Investigation of Thermal and Mechanical Response of Nylon-6 Filaments with the Infusion of Acicular and Spherical Nanoparticles

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ABSTRACT

It has been demonstrated in recent years that infusion of nanoparticles in thermoset as well as in thermoplastic polymers can help improve the chemical, thermal, and mechanical properties significantly. The improvement in properties can be achieved at very low nanoparticles loading (most of the cases ≤ 3% by weight). The shape of nanoparticles can be spherical, layered, irregular and acicular or rod-shaped. It is believed that the properties of the polymer can be maximized by aligning the rod-shaped particles along a preferred direction. The improvement in properties due to alignment of nanoparticles is influenced by two factors; (a) physio-chemical effect on the polymer structure, and (b) load transfer mechanism. In the present study infusion of vapor grown carbon nanofibers (CNFs), and multi-walled carbon nanotubes (MWCNTs) into a thermoplastic polymer, nylon-6 was first investigated. Carbon nanofibers were ≤200nm in diameter and 50-100μm in length. On the other hand MWCNTs were around 10-15 nm in diameter and about 5μm long. These nanoparticles with 1% wt loading were dry-mixed individually with nylon-6 by mechanical means, melted in a single screw extrusion machine, and then extruded through an orifice. Extruded filaments were later stretched and stabilized by sequentially passing them through a set of tension adjusters and a secondary heater. Stabilized filaments of about 80-150 micron dia were finally wound into spools in a filament winder. Two sets of filaments; one with CNFs and the other with MWCNTs were extruded. Individual filaments were then tested under tension. The enhancement in strength and stiffness were phenomenal. In both cases the enhancement in properties was in the 70-100% range. This remarkable increase in strength and stiffness was clearly due to the alignment of acicular reinforcements for MWCNT infused filaments. Although CNFs were relatively weaker than MWCNTs, the improvement with CNF was even more pronounced than MWCNTs. It is believed that since CNFs were larger in diameters, their alignment was much easier during the extrusion process. It is also observed that the improvement in stiffness is at the cost of sacrificing a significant amount of failure strain which is in no way beneficial for nylon. In an attempt to improve upon the breaking strain, spherical particles such as SiO_2 with identical loading were infused with nylon-6. Filament extrusion process was identical with the previous cases. Tensile test results of SiO_2 infused filaments has indicated that with spherical particle infusion a moderate but still significant improvement in strength and stiffness can be achieved without practically any loss of failure strain. Both TGA and DSC results also indicated that with identical loading the acicular nanopartilce infused systems are more thermally stable. Details of fabrication procedures, mechanical and thermal characterizations, and analyses of tension test results with respect to various reinforcements are included in the paper.

Keywords: nylon-6, carbon nanotubes, carbon nanofibers, silicon dioxide

1 INTRODUCTION

Nylon's toughness, low coefficient of friction and good abrasion resistance make it an ideal replacement for a wide variety of materials from metal to rubber. The amide groups of nylon are very polar, and can hydrogen bond with each other. Because of this, and because the nylon backbone is so regular and symmetrical, nylons are often crystalline, and make very good fiber [1, 2].

Extensive work concerning processing, modeling, morphology and thermal and mechanical properties of acicular shaped nano particles, specially multi-walled carbon nanotubes (MWCNTs) [3,4] and carbon nanofibers (CNFs) [5] reinforced filaments and nanocomposites, has been reported by various researchers.

Among several fiber aligning techniques, 'Extrusion' has been found as one of the most widely used fiber-aligning methods[3,4]. However, the end products totally depend on the starting materials and their chemical compositions, their mixing techniques, and type of extruder. In most of these cases, alignment of nanoparticles, specially the ones having high aspect ratios has been considered as a serious problem and decreasing in ductility is also an inevitable issue.

On the other hand, spherical-shaped silicon dioxide nanoparticles possess high thermal stability, have no alignment problems and are an excellent reinforcing agent for polymers [6]. So to get rid of alignment and ductility problem, silicon dioxide might be a better route to reinforce the polymer.

2 EXPERIMENTAL

2.1 Melt Processing

Nylon-6 nanocomposite filaments were synthesized using the following procedure: nanoparticles and nylon-6 were mechanically mixed (1:99 by wt) at 22000 rpm by using a blender with cooling system, then placed into a cylindrical drying chamber for 12 hours to driven out the moisture and finally extruded by a single-screw extruder at a rotational speed of 12 rpm. The temperature profiles of the barrel were 222-232-242 °C from the hopper to the die, respectively. Then the filaments were stabilized by using a set-up of two godet machines and a heater. Finally, the filaments are wound on a spool using *Wayne Desktop Filament Winder* at a winding speed of 70 rpm. The neat nylon-6 filaments were also extruded with the same extrusion condition.

2.2 Testing Procedures

To estimate the size and shape, the neat and nano infused filaments were examined using *JEOL JSM 5800* Scanning Electron Microscope (SEM). The filaments were placed on a carbon double-sided tape and coated with *JEOL Ion beam sputtering* unit before placing into SEM.

The characterization of nanoparticles dispersion and alignment in a filament has been carried out using Field emission scanning electron microscope (FE-SEM, Hitachi S-900). The FE-SEM samples were precisely cut with a carbon coated blade, and polymer was etched by using argon plasma with about 600 mtorr argon pressure and 2.5 W/cm^2 intensity for 1 hour.

In order to obtain the information on the thermal stability of the filaments samples, thermo gravimetric analysis (TGA) tests were carried out by using Hi-Res TGA 2950 TG analyzer under nitrogen gas atmosphere (70 ml/min). The samples were placed in the platinum sample pan, weighed (5 to 15 mg) and heated to 800^{0}C from room temperature at a heating rate of 10^{0}C/min.

The differential scanning calorimetry (DSC) tests were carried out non-isothermally by using TA Q1000 instrument under nitrogen gas atmosphere (50 ml/min). The samples were cut into small pieces, weighed (5-15 mg) and put into aluminum crucibles. All samples were held at 5 ^{o}C for 2 min, heated at a rate of 10 ^{o}C/min to 250 ^{o}C and subsequently held for 2 min, then cooled at a rate of 10 ^{o}C/min to 5 ^{o}C. The real time characteristic curves (for both TGA and DSC) were generated by *Universal Analysis 2000 -TA Instruments, Inc.* data acquisition system.

Tensile tests for individual filaments were conducted on a *Zwick Roell tensile* tester equipped with a 20 N Load Cell. The tests were run under displacement control at a crosshead speed of 0.01 1/s strain rate and gage length of 102 mm. At least ten specimens were tested in each category. The stress-strain curves were generated by *Zwick testXpert* software data acquisition system.

3 RESULTS AND DISCUSSION

3.1 Thermal Response

Figure 1 represents the TGA thermogram of neat and nanophased filaments. In the present study the 50% of the total weight loss is considered as the structural stability of the system.

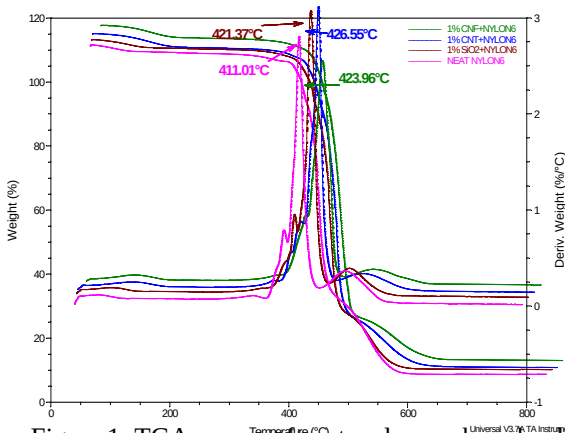

Figure 1: TGA curves of neat and nanophased nylon filaments.

It is clearly shown that the both acicular nanophased samples are more thermally stable (MWCNTs-427 ^{o}C and CNFs-424 ^{o}C) than neat (411 ^{o}C) and spherical SiO_2 (421 ^{o}C). This better thermal improvement indicates better bonding between the matrix and acicular nanoparticles. However, MWCNT nanophased has the highest thermal stability (427 ^{o}C). The reason for this high thermal stability is attributed to slight increase in cross-linking of nylon in the presence of CNT during extrusion process [7].

The DSC measurements (Fig. 2) indicate that the presence of nanoparticles specially both acicular-shaped increases the glass transition temperature (T_g, 62 ^{o}C) of the nylon-6 matrix (neat-49 ^{o}C, SiO_2 nanophased-55 ^{o}C). It is believed that MWCNTs or CNFs restrict the free volume motion of the matrix. The DSC melting peak (T_m) of the composites occurs at a slightly lower temperature (221 ^{o}C) than that of the neat nylon-6 (223 ^{o}C). This may be related to a slight reduction in crystallite size in the presence of nanoparticles [8]. It is also observed that the MWCNT /nylon-6 system has the highest crytallinity (30%) whereas CNF, SiO_2 and neat systems has 27%, 26% and 24% respectively. It might be the cause of high aspect ratio (L/d-500:1), high thermal conductivity and nucleation effect of MWCNTs.

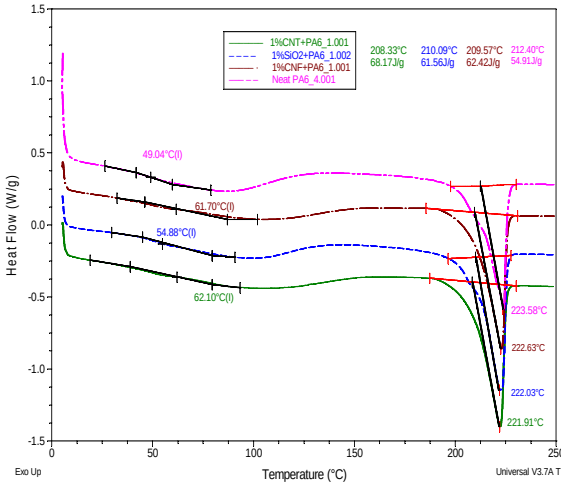

Figure 2: DSC heating curves of neat and nanophased nylon filaments.

All of the nanoparticles cause an increase in the crystallization temperature (Tc) relative to neat nylon-6 (WMCNT & CNF-197 ^{o}C, SiO_2-192 ^{o}C, Neat-190 ^{o}C). To various degrees, nanopartilces may act as nucleating agents causing a higher crystallization than that of the neat nylon-6 and crystallization starts earlier (Fig. 3). However, high

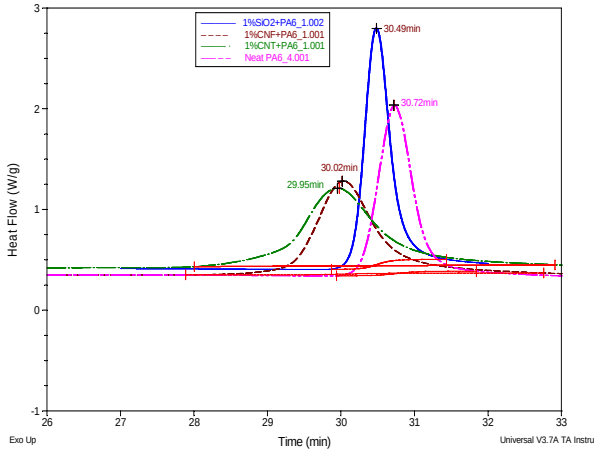

Figure 3: DSC cooling curves of neat and nanophased nylon filaments.

concentrations reduce the rate of crystallization. In some cases, the crystallization of the nanocomposites is slower than the pure extruded polyamide [9]. The combination of a larger number of nucleation sites and limited crystal growth is expected to produce crystals of fine grain size. [10].

3.2 Tensile Response

Stress-strain diagrams for neat and nanophased specimens are shown in Fig. 4. Tensile data in tabular form is shown in Table 1.

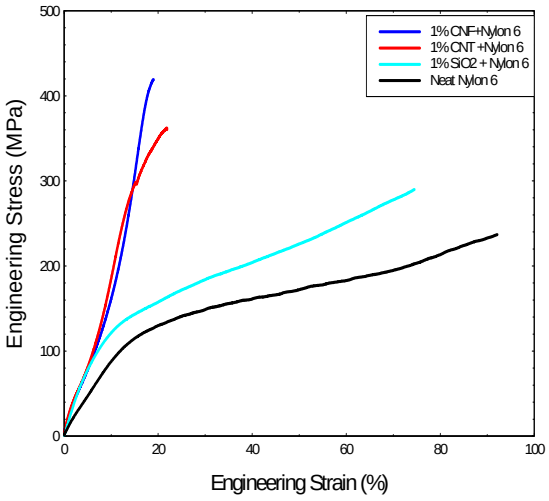

Figure 4: Tensile Stress-Strain curves of various samples.

The enhancement in strength and stiffness is phenomenal for both acicular systems. In both cases the enhancement in properties is in the 70-100% range. This remarkable increase in strength and stiffness is clearly due to the well dispersion and alignment of acicular nanoparticles into filaments (Fig. 5(b)) and higher crystallization with fine grain size. DSC and TGA data, SEM photographs also accord with this phenomenon. The enhancement in strength and stiffness for SiO_2 nanophased system is moderate (36% and 28% respectively). The FE-SEM micrograph (Fig. 5(a)) shows that dry mixing followed by extrusion with high shear force ensures the uniform dispersion of SiO_2 into nylon matrix.

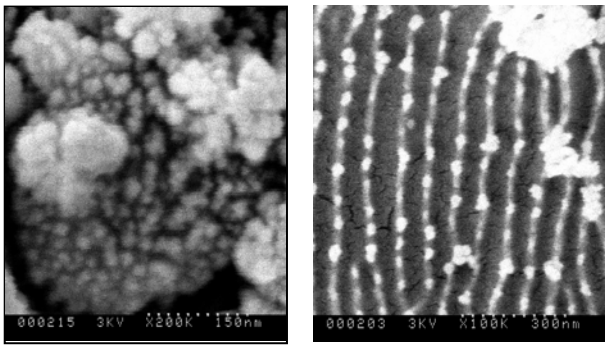

Figure 5: FE-SEM pictures (a) SiO_2/nylon-6 (b) MWCNT/nylon-6

The failure pattern of the MWCNT and CNF reinforced samples represents a different scenario. It is seen that the ultimate failure strain is reduced significantly (23%) whereas for SiO_2 nanophased is about 75%. Masayoshi et al. [11] showed that the deformation of nylon-6 is greatly affected by the crystalline formation. Kanamoto et al. reported [12] that the inter-crystalline network and entanglements of the original samples of polyethylene have a remarkable effect on ductility. Further, they suggested

that the interfacial friction and adhesion between crystalline lamellae is the primary mechanism for the deformation. In nylon-6 crystals, the chain sliding and /or slippage are severely restricted by the hydrogen bonding, which induces a high stress on draw.

The embedded MWCNTs within the matrix would have restricted the deformation of the polymer chains as well as chain extension more than SiO_2. The reason why such gain is attributed can be explained in the following way:

When polymers are filled with small particles, the load transfer is dominated by the shearing mechanism between the filler and the matrix. If a perfect bond is assumed between the two constituents, and if fillers within the composite remain highly oriented and its aspect ratio exceeds the critical length at an order of magnitude, the filler can bear 90 percent of the composite load, resulting in high composite strength. Although this model was developed based on the cases of micron size particles, they are still valid for the explanation of the nanoparticle filled composites [13]. The most recent studies related to carbon nanotube reinforced polymeric composites including molecular dynamics simulation and direct experiments also reveal the similar failure mechanism [14, 15].

Material	E-Modulus (GPa)	Gain/ Loss %	Tensile Strength (MPa)	Gain/ Loss %
Neat Nylon 6	1.10±0.10	-	210±10	-
SiO_2-Nylon 6	1.41±0.15	+28.18	285±8	+35.71
CNT-Nylon 6	2.10±0.10	+90.90	371±20	+76.67
CNF-Nylon 6	1.65±0.20	+50.00	410±15	+95.24

Table 1: Comparison of tensile properties of nanophased filaments.

4. SUMMARY

The following are the summary of the above investigation:

1. A comparison study between acicular-shaped and spherical-shaped nanopartilces infused composites has been introduced.
2. SEM studies show that initial dry mixing followed by extrusion under high shear force ensures uniform dispersion and alignment of nanoparticles in a unidirectional manner along the length of the filaments.
3. Filaments fabricated with acicular nanoparticles in this fashion were found to possess higher tensile strength and stiffness by about 70-100% when compared with neat nylon filaments. While the enhancement in modulus was expected, the gain in strength was somewhat surprising and is believed to have been caused by the alignment of nanotubes, and crystal size formation during the extrusion process.
4. It is believed that since CNFs were larger in diameters, their alignment was much easier during the extrusion process and thus CNF-nylon 6 system possesses higher tensile strength compare to MWCNT/nylon-6.
5. Tensile test results of SiO_2 infused filaments indicate that with spherical particle infusion a moderate but still significant improvement in strength and stiffness can be achieved without practically any loss of failure strain.

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