Effect of Layer Multiplying Extrusion on the Morphology and Properties of PS/CNT Nanocomposites

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ABSTRACT

Multilayer coextrusion has been used to produce extruded films having up to several thousand alternating layers with individual layer thicknesses ranging from several micrometers to only a few nanometers. In this work, the multilayer coextrusion process was used to orient carbon nanotubes in a polymer matrix. After 5 wt. % multiwall carbon nanotubes (MWCNTs) were melt mixed with polystyrene, polymer nanocomposites with three to over 4000 layers were extruded using a multilayer coextrusion process. The effects of the number of film layers on morphology evolution – i.e., MWCNT orientation and dispersion – were studied using transmission electron microscopy. Changes in the mechanical and electrical properties with increasing film layers were correlated with the morphological changes

Keywords: carbon nanotubes, extrusion

1 INTRODUCTION

Nanocomposites based on thermoplastics and carbon nanotube (CNT) have been studied for decades and some products had been commercialized. Due to the high aspect ratio and carbon structure of CNTs, thermoplastic/CNT nanocomposties exhibit excellent mechanical[1], electrical[2], and thermal[3] properties, even at low CNT concentrations.

These properties are affected by the CNT inherent quality, but also depend on the dispersion and orientation of CNTs in the polymer matrix[4, 5, 6]. Good dispersion is required for effective reinforcement and 3D conductive network formations. Orientation of fillers gives composites anisotropic properties and further enhances the reinforcement, electrical, and thermal conductivity in the alignment direction. To achieve good dispersion, three methods have been applied. Solvent solution processing[7] is when solvent is used to decrease system viscosity during mixing and then evaporated to get the composite. With in-situ polymerization[4] the monomer is first mixed with the filler and then polymerized. In melt mixing[8] fillers are mixed with a high temperature polymer melt, then solidified into the desired shape. Compared with the previous two methods, melt mixing is a preferred method for mass production with less environmental issues.

For CNT alignment control several methods have been used, such as aplication of a magnetic field[9], electrical fields[10] or flow[8]. The use of flow fields has the advantages of being more efficient and environmentally friendly, but it is difficult to achieve a high degree of CNT alignment using flow fields in conventional plastics processing.

In this work, a special melt processing method, the multilayer coextrusion process, was used to disperse and orient CNTs in a polystyrene (PS) matrix. Multilayer coextrusion technology utilizes a process flow through sequential layer multiplying elements to fabricate thin films with hundreds to thousands of alternating layers[11]. Previous work[12, 13] showed that with multilayer coextrusion, flow induced filler and polymer chain alignment was in the machine direction and confined in the layer structures. In this work we study the effect of layer multiplying elements on the orientation and morphology of a CNT/amorphous polymer system. The effects of layer multiplying elements (LMEs) on the nanocomposite's mechanical and electrical property changes were studied.

2 EXPERIMENTAL

2.1 Materials

In this work, polystyrene (PS) was used as the polymer matrix. The density and melt flow index of the neat PS (Ineos Nova 3601) was 1.04g/cm^3 and 12.5g/10min (condition G ASTM D1238). CNT were introduced by using 20wt% PS/CNT masterbatches (MB2020-00, Hyperion Catalysis). The CNT in the masterbatch was a vapor grown multiwall carbon nanotube, with diameter, length and density of 10-15 nm, 1-10 μm and 1.75g/cm^3 respectively.

2.2 Sample Preparation

Multilayer PS/CNT composites were fabricated by first diluting 20wt% PS/CNT masterbatch to 5wt% PS/CNT pellets using the twin screw extruder (Leistritz, ZSE18HP-400), then feeding the pellets into a coextrusion line with LMEs for layer multiplication.

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. 5wt% granules were fed into both extruders of coextrusion line, then two melt streams were pumped into the feedblock using gear pumps for tightly controlling the output. The customized

feedblock was designed to form a three-layer "sandwich" profile as shown in Figure 1. The melt streams were split, then stacked and merged.

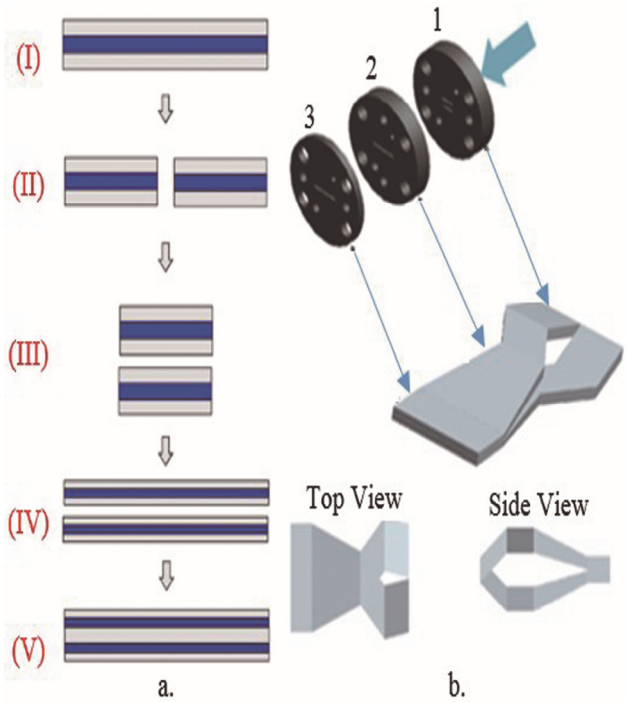

Figure 1. Schematic of multilayer coextrusion: a) Horizontal layer multiplication and b) The flow path of horizontal layering through LMEs.

By passing through more LMEs, the melt can have up to more than 16,000 individual layers. The number of individual layers in the extrudate, N, is directly proportional to the number of LMEs, n, added to the system:

$$N = 2^{n+1} + 1 \quad (1)$$

In this work, 0 to 13 LMEs were used to fabricate the PS/CNT sheet with nominal individual layers ranging from 3 to 16,385.

2.3 Morphology Characterization

Transmission electron microscopy (TEM) was used to characterize the dispersion, distribution and orientation of CNTs in the extrudate with different numbers of layers. Randomly selected extruded samples were cut into ultrathin sections; the cutting direction was parallel to YZ plan or XZ plan (X: machine direction, Y: transverse direction, Z: gravity direction). A Philips EM400T TEM was used to examine the morphology using an accelerating voltage of 100 kV. Five TEM images per trial were used for analysis.

2.4 Electrical Properties Measurement

Volume resistivity, ρ, of both the machine direction and transverse direction were tested using a programmable power source (2635 Source Meter, Keithley Instruments). 1-mm thick extrudate with different layer quantities were cut into specimens with length of 20 mm and width of 7 mm. For the machine direction specimens, the length direction was parallel to the X direction and for the transverse direction specimens the cutting was perpendicular to machine direction specimens. The current-voltage curves were obtained by using the voltage sweep mode to calculate electrical resistance, R. The volume resistivity, ρ, depended on R, sample length, l, sample width, w, and sample thickness, h:

$$\rho = R\frac{w \cdot h}{l} \quad (2)$$

The measurement direction was parallel to the length direction for all specimens. To eliminate contact resistance, the contact surface was coated with a silver paste. At least five specimens were tested for each sample.

2.5 Mechanical Properties Measurement

The mechanical properties were measured with a dynamic mechanical analyzer (DMA, TA Instrument's Q800-0603). Elastic and viscous moduli measurement were carried out using the tension mold clamp, and temperature ramp/ frequency sweep (-40ºC to 120ºC).

3 RESULTS AND DISCUSSION

3.1 Morphology

Morphology studies were carried out by analyzing TEM images in both the XZ and YZ planes. Images in the YZ plane, Figure 2, provided more CNT dispersion and distribution information, while images such as Figure 3 (XZ plane) provided more information about alignment.

Figure 2 shows that increasing the layer multiplying elements decreased the probability of observing large CNT agglomerates. To further analyze the mixing quality, Image J software was used to measure the large agglomerate area. Miquelard[14] used circle equivalent diameters >5 µm (aggregate area >19.6 µm^2) to examine the dispersion of the CNT in a PP matrix, according to the ISO-1855 standard (originally used for carbon black dispersion charactrization). For these composites, the TEM images did not show any structures larger than 3 µm, which indicated that the CNTs were dispersed well in the PS matrix.

Although agglomerates of CNT were still observed in all TEM images with different processing conditions, the particle size and distribution were more consistent with increased number of LMEs. This behavior was attributed to

blending effects[15] in the LMEs, which may act as a static mixer.

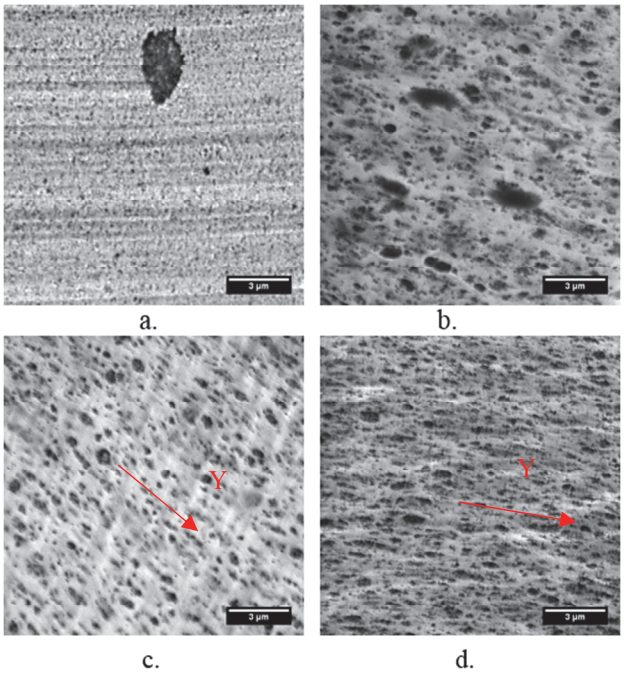

Figure 2. TEM pictures of 5 wt% PS/CNT nanocomposites (740× magnification) on the YZ plane: morphology of the a) pellets from the twin screw extruder; b) extrudate from the feed block (number of LMEs = 0); c) extrudate with three LMEs; and d) extrudate with 13 LMEs.

Shear flow in the extruder and die gives melt polymer chains alignment in the machine direction. The multilayer coextrusion process provides multistage melt stretching in the LMEs and a longer flow path, which may promote anisotropic filler orientation. The TEM images clearly show that the CNT bundles were stretched in both the X and Y directions. The design of the layer multiplying elements produces stretching in both the X and Y directions. Comparing three images in Figure 3, more oriented CNT or CNT bundles were observed when the quantity of LMEs was increased from 0 to 3, then remained nearly constant with further increases in LMEs. It is also noted that the CNT length is reduced with increased number of layer multiplying elements. This can be explained by the longer residence time and more shearing with increased number of LMEs that broke the long fibrils, which may be detrimental to the properties of the composite.

3.2 Electrical Properties

The volume resistivity ρ of composite was measured using the I-V plot from a voltage sweep in both the machine and transverse directions. Most samples showed ohmic behavior in the I-V plot. Figure 4 shows increasing the number of LMEs up to 2 slightly improved the electrical conductivity of the PS/CNT composites, but led to more consistent results, likely because of improved dispersion. New networks were formed by dispersion and alignment of CNT in both X and Y directions, while the fiber breakage may lead to reduced conductivity.

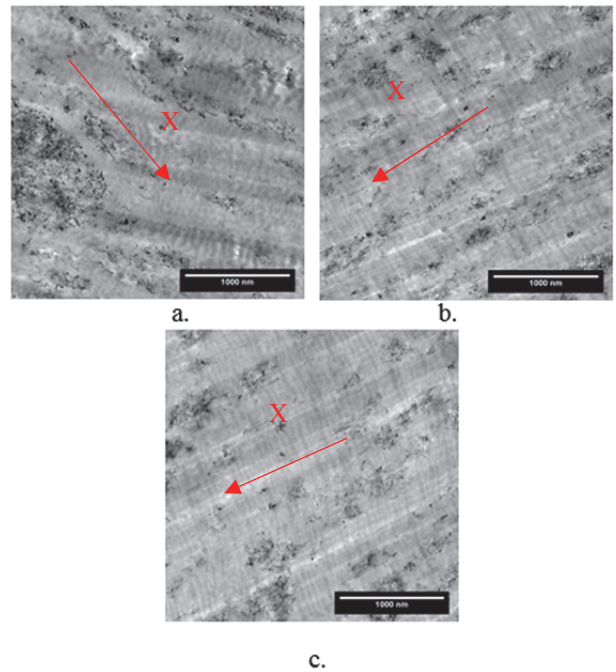

Figure 3. TEM pictures of 5wt% PS/CNT nanocomposites (7400× magnification) on the XZ plane: morphology of the a) extrudate from the feedblock (number of LMEs = 0); b) extrudate with three LMEs; and c) extrudate with 13 LMEs.

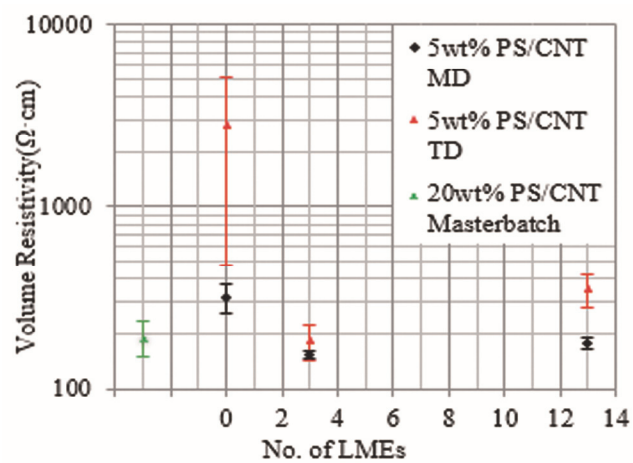

Figure 4. Volume resistivity as a function of the number of LMEs in both the machine direction (MD) and transverse direction (TD).

3.3 Mechanical Properties

Figure 5 shows that with increasing number of LMEs, the elastic modulus in the transverse direction increased significantly, but only slightly in the machine direction.

This may be the result of better dispersion and planar orientation of CNTs with increased number of LMEs.

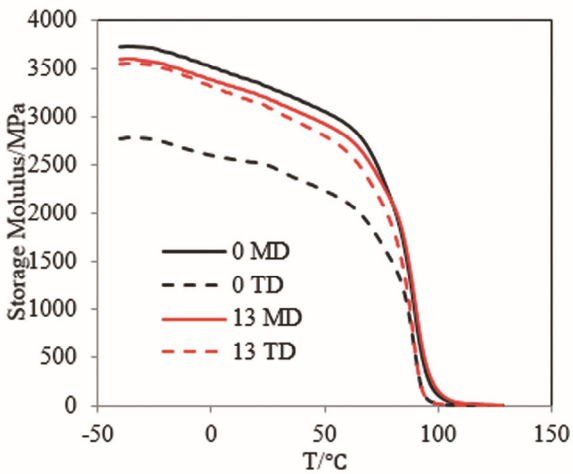

Figure 5. Dynamical mechanical properties of PS/CNT nanocomposites prepared by using 0 and 13 LMEs. The shera modulus was measured in the machine direction (MD) and transverse direction (TD).

4 CONCLUSIONS

The effect of LMEs in the multilayer coextrusion process was studied. Increasing the number of LMEs improved dispersion, but did not completely eliminate agglomerates. It also reduced fiber length. The mechanical properties in the transverse direction were significantly improved with increasing number of LMEs, but there was little change in the machine direction properties. The electrical properties improved up to three LMEs, but showed little change with more LMEs.

5 ACKNOWLEDGEMENT

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