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Rubber toughening of nylon 6 nanocomposites

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Abstract

The rubber toughening of nylon 6 nanocomposites prepared from an organoclay was examined as a means of balancing stiffness/strength versus toughness/ductility. Nine different formulations varying in montmorillonite, or MMT, and maleated ethylene/propylene rubber or EPR-*g*-MA rubber content were made by mixing of nylon 6 and organoclay in a twin screw extruder and then blending the nanocomposites with the rubber in a single screw extruder. In this sequence, the MMT platelets were efficiently dispersed in the nylon 6 matrix. The MMT platelets did not penetrate into the rubber phase. The addition of clay affected the dispersion of the rubber phase resulting in larger and more elongated rubber particles. The tensile properties and impact strength of these toughened nanocomposites are discussed in terms of the MMT and rubber contents and morphology. There is a clear trade-off between stiffness/strength versus toughness/ductility.

Keywords: Polyamide; Nanocomposite; Toughening

1. Introduction

Toughening of polyamides typically involves melt blending with a maleated elastomer wherein the grafted maleic anhydride readily reacts with the amine end groups of the polyamide to form a graft copolymer that strengthens the interface between the two phases and controls the morphology [1–7]. The size of the rubber particles in the blend is reduced because of the reduction in the particle–particle coalescence rate during melt mixing [8,9]. Rubber particle size is a key issue in achieving super-toughness of polyamides; generally, there are both lower and upper limits on particle size for optimum toughening depending on the polyamide type and molecular weight in addition to the rubber type [3,10–12]. It was shown that the rubber particle size should be generally controlled between 1 and 0.1 μm to give super-tough polyamide materials; these upper and lower critical particle sizes are known to depend on the molecular weight for nylon 6. The low temperature toughness of polyamide blends with styrene/hydrogenated butadiene triblock copolymers, SEBS, and ethylene/propylene random copolymers, EPR type elastomers depends on the molecular weight of nylon 6 and the type of elastomer [13]. The ductile to brittle transition temperature of such blends decreases as the molecular weight of the nylon 6 matrix increases and it can reach values as low as −50 °C for blends with maleated EPR elastomers or a block copolymer of low styrene content. Details of the fracture toughness of nylon 6 blends with maleated EPR rubber can be found in the literature [14].

Engineering polymers are often reinforced with glass fibers to obtain increased mechanical stiffness and strength; however, reinforcement with glass fibers, leads to reduced ductility and impact resistance. In some cases, it is useful to combine reinforcement with rubber toughening to balance end use performance. For glass–fiber reinforced, rubber-toughened nylon 6, the effects of glass fiber surface chemistry, glass fiber and rubber content, rubber particle size and rubber type on the impact and mechanical properties have been studied in detail [15–18]. Recently, there has been considerable interest in reinforcing polymeric materials using nanometer-sized particles with a high aspect ratio, i.e. nanocomposites. Fujiwara and Sakamoto [19] of the Unitika Co. described the first organoclay hybrid polyamide nanocomposite in 1976. One decade later, a research team from Toyota disclosed improved methods for producing nylon 6–organoclay nanocomposites using in situ polymerization similar to the Unitika process [20–23]. Vaia et al. proposed producing polymer nanocomposites by melt blending [24–27] which has great appeal since a conventional melt compounding process for forming nanocomposites would greatly expand the commercial

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opportunities for nanocomposites. Recently, there have been many studies reported on formation of nanocomposites by melt compounding [28–37]. The degree of exfoliation of the organoclay in a given polymer is strongly affected by the conditions of mixing, i.e. the viscosity of the matrix fluid, shear rate, residence time [32–34], and the structure of the organoclay [35].

The modulus of nanocomposites can be significantly increased compared to the neat nylon 6 [32,35] at low filler loadings, but the Izod impact strength is decreased and the ductile–brittle transition temperature is sharply increased as the content of nanosized particles is increased [32]. The use of nanocomposites can be limited by these losses in toughness; therefore, rubber toughening of nanocomposites becomes an interesting avenue to consider. The rubber toughening process used for neat nylon 6 and glass fiber/nylon 6 composites can also be applied for nanocomposites and is beginning to attract some interest [38–43]. This paper reports on a preliminary exploration of the rubber toughening of nylon 6 nanocomposites to better understand the balance of stiffness and toughness that can be achieved especially at low temperatures which is best expressed in terms of a ductile-to-brittle transition temperature.

2. Experimental

2.1. Materials

The nylon 6 used in this study was Capron B135WP from Honeywell (formerly AlliedSignal) with a number average molecular weight of 29,300 and a melt flow index of 1.2. The organoclay was Cloisite 30B supplied by Southern Clay Products. The montmorillonite (MMT) used to form this organoclay is refined from a Wyoming bentonite with a cation exchange capacity of 92 mequiv./100 g. Cloisite 30B is treated with 90 mequiv./100 g clay of Ethoquad T12, methyl bis-2-hydroxyethyl tallow quaternary ammonium chloride. The rubber used for toughening the nylon 6 nanocomposites was an ethylene–propylene random copolymer grafted with maleic anhydride (EPR-*g*-MA) obtained from ExxonMobil Chemical Company which contains 43 wt% ethylene, 57 wt% propylene, and 1.14 wt% grafted maleic anhydride.

2.2. Processing

The formation of the rubber toughened nylon 6 nanocomposites involved the following sequence of operations: first, melt compounding of the organoclay and nylon 6 to make a nanocomposite, and second, melt compounding of the nanocomposite with EPR-*g*-MA for toughening of the nanocomposite. The nanocomposites were prepared using a Haake co-rotating intermeshing twin screw extruder with 30 mm diameter screws having a centerline spacing of 26 mm and a screw length of 305 mm. The screw configuration contains two kneading disc blocks located at 37 and 127 mm, respectively, from the hopper. Both kneading disc blocks consist of one right-handed medium-pitched ($L/D=1$) and one left-handed medium-pitched ($L/D=1$) kneading disc elements and one mixing ring. The processing temperature was set at 240 °C and the screw revolution speed was fixed at 280 rpm. The organoclay powder and nylon 6 pellets were premixed in a tumbler and fed to the twin screw extruder using a microfeeder at the rate of 980 g/h. Prior to the melt processing, the pellets of neat nylon 6 were dried in a vacuum oven at 80 °C for a minimum of 16 h to satisfy the moisture content requirement of less than 0.2% for melt processing of nylon 6.

Blending of the nanocomposite with EPR-*g*-MA was carried out in a Killion single screw extruder having 25.4 mm diameter screw with an intensive mixing heads and a 762 mm screw length. The processing temperature was set at 240 °C and the screw speed was fixed at 40 rpm. Prior to the compounding, the pellets of nanocomposites were vacuum dried under the same condition as that for the neat nylon 6 and the EPR-*g*-MA pellets were dried in a hot air oven at 60 °C for several hours. Then, the two materials were mixed in a tumbler and supplied to the hopper of the extruder to obtain the rubber-toughened nanocomposites.

The extruded pellets of rubber-toughened nylon 6 nanocomposites were vacuum dried again in the similar manner before injection molding of the tensile and Izod impact specimens. The standard 0.318 cm (0.125 in.) thick tensile (ASTM D638 type I) and Izod (ASTM D256) bars were prepared using an Arburg Allrounder 305-210-700 injection molding machine. The barrel temperature was set to increase stepwise from 240 (hopper) to 270 °C (nozzle) with the mold temperature at 80 °C. An injection pressure of 70 bar and a holding pressure of 35 bar were used. A holding time of 9.0 s was needed to keep the materials in the cavity pressurized until cooling sealed the gate.

There are numerous other protocols that could be used to combine nylon 6, the organoclay and the maleated elastomer. The method used here was selected because it offers the best strategy for selectively placing the organoclay in the nylon 6 phase and not in the elastomer phase. Placement of the organoclay in the elastomer particles would not contribute as much to the overall modulus as having this reinforcement effect in the matrix phase and would diminish the toughening effect of the elastomer, particularly at low temperatures, by increasing its modulus. Thus, the best balance of stiffness and toughness dictates having the reinforcement in the matrix and not the dispersed phase. In commercial practice, one might use a twin screw extruder with multiple feed ports such that this same sequence of component addition could be achieved in a single step continuous process. In the absence of such an extruder, a two step process is the best route to the desired morphology.

2.3. Mechanical testing

Tensile tests were performed according to ASTM D638 using an Instron 1137, with an extensometer, upgraded with a computerized data acquisition system. Modulus and yield strength were measured at a crosshead speed of 0.51 cm/min. Elongation at break was measured at a crosshead speed of