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EFFECT OF MOLECULAR CHARACTERISTICS AND SILICA NANOPARTICLES ON VISCOELASTIC PROPERTIES OF FILLED POLYETHYLENE MELTS

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Abstract: Nanosilica filled polyethylenes were prepared by melt processing. Effects of polymer chain structure (linear and branched) and molecular weight as well as nanoparticle size (7 and 14 nm) and content (0-10 wt%) on the viscoelastic properties of the filled melts were investigated. It was found that the presence of nanosilica increased the storage and loss moduli and complex viscosity of the polyethylene melts. At the nanosilica content $\geq$ 5 wt%, the filled polyethylene melts showed the solid-like behavior in the terminal (low frequecy) region. Regardless of the difference in surface area, the viscoelastic results of the two sizes of the nanosilica were comparable. In addition, both linear and branched chain structures showed no significant difference in the moduli of the filled melts even the branched chains have the slower molecular dynamics. Good dispersion at low nanosilica contents was confirmed by Transmission Electron Microscopy (TEM).

1. Introduction

Polymer nanocomposites has been one of the most widely used materials as it could provide high strength at relatively low filler contents compared to conventional composites. By adding nanofiller to polymers, a direct consequence is the change in the polymer rheology. A rheological study of molten polymer nanocomposites is important to assess their processability. Moreover, viscoelastic properties of nanocomposites in the molten state are generally useful to understand their structure–propertyrelationships. The filler–filler and filler–polymer interactions can strongly influence both linear and nonlinear viscoelastic responses. Melt rheology is thus useful for the investigation of the polymer nanocomposites.

Many previous works have shown that the presence of nanoparticles in polymer melts could either increase or decrease the viscosity [1-2]. The general behavior reported in the literature for oscillatory shear rheological measurements at low frequencies is that the linear rheological properties evolve from a liquid-like behavior to a solid-like behavior as the nanoparticle concentration increases. In the case of viscosity reduction which is not common, one of the proposed criteria is that the size of the particle should be comparable to or smaller than the polymer molecular size[3].

For nanocomposites, the size of the polymer is comparable to or larger than the particle size. With the filler size down to the order of nanometers it can lead to substantial difference in the rheological properties of filled melts as compared to that reinforced with micron sized particles. At similar filler contents, the nanoparticles greatly influence the properties of system more than microparticles because of their higher specific surface areas [4].

Besides nanoparticle content and size, the rheological properties also depend on the polymer matrix. Here the effect of polymer chain structure is focused as well as the effect of nanoparticles. High density (linear chain) and low density (branched chain) polyethylenes with two molecular weights were used. To investigate the effect of nanoparticle size and content, hydrophilic nanosilica (fumed silica) with the size of 7 and 14 nm added at 0-10 wt% were chosen.Linear viscoelastic properties of samples were investigatedbysmall amplitude oscillatory shear measurements.

2. Materials and Methods

2.1 Material

High density (H) and low density (L) polyethylenes were supplied by Thai Polyethylene Co.,Ltd. Their melt flow indices are listed in Table 1. Hydrophilic fumed silica (SiO_2) nanoparticles with an average size of 7 and 14 nm were used. Both were purchased from Aldrich.

2.2 Sample Preparation

An internal mixer (Haake Rheomix 600p) was employed to mix PE and silica using a rotor speed of 50 rpm at 160°C. Before mixing, nanosilica was dried in an oven at 70°C for 8 hours. Contents of fumed silica in the range of 0.5-10% by weight were used. The disk-like samples with a diameter of 25 mm for oscillatory shear measurement were prepared by compression molding (Lab tech engineering Co.,Ltd. model LP20-B).

2.3 Rheological Testing

Oscillatory shear measurements were performed using an AR-G2 rheometer. Measurements were carried out using parallel plate geometry at a temperature range of 120-200°C under nitrogen atmosphere. Frequency sweep with an angular frequency in range of 0.1-100 rad/sec at low strain of 2% was applied.

Table 1: Melt flow index (MFI), complex viscosity and characteristic time of polyethylenes used

PE	MFI(g/10min)	η_0^*(Pa.s)	τ_cx10^3 (s)
H08	0.8	27.32 x10^3	16.0
H14	14	2.62 x10^3	3.2[a]
L5	5	5.0 x10^3	25.0
L30	30	0.9x10^3	1.3

[a]: extrapolated data

2.4 TEM Sample Preparation and Testing

Transmission electron microscopy (TEM) was used to examine the filler dispersion. The samples were microtomed to thin sections (~ 130–150 nm) using the Ultramicrotome with a diamond knife at -80 °C. Sections were placed flat on a copper grid coated with carbon. The samples were then brought up to room temperature. TEM was performed on the *FEI Tecnai G²20* (FEI Co., Eindhoven, Netherlands) with an accelerating voltage of 200 kV.

3. Results and Discussion

3.1 Rheology of polyethylene melts

The linear viscoelastic (LVE) results at various temperatures were shifted to 160°C by the WLF equation. Figure 1 shows a typical LVE behavior in the terminal region i.e. the moduli scale with angular frequency (ω) where G' ~ ω^2 and G" ~ ω^1. The angular frequency at which G' crosses over G", so-called thecrossover frequency (ω_c) is determined.

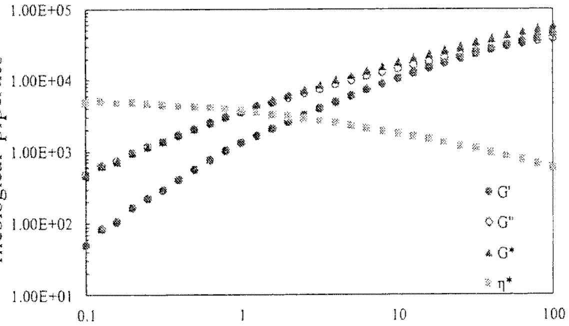

Figure 1. Typical LVE behavior in the terminal region of polymer melts (here is neat L5 at temperature of 160°C).

The characteristic time (τ_c) is then calculated from the inverse of ω_c, $\tau_c = 1/\omega_c$. This $\tau_c$can relate to the longest relaxation time of the polymer chain. In this work, the frequency range below and beyond $\omega_c$was considered the terminal region and rubbery region, respectively.

The master curve of storage and loss moduli as a function of frequency of these polyethylenes is presented in Figure 2. Only low density polyethylene melts could show the terminal behavior. The crossover frequency (ω_c) of these polyethylenes except H14 was obtained. Experimentally, H14 was solidified at low temperature before the crossover frequencycould be reached. The ω_c was thus extrapolated. The characteristic time (τ_c) was then calculated and also listed in Table 1. For the same chain structure the polyethylenes with the higher zero viscosity (i.e. higher molecular weight) showed longer τ_c. It means that H08 takes longer time to relax than H14, and L5 longer than L30.

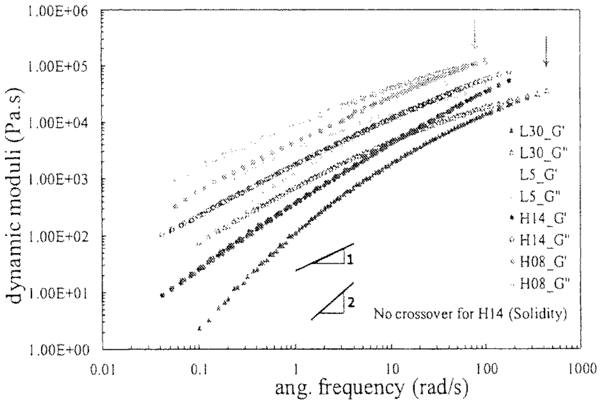

Figure 2.Master curve of dynamic moduli versus frequency of long-chain branched (L30 and L5) and linear (H14 and H08) polyethylenes at 160°C.

3.2 Rheology of fumed silica filled polyethylene melts

Figure 3 presents G' and G"moduli of the filled L5 melts. At low loadings, both moduli increased with increasing ω and in the low frequency region G" is larger than G', displaying the viscous nature.With increasing the filler loading, the moduli increased over the whole frequency range by which the increase was more pronounced in the low frequency region and in G' more than in G".It was also noticed that the crossover frequency (ω_c) was shifted to lower values, indicating an increase in the longest relaxation time. It could mean that the presence of fumed silica contributes to the elasticity of the polyethylene melts. At 10 wt% loading for L5, both G' and G" became almost frequency independent (log–log plot). Similar results were also obtained for H-08, H-14, and L-30 (not presented here).Generally, frequency-independent moduli are characteristic for solids and indicate that the polymer chain relaxation is slowed down and the chain reptation is stronglyrestrained [4].

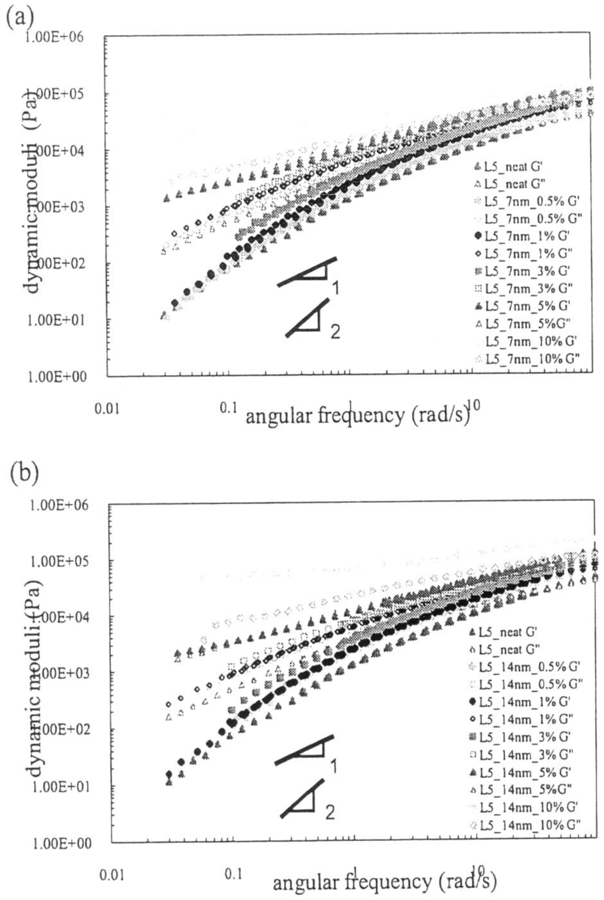

Figure 3.Storage and loss moduli of the fumed silica (a) 7 and (b) 14 nm filled L5 melts at various contents (wt%) as a function of the angular frequency at the temperature of 160°C.

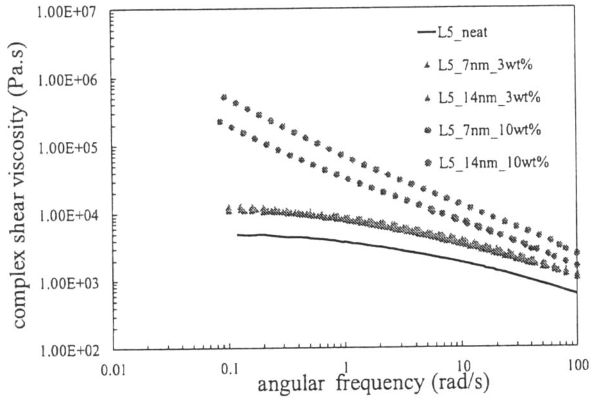

Figure 4.Complex viscosity versus frequency for 7 and 14 nm fumed silica filled L5 at 0, 3, and 10wt%

Besides the viscoelastic moduli, the complex viscosity of the neat and the filled L5 is plotted. Figure 4 displays the complex viscosity versus frequency at 3 and 10 wt% loadings.As shown, at low filler loading the samples show a frequency-independent behavior in the low frequency region, whereas at high loading the viscosity diverges. This diverge corresponds to the solid-like behavior observed in the storage modulus. Similar results were also obtained for L-30, H-08and H-14 (not presented here).In terms of the silica particle size, with the larger surface area smaller size should have more effect on the viscosity. However, the results were inconclusive that the viscosity was higher in the presence of 7-nm silica particles.

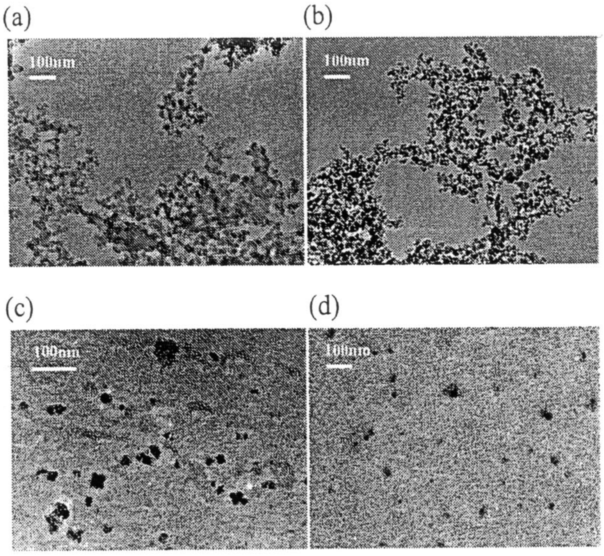

Figure 5. TEM images of (a) pure 7 nm, (b) pure 14 nm, (c) 0.5 wt% of 7nm filled H14, and (d) 1 wt% of 14 nm filled L5 at the scale bar of 100 nm.

Preliminary study on the dispersion of silica nanoparticles in polyethylenes was examined. TEM images of the fumed nanosilica 7 and 14nm (as obtained from evaporating the silica dispersion) and their filled L5 (0.5 wt%) and H14 (1 wt%) are shown in Figure 5. Relatively good dispersion was observed at the low loadings.

4. Conclusions

Typical linear viscoelastic behavior at low frequency was generally obtained for both linear and branched polyethylene melts. The branched structure though showed stronger viscosity-characteristic time relation as due to the additional mode of molecular relaxation. The addition of fumed silica to polyethylene increased bothstorage and loss moduli as well as complex viscosity especially at low-frequency. It suggests that silica nanoparticles influence the relaxation dynamics more than the plateau elastic modulus. The change from liquid-like behavior to solid-like behavior (independent of frequency) was observed at high loading (≥ 5 wt%). It indicates that in the presence of nanofillers at particular loading some reinforcing network must be formed. The 7 nm and 14 nm showed relatively the same behavior, implying that the filled melts may not differentiate these two sizes.

Acknowledgements

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