Impact of Nanoparticles on the Mobility of the Host Polymer and the Viscosity of Polymer Nano-Composites (PNC's)

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ABSTRACT

Reports as early as 1974[1] have indicated that polymer nanocomposites(PNCs) can exhibit viscosities that decrease with particle addition counter to the classical behavior for filled systems originally described by Einstein[2]. Schmidt et. al.[3] previously reported that PNC's prepared from trimethylsiloxy-treated polysilicate nanoparticles of $0.75 \leq R_g \leq 2.1$nm and a series of narrow molecular weight distribution polydimethylsiloxane (PDMS) polymers exhibited a critical size ratio (Rg(particle)/Rg(polymer) ~0.13) for viscosity reduction behavior. In this paper we will discuss potential physical phenomena responsible for the viscosity behavior. Also, some initial observations on the impact of tethered particles compared to blended particles on the mobility of the host polymer will be made, using mono-functional polyoctahedral silsesquioxane (POSS) particles tethered to PDMS chain ends and NMR relaxation analyses.

Keywords: polymer nanocomposite, viscosity reduction, PNC, critical size ratio, NMR relaxation

1   PNC VISCOSITY REDUCTION

A series of trimethylsiloxy-treated polysilicate particles of varying molecular sizes ($0.75 \leq R_g \leq 2.1$nm where R_g is the radius of gyration) were prepared using super critical fluid extraction techniques[3]. The resulting particles were characterized using Small Angle Neutron Scattering (SANS) and blended at 30 vol% loadings with four different narrow molecular weight trimethyl siloxy terminated pdms polymers and the viscosity of each measured at 25C using cone and plate rheometry. Figure 1 shows that the viscosity of the blend PNC's increased steadily as the size of the particles increased from 0.7 to 2.1nm.   However, for the three largest polymers the smallest particles actually lowered the viscosity of the PNC's relative to the polymer alone ($\eta/\eta_0 < 1$) at 30 vol% particle loading.   Also, the particle size necessary to achieve a viscosity increase ($\eta/\eta_0 > 1$) increases as the Mw of the pdms polymer increases. This suggests that the relative size of the particle and polymer are important in dictating whether or not non-Einstein viscosity behavior will be accessible. The authors hypothesize that in these compatible, but weakly interacting particle/polymer PNCs, the ratio of particle and polymer sizes determines if the polymer expands ($\eta/\eta_0 < 1$) or collpses($\eta/\eta_0 > 1$) in the presence   of   the   nanoparticles.
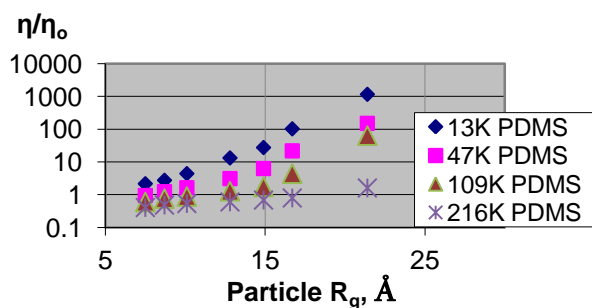

Figure 1 Impact of trimethylsiloxy-treated polysilicate particle size on the specific viscosity of blended 30 vol% particles in pdms PNC's.

2   RELAXATION OF THE POLYMER COMPONENT IN TETHERED AND BLENDED COMPOSITES

The utility of the ^{1}H NMR relaxation measurements is predicated on the assumption that the polymer protons have much greater mobility than the particle protons and hence dominate the relaxations detected from the spin-echos of the pulse sequence. To confirm this hypothesis blended PNC's based on 45wt% $R_g=1.5$nm , trimethylsiloxy-treated polysilicate particles (R2) in 15k (Mw) per-deuterated pdms and 13k standard pdms were prepared and subjected to ^{1}H spin-spin relaxation measurements. Magnitization was only observed with the PNC containing standard pdms confirming that the relaxation measurements are sensitive to the protons of the polymer component as hypothesized.

Monofunctional POSS molecules were used to tether particles (molecules with minimal degrees of structural freedom) to both ends of a flexible pdms chain (synthesis scheme figure 2). ^{1}H NMR relaxation measurements (^{1}H spin-spin relaxation measurements using Carr-Purcell-Meiboom-Gill (CPMG) pulse sequences[4]) were used to evaluate the relative mobility of the polymer component for a series of tethered and blended PNC's with the tethered particle content increasing with reduced polymer chain length.
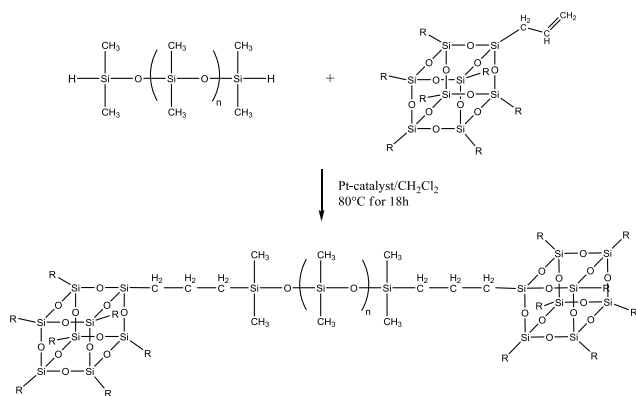
Figure 2 General scheme of hydrosilylation reaction to synthesize POSS-PDMS-POSS triblocks. (Reaction performed under inert conditions)

The specific relaxation rates of the POSS-PDMS-POSS triblocks as a function of the weight fraction of the POSS component (phenyl and t-butyl POSS particles) with respect to the pure polymers are shown in figure 3. Clearly the relaxation rates increase with increasing POSS content indicating that the mobility of the pdms component of the triblock is reduced (especially above 20 wt% POSS) by the tethered POSS particles. Also, it is apparent that the phenyl POSS molecules reduce the mobility of the polymer component more efficiently than the t-butyl POSS particles.

For comparison, blended PNCs based on R2 polysilicate particles were analyzed in the same manner and found to have a lesser impact on reducing the mobility of the pdms component at loadings up to 60 weight percent particle loading. However, between 60 and 70 weight percent particle loading the blended particles appear to start restricting the pdms component mobility severely resulting in specific relaxation rates that are greater than the analogous tethered PNC's (data not shown).
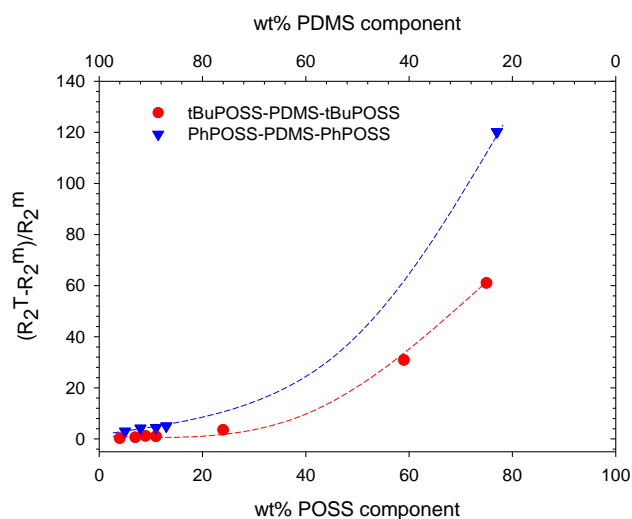
Figure 3 The impact of particle content on the specific relaxation rate of the pdms component in tethered PNC's.

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