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Thermoplastic nanocomposites

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Abstract

A compound containing 75 wt% of high-density polyethylene (HDPE) and 25 wt% of polypropylene (PP) was melt-mixed in an extruder. The resulting compound was fibrillated by drawing it through a pair of steel rollers at 138°C. The fibrillated tape was cut into small pieces and then re-molded at temperatures above the melting point of HDPE. TEM results indicate that PP fibrils of about 30–150 nm in diameter were created in the HDPE matrix. The mechanical properties of HDPE were greatly improved with a yield stress above 60 MPa and a Young modulus of 3.5 GPa. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polypropylene; Polyethylene; Nanocomposites

1. Introduction

Plastics are widely used because of their low density, good processability and low cost. One of the most important markets in which the plastics have difficulty to penetrate is the market in structural applications. Composites prepared by incorporating glass or carbon fibers into plastics have experienced a significant growth in this area but such composites have several drawbacks, including higher density, higher cost and poorer processability.

Recently, a new method has been developed in our laboratory by which common crystalline polymer blends are converted into stiff and strong nanofiber reinforced composites. A commercial high-density polyethylene (HDPE) and polypropylene (PP) were melt-mixed and extruded into thick tapes, which were then drawn through a pair of steel rollers. After roller drawing, the fibrillated tapes were melt-molded again above the melting point of HDPE. When the molding temperature was below the melting point of PP, the resultant samples behave like a tough engineering plastic with a yielding stress of 60 MPa and a Young's modulus of 3.5 GPa. These values are much higher than those of pure HDPE.

A polymer consists of long-chain molecules. The atoms constructing the backbones of these chains are held together by covalent bonds. Though covalent bonds are one of the strongest in nature, their strength is not realized in polymers because the molecular chains exist primarily as random coils [1–2]. The response of a polymer to an external force is mainly through the motion of the chain segments of the coils which dominates the yielding behavior of the polymer. When a semicrystalline polymer is subjected to an external load, the chain segments in the crystalline regions slip, causing the lamellae to disintegrate locally and the polymer to yield and neck [3–4]. This gives rise to a low stiffness and strength.

Polymer scientists and engineers have been working to develop stiff and strong polymer materials by restricting the motion of the chain segments. Two avenues that they have been pursued are chemical construction of new polymers with a rigid backbone chain [5], such as ladder polymers and liquid crystal polymer and physical optimization of the internal structure (conformation) of traditional semicrystalline polymers [6–9] through such processes as gel-spinning, die drawing and roller drawing. In the latter method, a semicrystalline polymer with flexible chains is drawn at temperature below its melting point. After the polymer coils are stretched, the extended flexible chains are frozen rapidly, producing orienting crystals or fibrils. As a result, the mechanical properties of the common crystalline plastics are enhanced greatly in the stretching direction. Using this method, polymer fibers, plates, rods and tubes with high longitudinal stiffness and strength have been developed [10–11].

Following the idea of the latter method, a blend consisting of two semicrystalline polymers is fibrillated by die/roller drawing and then the fibrillated profiles are processed at a

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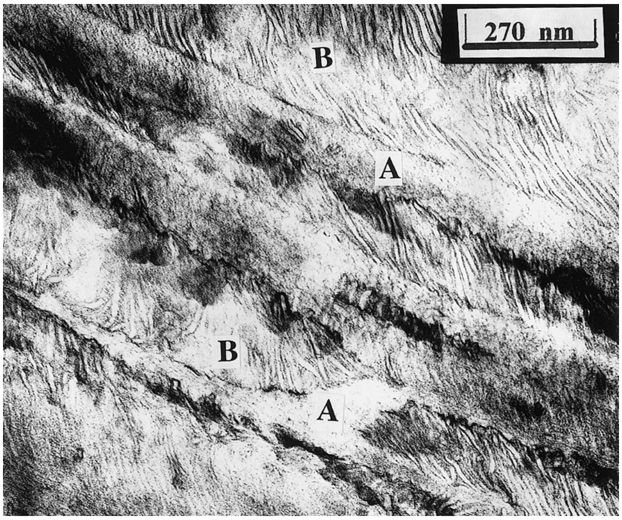

Fig. 1. TEM micrograph of the HDPE/PP composite: A—PP fibrils and B—PE trans-lamellae hatched on the PP fibrils; the sample was stained with ruthenium tetroxide.

high temperature between the melting points of the two components. The fibrils of the polymer with the higher melting point should survive in the molding process and reinforce the polymer matrix that is formed due to the melting of the component with the lower melting point.

2. Experimental

A commercial HDPE (Philips HMMPE) was blended with 25 wt% of PP (Himont 6501) and the resulting material was extruded into 2.4 mm tapes. The extruded PE/PP tapes were pulled through a gap between a pair of steel rollers at about 138°C and the thickness of the tapes was reduced to approximately 0.3 mm. The draw ratio (the ratio of the cross section areas before and after drawing) was about 10. At this draw ratio, the lamella-spherulite structure of the tape was transformed into a fibrous structure. The melting points of the PE and PP components of the fibrillated tape were measured to be 139 and 167°C, respectively, by differential scanning calorimeter. To prepare the HDPE/PP nanocomposites, the fibrillated tapes were cut into short pieces and melt-processed again by compression molding or extrusion. In compression molding, the fibrillated sheets were arranged in two orientation modes—the tapes were all aligned parallel respect to the fibrillation directions (single-axial orientation) or arranged parallel in the same layer but perpendicular between the adjacent layers (biaxial orientation). The extruded sample was prepared on a twin-screw extruder at 155°C.

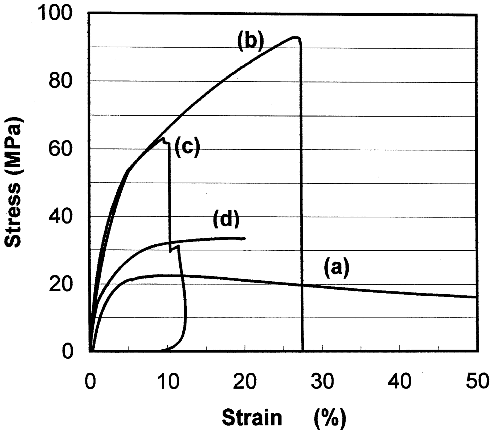

Fig. 2. Tensile behaviors of PP-fiber reinforced HDPE produced at the processing temperature of 165°C: (a) HDPE; (b) single-orientation PE/PP composite; (b) biaxial-orientation PE/PP composite; and (d) extruded PE/PP composite.

3. Results and discussion

Fig. 1 is a TEM micrograph of a sample prepared by molding the fibrillated HDPE/PP tape at about 165°C. Though the molding temperature is close to the melting point of the PP component, the PP component still exist as fibrils with a dimension ranging from 30 to 150 nm (c.f. A in Fig. 1); while the HDPE matrix exhibits a lamellar structure. The PP fibrils are connected to the PE matrix through the hatched trans-lamellae. This morphology is similar to the trans-crystalline structure as observed in glass/carbon fibers reinforced crystalline plastics [12], except the PP fibers are in nanometer scale and much finer than the glass or carbon fibers.

Fig. 2 shows the typical stress–strain curves of the single- and biaxial-orientation samples, the extruded sample as well as the pure HDPE sample molded at 165°C. Under the action of a tensile load, the stress–strain curve of the HDPE begins to deviate from the linear response under low stress and gives a maximum stress of approximately 23 MPa at a strain of around 14%. The Young's modulus was calculated to be 1.45 GPa. After hitting the maximum point, strain softening is observed. Then the material necks and is cold-drawn under further strain. For the single-orientation sample, the stress–strain deviates from the linear response only under a much higher stress. There is no obvious necking, but a yield point is observed under a stress of about 55 MPa. The yield strength of the HDPE/PP nanocomposite is comparable to that of some of the popular engineering plastics (Nylon 66: 55 MPa, poly(butylene terephthalate)(PBT): 56 MPa, poly(ethylene terephthalate)(PET) and polycarbonate (PC): 60 MPa). After the yield point, straining hardening is observed. The stress increases continuously as the strain increases until the breaking point, giving a maximum tensile strength of about 90 MPa at a strain of about 25%. The tensile strength of the HDPE/PP nanocomposite is much higher than that of most engineering plastics, including PET, PBT and PC at ambient temperature. It is comparable to that of poly(ether ether ketone) (70–103 MPa). The Young's modulus was

Table 1
Effect of molding temperature on tensile properties of HDPE reinforced by PP-fibrils generated in situ

Molding temperature (°C)	165	165	175	185	165[a]
	HMMPE	*Single-orientation samples*			
Stress at max. load (MPa)	23.0	88.2	82.0	59.9	27.6
Strain at max. load (%)	14.2	21.6	22.5	25.6	8.0
Young's modulus (GPa)	1.5	3.5	3.7	3.0	2.5
		Biaxial-orientation samples			
Stress at max. load (MPa)		63.8	50.6	28.8	45.0
Strain at max. load (%)		12.2	18.7	10.0	39.0
Young's modulus (Gpa)		3.5	2.4	1.5	1.8

[a] Testing direction is 90° and 45° to the fibrillation directions for the single- and biaxial-orientation composites, respectively.

calculated to be 3.5 GPa. This modulus value is higher than that of most of engineering thermal plastics and a general purpose epoxy resin. The HDPE/PP composite thus behaves like a tough and rigid engineering plastic. The biaxial-orientation sample of the composite gives a maximum stress of about 64 MPa and a Young's modulus 3.5 GPa. The strain–stress curves of the single- and biaxial-orientation sample are nearly identical except that the single-orientation one has a higher strength and ultimate strain. Although the extruded samples were prepared by processing the small fibrillated HDPE/PP tapes at 155°C, a maximum stress of 33 MPa and a Young's modulus of 2.0 GPa are obtained. The mechanical properties of the sample reflect the effect of the reinforcement of the PP nanofibrils to the HDPE, because under the same processing conditions the extruded pure HDPE tape only gives a maximum stress of about 17 MPa and a Young's modulus of 1.3 GPa.

The single- and biaxial-orientation compression-molded samples were also tensile-tested, respectively, in the directions 90 and 45° with respect to the fibrillation direction. It is anticipated that the mechanical properties should be weaker in these directions. The yielding stress and Young's modulus were measured to be 27.6 MPa and 2.5 GPa, respectively, for the single-orientation sample, and 45 MPa and 1.8 GPa, respectively, for the biaxial-orientation sample. These values are still higher than those of the pure HDPE. The above results clearly demonstrate that the tensile properties of the HDPE could be enhanced greatly by the PP fibrils generated in situ in the fibrillation direction without any sacrifice in other directions. Table 1 summarizes the tensile properties of the samples molded at different temperatures. Even when the molding temperature was 175°C (higher than the melting point of PP, 167°C), the resulting samples still show a very high strength and modulus. However, when the processing temperatures is above 185°C, the tensile properties decrease rapidly.

It is easy to understand why the samples molded below the melting point of PP possesses excellent tensile properties, because at such processing temperature only the PE component is melt. As the sample is cooled to a temperature below the crystallization temperature of PE, trans-crystallization of the PE component is induced at the PP fibril surface. The PP-fibrils are connected to the PE matrix through the hatched trans-lamellae, as shown in Fig. 1. However, it is surprising to find that the sample molded at 175°C that is higher than the melting point of PP still exhibit superior properties. This is probably caused by the molecular shape-memory effect. The PP fibrils disintegrate above the melting point of PP, but completed randomization of the extending chains doses not occur within the processing time. Some traces of extending chains will survive and may induce the crystallization of PP component and the formation of orientation fibers during cooling. Consequently, the resultant samples still possess some of the enhanced properties of the nanofibril-reinforced composites prepared at temperature below the melting point of PP.

The main problem associated with this system is that the mechanical properties of the samples are sensitive to processing temperature. However, a pair of semicrystalline polymers with more widely spread melting points can provide a much wider processing window. This work thus has demonstrated a method of converting a blend of semicrystalline polymers into higher performance nanocomposites.

Acknowledgements

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