

## Mechanical and Molecular Behavior of Nanoparticle/Polymer Composites

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The addition of nanoscale fillers to polymers can have a dramatic effect on the mechanical properties [1,2] compared to micron scale fillers. This may be in large part due to the small size of the filler and the large surface area of nanoscale fillers. The role of the surface in mediating polymer response is under debate. It may be that the mobility of the chains within a few mers of the surface is reduced while leaving the bulk relatively unaffected and this has been termed a “bound polymer layer.” On the other hand, the surface may act to trap entanglements and result in a restriction on the overall chain mobility of the polymer molecules both near and far-field to the filler surface. This project, therefore, has two goals. The first is to fabricate nanofilled polymers and investigate their properties for engineering applications. The second is to gain a fundamental understanding of the interactions of polymer chains with nanofiller surfaces.

We are using solid state nuclear magnetic resonance, rheology and bulk mechanical studies to achieve some fundamental understanding. The composite systems we will report on in this document are fumed silica filled polyvinyl acetate (PVAc) in which the nanofillers are in fractal like aggregates, and crystalline alumina filled polymethyl methacrylate (PMMA) in which the fillers are processed using the gas condensation method and for the most part not aggregated. The samples are processed either by dispersing the nanofillers in monomer or by dispersing them in dissolved polymer. They are subsequently molded into the appropriate geometries for testing. We have altered the interface to control the level of interaction between the nanofiller and the polymer matrix.

A sampling of our rheology results is shown in Figures 1-4. Simple shear tests around and above the glass transition temperature,  $T_g$ , were performed using two special fixtures, each designed for a particular temperature regime. Figure 1 shows the effect of the addition of nanoscale silica to PVAc around  $T_g$ . Note that the  $T_g$  increases by several degrees. This implies that there has been a decrease in the conformational mobility of the polymer chains. In addition, the normalized data in Figure 2 shows that there has been no broadening of the relaxation spectra. This implies that the nanofiller has not created a bound polymer layer, but has caused both a near and far-field effect. In addition, studies above  $T_g$  (Figure 3) show a response strikingly similar to the Payne effect [3]. As the filler content increases, the non-linearity (decrease in storage modulus with strain), starts earlier and decreases more dramatically. There is also an effect of filler surface chemistry on the melt rheology as shown in the plot of loss factor vs. shear strain in Figure 4. The increasing loss factor with strain amplitude is thought to be the result of increased slippage of the polymer entanglements “trapped” by the fillers. These results suggest that polymer/filler interactions strongly modify the far-field polymer behavior with respect to chain entanglement slippage at large strains.

Figures 5-8 show the results of our work on nano-alumina filled PMMA [4]. Note that in Figure 5 the addition of 5 wt% of filler increased the strain to failure by almost an order of magnitude. This increase in strain to failure is accompanied by a change in failure mode from crazing in the unfilled PMMA (Figure 6(a)) to shear yield followed by fast fracture (Figure 6(b)). Figure 6(c) shows that one probable mechanism of deformation is cavity growth around the nanoparticles. Accompanying the change in mechanical properties is a large decrease in  $T_g$ , (Table I). This change is not due to changes in molecular weight, tacticity or residual monomer. The NMR results shown in Figure 8 depict a larger mobile fraction in the filled polymer (an increase in the intensity of the center peak) even at room temperature. Below  $T_g$ , the outer peaks of the Pake pattern, separated by 120kHz are the  $CD_2$  groups and the inner peaks separated by 40kHz are the  $CD_3$  groups. The heights of these peaks remain relatively constant below  $T_g$ . The increase in mobility is probably due to freer mobility of the  $OCD_3$  (methoxy) group – possibly those motions associated with the  $\beta$  transition. At temperatures above  $T_g$ , the  $CD_2$ , and  $CD_3$  peaks decrease because these groups have also become mobile, contributing to the center peak. This decrease and the narrowing of the  $CD_2$  pattern is consistent with the onset of the glass transition. This change in  $T_g$  is not observed for fillers with fractal like agglomerates or strong bonding to the matrix. Therefore, we tentatively conclude that in this system, we have created PMMA filled with poorly bonded nanofiller that essentially creates a large volume of voids and thus internal free surface in the sample. This could account for both the decrease in  $T_g$  and the delocalized damage development leading to shear yield instead of crazing.

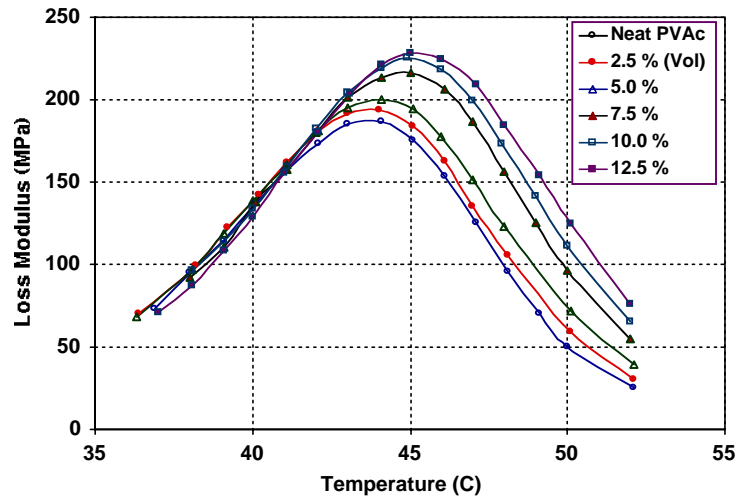


Figure 1.  $G''$  vs temperature for untreated nanoscale silica filled PVAc at 2Hz. The filler has a surface area of  $380 \text{ m}^2/\text{g}$ .

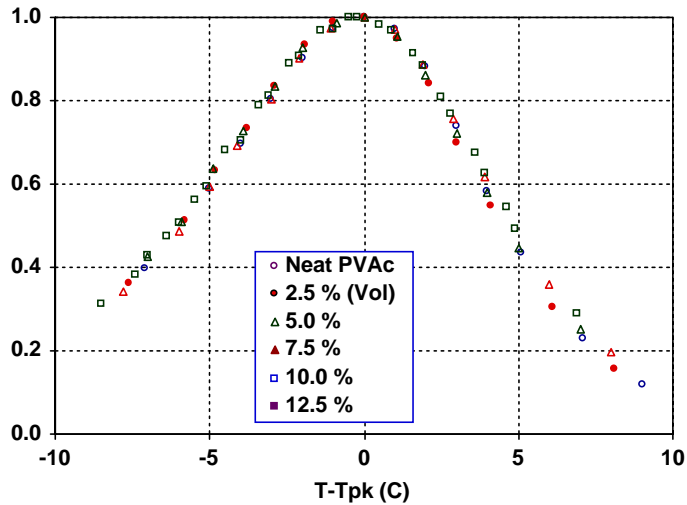


Figure 2. Normalized  $G''$  vs temperature for untreated nanoscale silica filled PVAc at 2Hz. The filler has a surface area of  $380 \text{ m}^2/\text{g}$ .

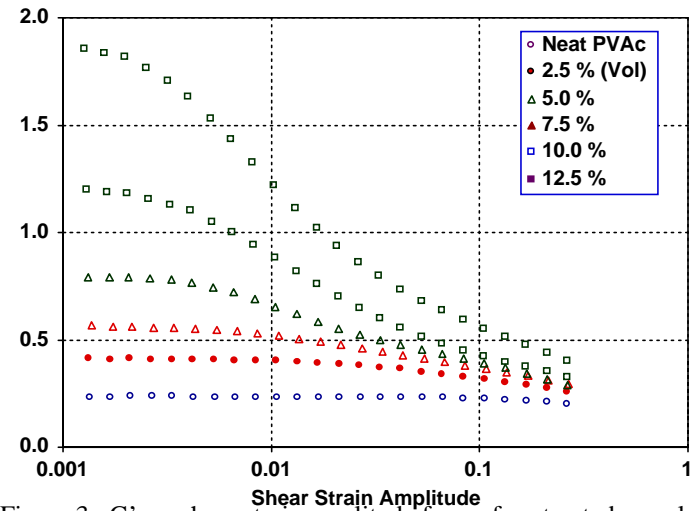


Figure 3.  $G'$  vs. shear strain amplitude for surface treated samples at  $90 \text{ C}$  at  $5\text{Hz}$ . The filler was treated with X and has a surface area of  $200 \text{ m}^2/\text{g}$ .

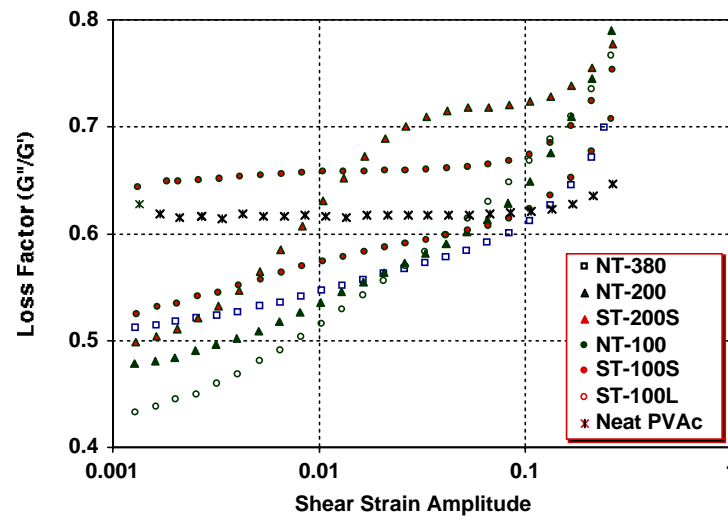


Figure 4. Loss factor vs shear strain amplitude for all fillers at 20 phr,  $90\text{C}$  &  $5\text{Hz}$ . Neat PVAc is included for comparison.

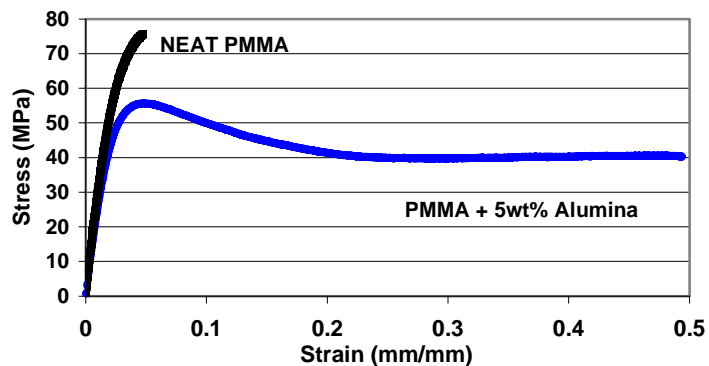


Figure 5. Typical stress-strain curves for neat and filled PMMA showing yielding vs. non-yielding behavior ( $4\% \text{ min}^{-1}$  strain rate).

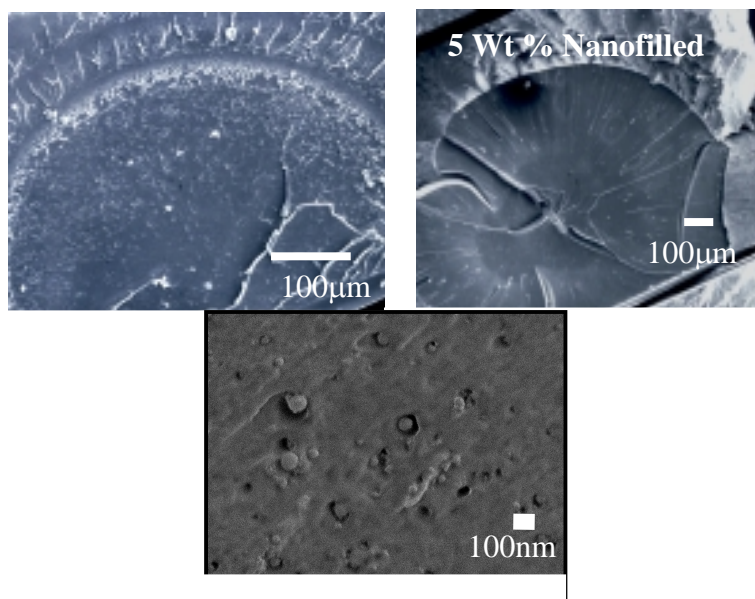


Figure 6 SEM micrographs showing (a) Fracture surface of neat PMMA showing the results of a crazing failure mode, (b) the shear yielding failure of 5 wt% nanoalumina filled PMMA, (c) the cavity growth that occurs during deformation of 5 wt% nanoalumina filled PMMA.

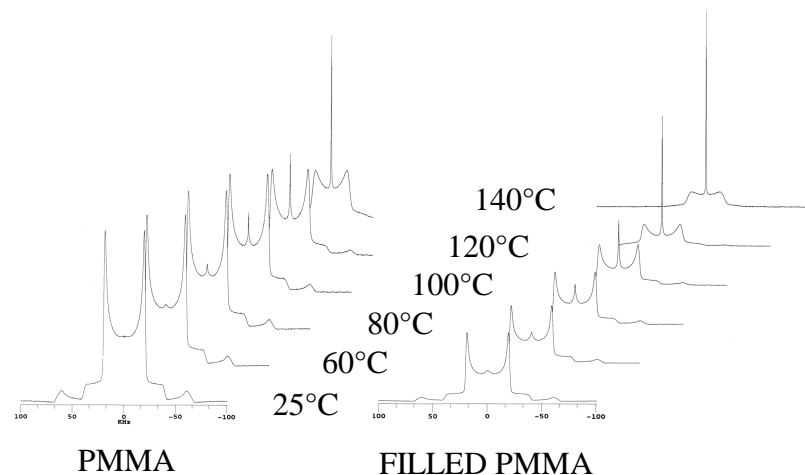


Figure 7.  $^2\text{D}$  solid echo spectra of fully-deuterated PMMA samples. The spectra on the left are scaled by a factor of 2.

**Table I.** Chemical and Transition Temperature Data PMMA/Alumina Nanocomposites.

	Neat PMMA	PMMA/Coated $\text{Al}_2\text{O}_3$	PMMA/Uncoated $\text{Al}_2\text{O}_3$
Molecular Weight (Mn)	142,000	155,000	153,000
Polydispersity Index	1.5	3.0	1.6
Tacticity % Iso	4.2%	4.9%	3.2%
% Hetero	35.1%	33.9%	31.5%
% Syndio	60.7%	61.2%	65.3%
Tg by DSC	119°C	96°C	
Tg by DMA	126°C	104°C	106°C

## REFERENCES

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