile strength about twice higher than the non-reinforced PET processed under the same condition.

Introduction

Although the mechanical properties of polymer composites are governed by the individual properties of the components, the interface formed between the matrix and the fiber strongly influences the performance of the composite [1-3]. For thermosetting composites, it has been a standard routine to utilize various coupling agents to strengthen the adhesion between fibers and matrix [4-5]. However, the known coupling agents for glass and carbon fibers typically do not work well for common thermoplastic polymers, and therefore the chemical compatibility between fibers and matrix is of a major concern for thermoplastic composites [6].

Capiati and Porter [7] first published the concept of a single-polymer composite, a composite with matrix and reinforcement from the same polymer. The method utilized the noticeable difference in melting temperature between high-density polyethylene (HDPE) matrix and HDPE reinforcement to fabricate an HDPE homocomposite. Since the extent of adhesion between fibers and matrix is largely influenced by their physical and chemical compatibility, the polyethylene homocomposite concept has been discussed in several studies [8-10] following Capiati and Porter's work. It has been shown in these studies that

excellent bonding between fibers and matrix are achieved in the polyethylene homocomposite, with the interfacial shear strength on the same order of that for glass fiber reinforced epoxy resins. Morphological investigations [8,11,12] further revealed that, under appropriate processing conditions, transcrystalline interphases are formed at the fiber-to-matrix interface, which can be used to explain the enhanced fiber-matrix adhesion.

Despite the advantages of polymer homocomposites over heterogeneous composites in terms of chemical compatibility and recyclability, the small difference in the melting temperature between the fiber and the matrix poses a challenge during fabrication. For instance, the melting temperatures for HDPE matrix and fibers reported by Mead et al. [8] were 132°C and 139°C, respectively. With a temperature window of only 7°C, it is difficult to process the resultant homocomposite under normal processing conditions without significantly annealing the fiber. In the case of ultrahigh molecular weight polyethylene (UHMWPE), the difference of melting temperature between fiber and matrix is in the range of 5-9°C [9]. It is known that polyethylene fibers annealed at a temperature close to its melting temperature have a much reduced modulus toward the modulus of bulky HDPE of about 1 GPa [8].

To enlarge the process window, the original concept of single-polymer composites has been relaxed and extended to the incorporation of polymers with the same chemical composition but different chemical structures. Examples are HDPE matrix reinforced by UHMWPE fibers [12,13] and low-density polyethylene (LDPE) matrix reinforced by HDPE fibers [8]. In both cases, a process window of about 20°C results. When LDPE is reinforced by UHMWPE fibers [14], the process window can be further enlarged to about 40°C. Although manufacturability is greatly enhanced in these composite systems, the interfacial adhesion was found to be much lower than the original HDPE homocomposite [8,14]. It should be noted that, except for different molecular weight, HDPE, LDPE and UHMWPE also bear different chain configurations. The difference in chain configuration, e.g. branched or linear chains, plausibly deteriorates the compatibility between the fiber and the matrix through steric interactions.

The single-polymer composite concept has also been applied to polypropylene (PP) [15,16] and poly(methyl

methacrylate) (PMMA) [17-19]. Being a fast-crystallizing polymer as polyethylene, PP faces the same dilemma between processibility and fiber-matrix compatibility in homocomposite applications. With regard to the essence of the single-polymer composite concept, PMMA, as an amorphous polymer, is certainly not a good system in homocomposite applications because the system is now subjected to an additional drawback resulting from low strength of amorphous PMMA fibers except for the narrow processing window.

It can be seen that most of the previous work on homocomposites involves fast crystallizing polymers such as polypropylene and polyethylene. However in these polymers, the proximity of the melting temperatures between the fiber and the matrix pose a considerable difficulty during homocomposite processing. In the present study, poly(ethylene terephthalate) (PET), a slowly crystallizing polymer, is employed for homocomposite manufacturing. The conceptual design and advantages of such a homocomposite system and some preliminary results are presented in the paper.

Conceptual Design of PET Homocomposite

The key issue in thermoplastic homocomposites is how to melt-process the matrix without melting the fiber. It is well known that the melting temperature of a polymer depends on its physical form, i.e., amorphous state, crystalline state and amount of crystallinity. Commonly used polymer fibers, such as PP, PE and nylon fibers, are highly crystalline and have melting temperatures close to those of single crystals. These polymers, however, have disadvantages in homocomposite applications owing to their fast crystallization rate. Because of fast crystallization, the products derived from PE, PP and nylon are highly crystalline, resulting in closeness of melting temperature of these products. With unique properties and economical and environmental advantages, PET stands out for homocomposite applications. PET is a slowly crystallizing polymer, with typical half-crystallization time around 2 minutes [20]. Amorphous products will result if molten PET is rapidly cooled. Amorphous PET is very stable at room temperature because its glass transition temperature is about 80 °C. Examples are injection molded amorphous PET articles. On the other hand, if PET is heated to above its crystallization temperature and kept for a few minutes or a shorter period under elongational stress, highly crystalline PET will be formed. Examples are PET fibers and heat-set PET films. The melting temperature of highly crystalline PET fibers is above 250°C. If a lamination of amorphous PET films and crystalline PET fibers is rapidly heated to above the softening temperature of the amorphous phase, the amorphous PET will gain enough fluidity for compression molding.

Experimental

Materials:

PET woven fabrics, meshes, and amorphous films were obtained from Goodfellow Corporation. The PET fabric (Figure 1.a) is plain weaved, 0.15 mm thick, with 33% open area, and have 55 threads per cm. The monofilament diameter is 70 μm . The nominal aperture size is 100 μm . The PET mesh (Figure 1.b) is made of yarns interlacing at right angles. It is 0.127 mm thick and has 50% open area. The amorphous PET film is 0.25 mm thick. The mechanical properties of the three physical forms of PET were obtained using tensile test with a rectangular sample geometry of 70 mm \times 15 mm. The tensile strengths for the fabric, the mesh and the amorphous film are 160, 95 and 65 MPa, respectively.

Manufacturing:

The crystalline PET fabric laid between two amorphous films was compressed between platens on a Carver press, as shown in Figure 2. Spacers were used to control the thickness of the fabricated composite film. The compression speed employed was 1.58 mm/sec. The adhesion property of the matrix and the fiber were studied by varying the platen temperatures, the compression force and the holding time. The platen temperatures were varied from 170°C to 200°C, compression force from 5,000 to 10,000 lbf and the holding time from 30 to 100 seconds. The PET homocomposite obtained was rapidly quenched in water. This procedure was repeated for the fabrication of PET homocomposites using the PET mesh as the reinforcing material. Non-reinforced PET was fabricated by compressing two amorphous PET films at 180°C on the carver press and subsequently quenching in water. The same compression force and holding time as used in homocomposite fabrication are used.

The fabric/mesh reinforced homocomposites and the non-reinforced PET all have a thickness of 0.46 mm. Tensile specimens of standard dimensions were punched from the samples. The ends of the tensile specimen were glued using an epoxy adhesive between two nylon stubs, as shown in Figure 3. Tensile tests were carried out on an Instron machine at a crosshead speed of 0.05 mm/sec.

Results and Discussion

The interfacial adhesion between the matrix and the reinforcements was found to be a function of temperature and compression force. Excellent bonding between the matrix and the reinforcements were observed at 180°C, under compression force of 9,000 lbf, and with a holding time of 90 seconds. The compression-molded sample is translucent or milky, signifying significant amount of

crystallinity gained during the holding stage. During the process, the amorphous PET fluidizes first and then crystallizes to solidify. It is interesting to point out that the sequential fluidization and solidification stages occur under the same isothermal molding condition. At the end of 90 seconds, enough crystallinity is gained and the lamination is rigid enough for platen separation. Prolonged holding stage was found to be detrimental to the mechanical properties of the composite because the sample becomes brittle. The embrittlement is believably caused by thermal degradation and overgrowth of the spherulites. Samples fabricate at temperatures lower than 180°C showed weak interfacial bonding. The lamination can be separated by peeling off the PET films. The decreased bonding strength at lower platen temperatures may be attributed to the significant amount of crystallization occurring during the relatively slow heating stage with a lower platen temperature. It should be stated that, for an amorphous PET film, softening and crystallization are two competing processes during heating. If amorphous PET is heated slowly, crystallization will dominate during the heating stage, thus prohibiting softening and fluidization of the material. On the other hand, further increase of the platen temperature to above 180°C will result in very slow crystallization during the hold stage. As a result, the platens cannot be separated with a short holding time, with which embrittlement of the sample can be suppressed; otherwise the still molten amorphous PET will stick to the platen during platen separation.

Figure 4 shows the load displacement curves of the PET homocomposites and the non-reinforced PET. The strength of the fabric reinforced PET homocomposite, the mesh reinforced PET homocomposite, and the non-reinforced PET are 90, 64, and 54 MPa, respectively. The initial linear elastic region shows a higher yield for the mesh reinforced composite than the fabric reinforced and the non-reinforced PET. Figure 5 and Figure 6 compare the different failure mechanisms of the fabric reinforced homocomposite and the non-reinforced PET. Creeping is suppressed in the homocomposite, while the non-reinforced PET is subjected to a large degree of flow under a constant load. The fracture of the PET homocomposite was initiated by the failure of the fiber.

Conclusions

A new approach to polymer homocomposite preparation using a slowly crystallizing polymer was investigated. Derived from the same PET with the same chemical composition and chain configuration, the amorphous PET has a fluidization temperature more than 70°C lower than the melting temperature of the highly crystalline PET fiber, thus providing a wide process window for homocomposite fabrication. The interfacial adhesion in PET homocomposite was found to be temperature and pressure dependent. The fabric reinforced

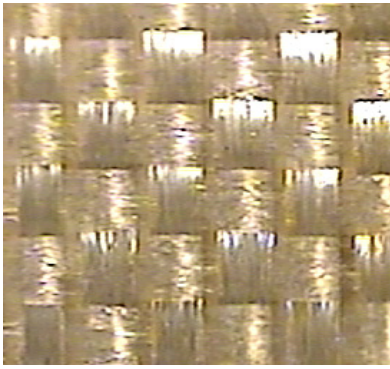
PET homocomposite has a strength more than twice higher than that of the non-reinforced PET. Creeping is suppressed in the homocomposite, while the non-reinforced PET is subjected to a large degree of flow under a constant load. With considerable amount of research in the future toward a better understanding on the interfacial bonding and with the utilization of higher modulus PET fibers, PET homocomposites with greatly enhanced mechanical properties could be attained.

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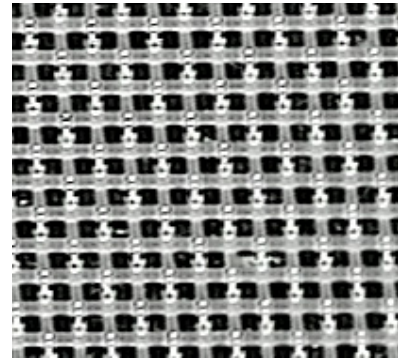
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Key Words

Polymer homocomposites, single-polymer composites, polyethylene terephthalate, slowly crystallizing polymers.



a)



b)

Figure 1: Reinforcements used for composite fabrication: a) PET fabric and b) PET mesh.

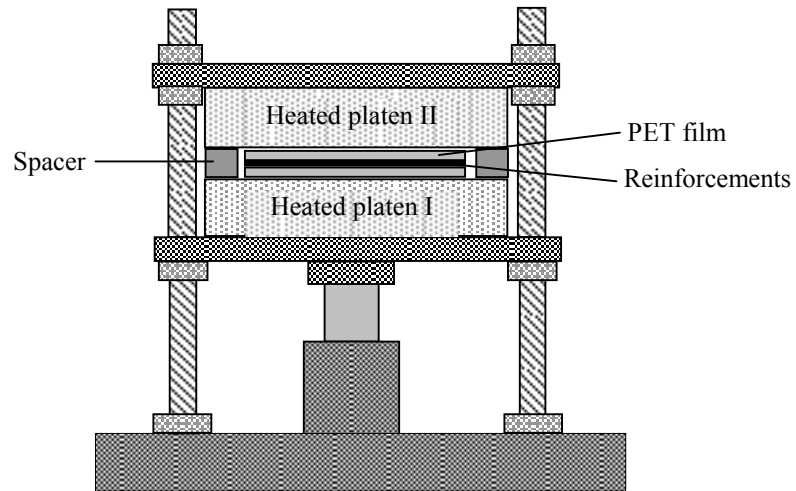


Figure 2: Experimental setup for PET homocomposite fabrication.



Figure 3: Tensile specimen with nylon stubs on both ends.

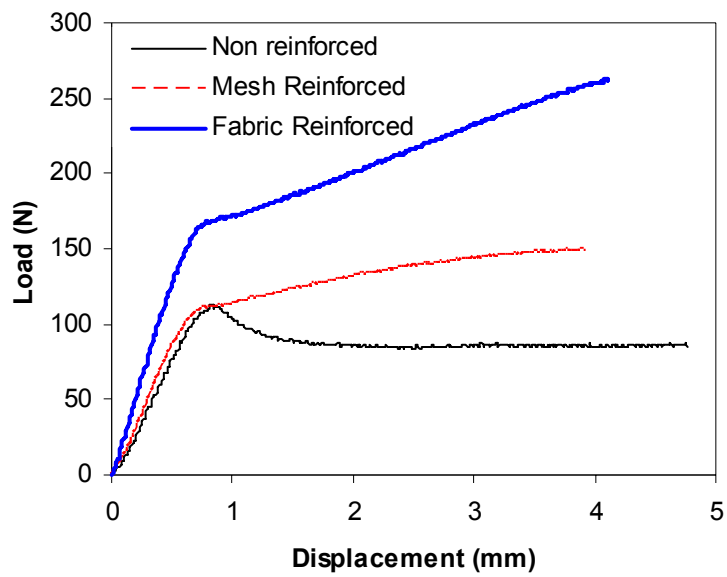


Figure 4: Load displacement curves of the two PET homocomposites and the non-reinforced PET at a crosshead speed of 0.05 mm/sec.

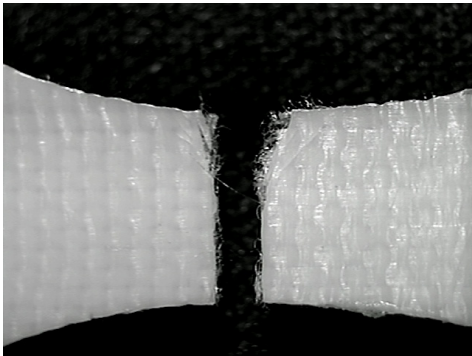


Figure 5: Brittle fracture of PET homocomposite.

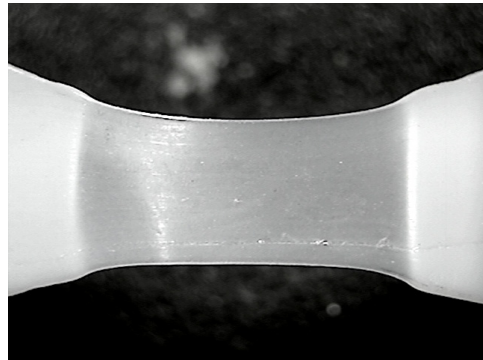


Figure 6: Creep of Non-reinforced PET.