

Multilayer co-extrusion processing of PS/TPV/CNTs nanocomposites

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ABSTRACT

The development of layer multiplying technique using coextrusion is able to create polymer films having several thousand layers with individual layer thickness ranging from a few microns to several nanometers. The number of individual layers in the films is controlled by the number of layer multiplying elements (LMEs) added to the system. The main focus of our research is to investigate the effects of polymer based nanocomposites combinations, layer quantity, processing files and flow path design on the morphology, bulk properties and layer stability of the coextruded films. In this research work, CNTs filled PS and TPV blends with different number of layers were compounded using Coextrusion technique. The effect of number of layers on the localization of CNTs in the polymer blends was evaluated. Further nanocomposites were also characterized for their mechanical properties.

Keywords: multilayer co-extrusion, nanofillers, carbon nanotubes

1 INTRODUCTION

Polymer nanocomposites comprising of a filler and polymer matrix are prepared using a variety of fillers such as nanoclay, carbon nanotubes, nanoparticle silver, nanoalumina, nanogold, nanozinc etc[1-4]. These materials exhibit unique property enhancement such as improved barrier properties, flame retardance, electrical conductivity and mechanical properties, depending on filler choice. The primary reason for the improvement in properties is due to the high surface area of nanofillers and their uniform distribution and dispersion in the polymer matrix.

The polymer nanocomposites can be prepared by in-situ polymerization [5-7], solution blending [8-12] and melt intercalation. Among these melt intercalation is considered to be more industrially relevant process as there is no need of any solvent. It also provides more shear to polymer while mixing which enables better distribution and dispersion of nanofillers inside the matrix. A wide range of materials have been reported as matrix materials in polymer nanocomposites; polyethylene oxide (PEO) [13-16], poly(dimethyl

siloxane) (PDMS) [17], polyimide [18-20], poly(methyl methacrylate) (PMMA) [21, 22], polystyrene (PS) [23-25], polypropylene (PP) [26, 27], and polyethylene (PE) [28-30].

Nanocomposites based on polymer and carbon nanotubes (CNTs) have been studied for decades and various products have been commercialized. Due to high aspect ratio and carbon structure of CNTs, polymer/CNTs nanocomposites exhibit excellent mechanical [31] electrical [32], and thermal [33] properties, even at low concentrations. These properties are affected by the CNT inherent quality, but also largely depend on the dispersion and orientation in the polymer matrix¹.

Besides achieving uniform dispersion of CNT in polymer matrix, CNTs can also be selectively localized in specific phase or even interphase of immiscible polymer blends [34, 35] by controlling the morphology. Moreover, multiphase polymer blends are able to combine the attractive features of each component while at the same time reducing their deficient characteristics [36]

There are different approaches to have localized CNTs in the polymer matrix using melt mixing method such as applying shear forces, annealing, blends, foaming and addition of different fillers. A few include introduction of foamed structures in the polymer matrix, which could tailor CNTs morphology [35]. It is also reported to use polymer blend system so as to create phase separation in the compounded product. There are a few reports on effect of blend system on conductivity morphology of nanocomposites [35]; however, very few reports are available on the effect of number of layers onto mechanical properties of the system.

In the present work, mechanical properties of CNT filled binary blends was studied and compared with unfilled neat blends. Polystyrene (PS) was used as hard phase material, and thermoplastic vulcanizates (TPV) was used as soft phase material. A special melt processing method, the multilayer coextrusion process, was used to fabricate multilayered samples. Multilayer coextrusion technology utilizes a process flow through sequential layer multiplying elements to fabricate thin films with hundreds to thousands of alternating layers [37]. Here only 3, 33 and 513-layer sample were selected

in order to prepare individual “macro-layer” (>100 μm, 3 layer structure), micro-layer (1 to 10 μm, 33 layer structure) and “nano-layer” (<1 μm, 513 layer structure). The effect of layer multiplying elements (LMEs) on the mechanical properties of nanocomposite was also studied.

2 MATERIALS AND APPROACH

In this work, polystyrene (PS) was used as rigid phase polymer. The density and melt flow index of the neat PS (Ineos Nova 1301 High Heat) was 1.04g/cm³ and 3.5g/10min (condition G ASTM D1238). TPV (Viprene™ G45A-32U-NAT), purchased from Alliance Polymers, was designed as ductile phase. The density of elastomer was 0.97g/cm³.

CNT were introduced into hard phase by using 20wt% PS/CNTs masterbatch (MB2020-00, Hyperion Catalysis). The CNTs in the masterbatch were vapor grown multiwalled carbon nanotubes, with diameter, length and density of 10-15 nm, 1-10 μm and 1.75g/cm³ respectively.

2.1 CNTs Filled Polystyrene Nanocomposites

CNT filled PS used as hard phase was fabricated by first diluting 20wt% PS/CNTs masterbatch to 3wt% PS/CNTs using twin screw extruder (Leistritz, ZSE18HP-400). Masterbatch and neat PS pellets were fed into the extruder by using volumetric feeder as designed ratio; then extrudates were cooled and granulated into pellets for coextrusion.

Table 1. Formulation of the multilayer thin sheets

Sample Name	No. of layers	Recipes in PHR		
		TPV	PS	CNTs
PS/TPV	3	100	25	0
	33	100	25	0
	513	100	25	0
PS + CNTs/TPV	3	100	24.25	0.75
	33	100	24.25	0.75
	513	100	24.25	0.75

PHR – parts per 100 of the elastomer

2.2 Multilayer Composite Preparation

Figure 1 a shows schematic presentation of multilayer extruder. The coextrusion line had two 25-mm Wayne single screw extruders (L/D=30:1), two Zenith PEP gear pumps, a customized feedblock and LMEs. The customized feedblock was designed to form a three-layer “sandwich” profile, which was continuously split, then stacked and merged by passing through the LMEs forming horizontal multilayer structures. The number of individual layers in the

extrudate, N, increases at an exponential function with the number of LMEs, x, in the multilayered structure.

In our case, PS/CNTs pellets were fed into one extruder which formed the core layer (blue in Figure 1 a), and TPV was pumped through the other extruder and slipped in the feedblock to form the skin layer. This three layer stream went through the LMEs and die to shape into thin sheet, which were cooled and pulled by a chilling roll. All the formulations and control samples were extruded as tape of about 40 cm wide and 0.5mm thick. The ratio of PS:TPV was also carefully controlled at 1:4.



Figure 1. Schematic presentation of multilayer coextrusion: (a) Horizontal layer multiplication; (b) The side view of coextrusion line; (c) Layer quantities relationship with numbers of LMEs used in process.

The temperature file of extruder from rare to LMEs was 150, 180, 190, 205°C and 205°C for die zone. In order to achieve better surface finish and efficient cooling, samples were pulled at the speed of 5ft/min.

3 CHARACTERIZATION

The tensile properties, such as tensile strength and elongation at break, were measured using a universal testing machine (Instron, model: 4400R) at a strain rate of 500 mm/min according to ASTM D882-12. The tensile specimens used for testing were die cut into a 150cm long and 12.5cm wide ribbon which were along the machine direction. Specimens were clamped using 50cm gauge length, and the average of at least five tests was reported.

The dynamic mechanical properties of the multilayer sheets were analyzed using the Dynamic Mechanical Analyzer (DMA) Q800 (TA Instruments). Samples used for the testing were rectangular shaped strips cut from as coextruded sheets. The dynamic mechanical behavior was studied using the temperature range of -90 to 140 °C in tension mode. Using the TA instruments universal analysis software, storage modulus (E'), loss modulus (E''), and tan delta (tan δ) values were analyzed as a function of temperature.

In order to analyze the morphology of the specimens were fractured in the liquid nitrogen, keeping the fracture surface perpendicular to the machine direction of extrusion. The samples were sputter coated with gold and examined using a field-emission scanning electron microscopy (SEM, JEOL, model: 7401F).

4 RESULTS AND DISCUSSION

In the Figure 2, tensile strength and toughness were plotted to nominal single layer thickness. The addition of PS layer into TPV did not show any reinforcing effect for 3-layered structure which had 100 μm -thick PS layer. While for unfilled system, with decreasing layer thickness, the tensile strength increased. This might be due to the fact that PS suppressed crazing and cracking by the TPV layer [38]. The CNTs filled PS and TPV structure showed maximum tensile strength at 8 μm thickness of PS and decreased further. The decline of the tensile strength is due to the morphology change from layered structure to PS dispersed structure (Figure 3).

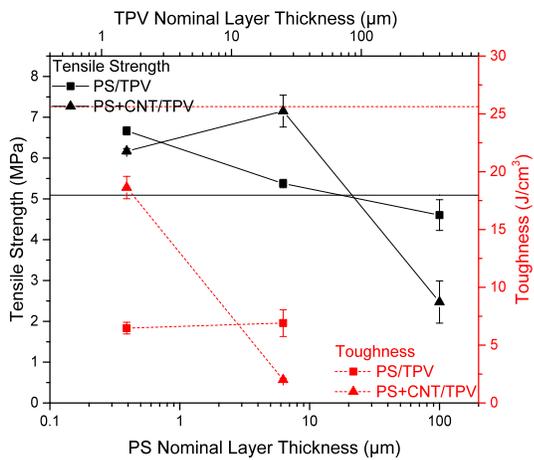


Figure 2. Tensile properties (Tensile strength and Toughness) in flow direction of multilayered sheet with different layer quantity vs. nominal layer thickness (tensile strength and toughness are black solid lines and red dash lines respectively)

PS was not continuous phase, and load was not effectively transferred to CNTs. Adding CNTs to PS phase would increase the melt viscosity of PS layer. The big viscosity contrast of PS and TPV layer may result instability causing PS layer to break up [39]. On the other hand, cross-linked rubber particles in the TPV, which usually were 1-2 μm [40], may also have facilitated breaking of the PS layer. It was observed during the experiment, for 3-layered sheets for both formulations that the samples broke at very low strain. It was particularly PS layer which broke while TPV layer looked delaminated and stretched to break at higher strain. However, 33 and 513-layer sheets exhibited macroscopic yielding, and more homogeneous behavior. Strain density was utilized to represent the toughness, which is the area under stress-strain curve. For unfilled system, decreasing the layer thickness did not change the toughness. However, for CNTs filled system, toughness increased significantly from 33-layered structure to 513-

layered structure. With breaking up of PS layers, TPV turned into the matrix phase and gave more ductility to the nanocomposite.

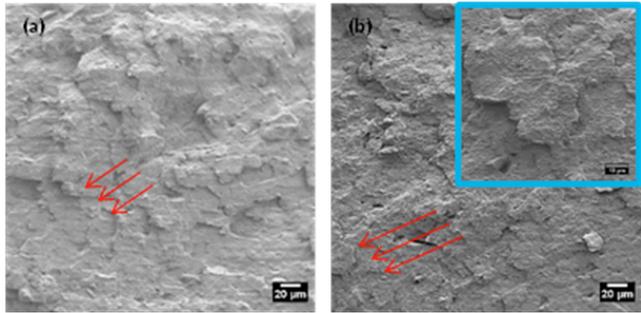
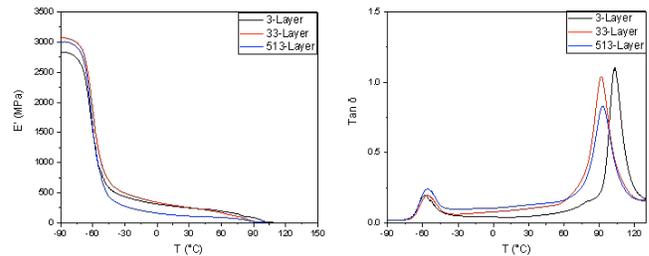


Figure 3 SEM of cross section of PS+CNTs/TPV sheet with 33-layer (a), and 513-layer (b). The arrow pointed the PS layers

The DMA results are shown in Figure 4 only for PS+CNT/TPV system as PS/TPV gave the similar trend. At room temperature, 3 and 33-layered sheet had approximate same storage modulus (Young's modulus), but 513-layer had lower modulus. Burt reported similar modulus decrease after approaching nanoscale thick layers, due to more volume of interphase layers occupying single layer volume, which had lower modulus and more free volume [41, 42]. For the same reason, the peak of PS glass transition shifted to lower temperatures from 3 to 33-layered sheet and then slightly increased due to destruction of continuous layered structure.



Also

Figure 4. DMA test results, (a) storage modulus of PS+CNT/TPV vs Temperature; (b) Tan δ vs. Temperature

5 CONCLUSION

PS/CNTs/TPV multilayered structures were successfully prepared using multilayered coextrusion. Three types of structures were prepared by varying the number of layers. The three layered structures were not stable and broke at very low strain. Whereas 33 and 513 layered structures showed macroscopic yielding and more homogeneous behavior.

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