

Melt Rheology of Nylon Nanocomposites based on Polymer Nanoparticles

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1. Abstract

The incorporation of nanoparticles into polymeric materials can lead to dramatic improvements in polymer properties. These enhancements have been shown to apply to a wide range of thermoplastics and a few thermoset systems. We have incorporated polymer nanoparticles into a commercial injection grade Nylon 6 by melt extrusion and studied the rheological behavior, microstructure and thermal properties of the neat polymer and the nanocomposites. In order to address the influence of nanofiller, two types of polymer nanoparticle were investigated whereas the concentration was maintained constant at 3 wt %. The results showed that although the nanoparticles did not influence the melting temperature, the decomposition temperatures were increased. Moreover, the degree of crystallinity was reduced relative to the neat polymer. The rheological properties showed that the nanoparticles induced greater elastic behavior in an otherwise viscous melt.

2. Introduction

Nanofillers have an important role in modifying the properties of polymers and affording the development of new applications. The effect of the nanofillers on the polymer matrix properties depends on concentration, the shape and particle size, aggregate size, surface characteristics and degree of dispersion [1, 2]. However, the homogeneous dispersion of nanofillers is very difficult because they have a strong tendency to agglomerate. Different types of nanofillers are currently utilized, for instance, nanoclays, carbon nanotubes, and hybrid organic-inorganic nanoparticles, i.e., polyhedral silsesquioxane (POSS) [3-5]. This research focuses on the influence of polymer nanoparticles (PNPs) on the microstructure, thermal and rheological behavior of commercial polyamide nylon 6.

3. Experimental

3.1 Materials

Nylon 6 Capron (BASF) was melt compounded in a single screw extrusion machine. Two types of polymer nanoparticles (PNPs) especially synthesized by the Rohm & Haas Co., and whose chemical compositions are proprietary, were added. The PNPs have typical diameters of 4 nm (as determined by SAXS); PNP2 has attached maleic anhydride groups to its surface. The samples are listed in Table 1.

Table 1 Nylon-PNP nanocomposites

Sample	Nanofiller	c (wt%)	H ₂ O uptake (%/hr)	T _m (°C)	T _{dec} (°C)	χ (%)
Nylon 6	-	0	0.090	220.7	401	36
Nylon-PNP1	Nanopolymer 1	3	0.055	218.5	400	30
Nylon-PNP2	Nanopolymer 2	3	0.013	219.1	417	28

3.2 Thermal Analysis

The thermal transitions were determined by differential scanning calorimetry (DSC) using the Pyris1 (Perkin Elmer, CT, USA). Samples of 10 mg were prepared, and data from the second heating scans are reported. The thermal scans were carried out at a heating rate of 20°C/min under nitrogen atmosphere. The decomposition temperatures, T_{dec} , were determined by thermogravimetric analysis (TGA), at 20 °C/min, using the TGA7 analyzer (Perkin Elmer). The experiments were carried out under air scanning from 30 °C up to 950 °C.

3.3 Rheology

The rheological properties of the composites were studied with a stress-controlled CVO Rheometer manufactured by Malvern Instruments. The rheometer was equipped with 25 mm diameter parallel plates, and a gap of 1 mm was utilized throughout.

3.4 Microstructure

Isothermal recrystallization was carried out using a Leitz microscope and a Mettler FP-90 hot-stage. Images were acquired using a Moticam 100 digital camera manufactured by Motic Inc. H_V small-angle light scattering patterns were obtained using a He-Ne laser. Image analyses were carried out using ImageTool software, v3.0 (UTHSCSA, Texas, USA).

4. Results and discussion

Thermal transitions were determined by DSC, Figure 1a,b shows the heating and cooling scans. The results show that the PNPs do not change the thermal transitions (melting T_m and crystallization T_c) of the matrix. However, the decomposition temperatures T_{dec} were increased. The results are listed in Table 1. Polyamides are susceptible to water uptake as they are hydrophilic. The water uptake was monitored for Nylon and the nanocomposites, Figure 1c shows a plot of weight gain vs. time obtained at room temperature. The results (Table 1) showed that the rate of water uptake is less than 0.1%/hr for all the materials studied.

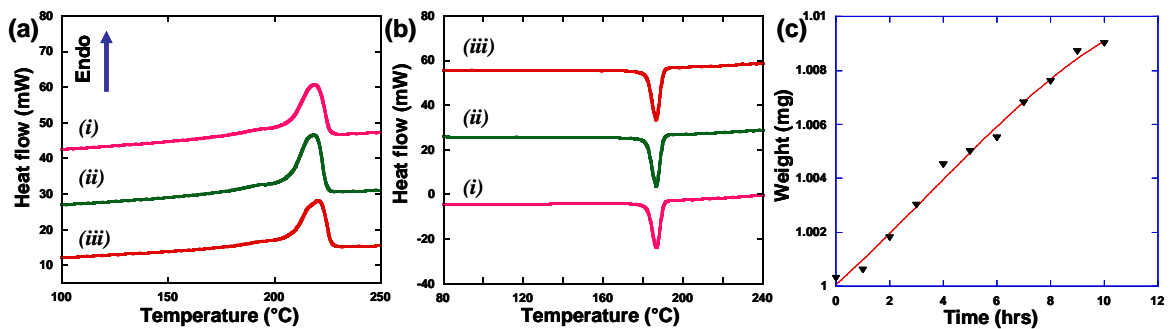


Figure 1. DSC scans of Nylon-PNP nanocomposites (i) nylon, (ii) nylon-PNP1 and (iii) nylon-PNP3. (a) heating and (b) cooling. (c) Water uptake of Nylon as a function of time, at room temperature.

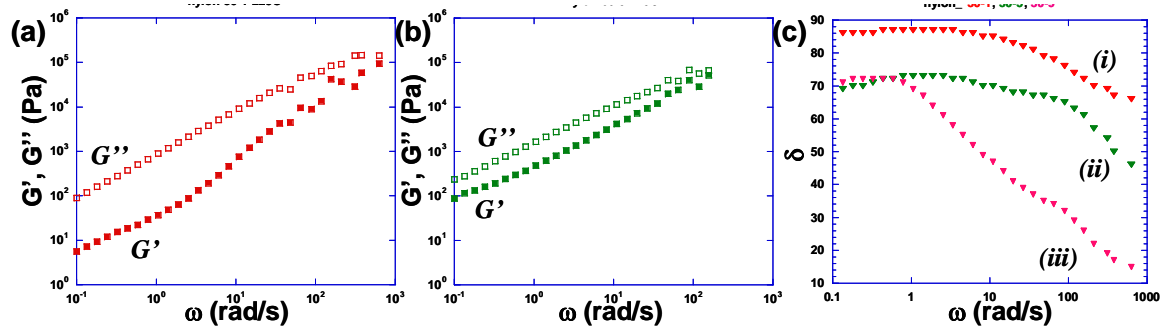


Figure 2. Linear viscoelastic properties of nylon-PNP nanocomposites. (a) nylon (b) nylon-PNP1, (c) Loss angle δ for (i) nylon, (b) nylon-PNP1 and (iii) nylon-PNP2. $T=225^{\circ}\text{C}$.

Figure 2 shows plots of dynamic shear moduli as a function of strain rate obtained at 225°C . Nylon displays a predominantly viscous behavior, where $G'' > G'$, Figure 2a. Addition of PNP1 produced an increased of moduli (data shifted upwards) and G' approached G'' . Thus, the elastic modulus G' was enhanced by the addition of PNP to the matrix [3]. The loss angle $\delta = G''/G'$ measures the viscoelastic behavior of the melt ($\delta=0^{\circ}$ perfectly elastic, $\delta=90^{\circ}$

perfectly viscous). Figure 2c shows δ vs. strain rate ω , the results show that the PNPs indeed enhanced the elastic behavior of the molten nanocomposites, PNP2 being more effective. Figure 3a shows a plot of recrystallization time under isothermal conditions for each material studied. It can be seen that the PNPs increased the crystallization times, and these results correlate with the reduction of degree of crystallinity, as determined by DSC (using $\Delta H_m^o = 190$ J/g, 100% crystallized Nylon 6). The neat nylon and the nanocomposites crystallize into a spherulitic superstructure, figure 3b shows the HV SALS pattern of Nylon-PNP2; the pattern displays central diffuse intensity and an intensity maximum arising from the spherulite's mean size.

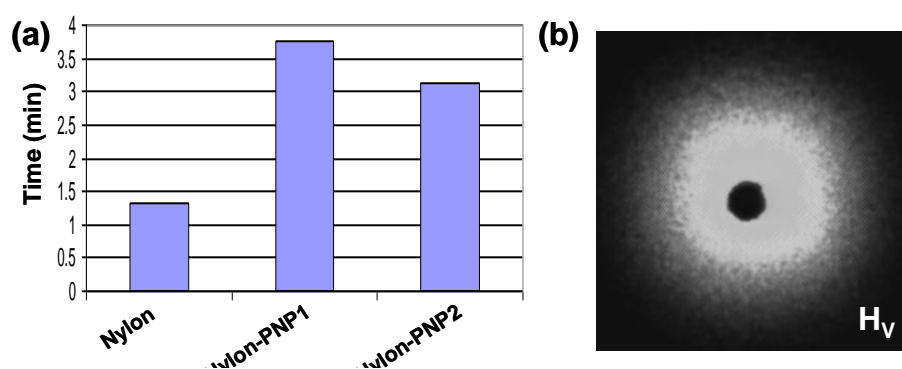


Figure 3. (a) Crystallization time for nylon and the nanocomposites when cooling from the molten state. (b) SALS pattern of recrystallized nylon-PNP2 nanocomposite showing spherulitic morphology.

5. Conclusions

Addition of polymer nanoparticles to nylon 6 did not change the transition temperatures T_m and T_c , however the decomposition temperature T_{dec} was increased. The rate of crystallization was compromised by the presence of PNPs and this reflected in a reduction of the degree of crystallinity χ . Rheology showed an increase in the elastic component of the molten polymers suggesting the formation of a molecular network.

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6. References

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