Investigation into the Thermal and Mechanical Behavior of PMMA/Alumina Nanocomposites

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Abstract

Polymethylmethacrylate (PMMA) nanocomposites were synthesized by free radical polymerization in the presence of various weight percentages of alumina (Al$_2$O$_3$) nanoparticles. The resulting nanocomposites show an average increase of 600% in strain-to-failure and the appearance of a well-defined yield point. Concurrently, the glass transition temperature (T$_g$) of the composites decreased 20ºC, while the ultimate strength and the Young’s modulus decreased by 20% and 15%, respectively.

Introduction

Nanocomposites make up a particular class of polymer composites that have recently garnered much attention. This growing class of materials can lead to reinforcement of a polymer without the undesirable property changes exhibited by micron particle filled systems. For example, Sumita found dramatic improvements in the yield stress (30%) and Young’s modulus (170%) in nano-filled polypropylene compared to micron-filled polypropylene that lowered the yield stress and provided only modest improvements to the modulus [1]. Similarly, Ou et al., filled Nylon 6 with 50 nm silica particles and reported increases in tensile strength (15%), strain-to-failure (150%), Young’s modulus (23%), and impact strength (78%) [2].

One of the key aspects of nanoparticles as a filler is their significant surface to volume ratio. When any particle is well dispersed in a polymer matrix, the volume directly surrounding the particle has polymer chains in contact with the particle surface. If the particle has a strong affinity for the matrix, these chains can lose some of their mobility and a region of low-mobility polymer will exist around each particle [3]. This layer of affected polymer has been estimated to be somewhere between 2 and 9 nm thick [4] and is generally termed the “bound polymer” (BP) layer. In conventional micron-filled composites, the volume fraction of BP is insignificant due to the relatively large diameter of the particles and the corresponding low surface to volume ratio. In the case of nanocomposites, however, this region of affected polymer can represent a significant volume of the total matrix polymer. Therefore, the BP’s behavior will directly impact the observed mechanical and thermal behavior of the composite [5]. For example, Becker found an increase in the T$_g$ and a 100% increase in storage modulus above T$_g$ in a nano-size silica/PMMA-HEMA system [6]. Iisaka and Shibayama also reported an increase in T$_g$ directly related to the strength of interaction between glass beads and PMMA [5].

The presence of the nanoparticles changes the overall mechanical properties of the polymer matrix. In general, well-dispersed particles or voids can change the stress state of a large volume fraction of the polymer. This can lead to a change in the mode of deformation. For
example, in rubber-filled epoxies, an applied stress can induce microvoid formation in the lower modulus filler particles through cavitation that in turn alters the stress state in the surrounding matrix, and results in a tougher matrix [7]. Wu, has hypothesized that the stress fields associated with each rubber particle could interact, leading to a change in stress state from plane strain to plane stress at a critical interparticle distance (ligament thickness) [8]. This would allow sections of the polymer between particles to relieve the applied stress and toughen the matrix. Sternstein et al., observed that judicious placement of machined holes in a sheet of PMMA would cause the material to exhibit ductile behavior [9]. In fact, crazes that formed when holes were an optimum distance apart would thicken and lengthen instead of reaching a critical length to initiate brittle fracture. The stress state of the polymer was altered in each case to promote energy dissipation and tough behavior.

The present study focused on the in-situ polymerization of PMMA/alumina nanocomposites and a comprehensive analysis of the mechanical and thermal behavior of the resulting materials. While still preliminary in nature, we have uncovered some rather unique behaviors.

**Experimental Procedure**

Alumina nanoparticles (39 nm average diameter obtained from Nanophase Technologies Corporation) were used in composite preparation in their as-received state (uncoated) or coated with (3-acryloxypropyl) dimethylmethoxysilane (95% SIA 0190.0, Gelest Inc.). The monomer, methylmethacrylate (99% stabilized with 100ppm MEHQ, Acros Organics), initiator, 2,2 azobisisobutyronitrile (98% Aldrich), and chain transfer agent, 1-decanethiol (96% Aldrich Chemical), were used without further purification.

The nanoparticles were coated similarly to the procedure found in reference 10. The polymerization procedure was developed based on the work of Balke and Hamielec [11]. Coated or uncoated nanoparticles were added to MMA monomer and dispersed via sonication at 70% (VCX-400 Sonics Materials Vibracell) for 10 minutes. During the last two minutes of the sonication, the initiator (AIBN) and chain transfer agent (1-decanethiol) were added. The polymerization was carried out at 55°C under a nitrogen blanket for 21 hours. The polymer was then broken into small pieces by mechanical means and dried in a vacuum oven for 2 hours at 115°C to drive off adsorbed water and residual monomer. The resulting nanocomposite was compression molded into tensile specimens (ASTM D638-95 Type IV) in a hydraulic press (Carver 12 Ton) at 190°C and 3.5 mTons. Specimens were allowed to cool to room temperature under pressure for a period of 6 hours. Finished specimens were sanded with fine sandpaper (400 grit) to remove flashing. Alumina nanocomposites were light yellow in color and translucent up to a thickness of 5 mm.

**Composite Testing**

Uniaxial tension testing was performed in accordance with ASTM D638-95 [12] at a constant strain rate of 0.04 min⁻¹. At least six samples of each material were tested. Dynamic mechanical analysis (DMA) was carried out on a Rheometric Scientific DMTA V using tensile mode at 5 Hz, with 0.01% strain. Temperature ramps from 15°C to 200°C at 2°C/min were conducted to determine the $T_g$ of the materials. The $T_g$ is reported as the corresponding peak of
the loss modulus curve in each case. $T_g$ was also obtained through differential scanning calorimetry (DSC) (Seiko Instruments SSC5200) with a temperature ramp from 25°C to 190°C at 10°C/min. The fracture surfaces were observed using scanning electron microscopy (SEM) and field emission SEM. Molecular weight analysis was performed on a Waters HPLC calibrated by a narrow polystyrene standard. Tacticity and retained monomer percentages were determined using a Varian liquid NMR (500 MHz) by dissolving 200 mg of the composite in 1 ml deuterated chloroform and performing both $^1$H and $^{13}$C NMR.

**Results and Discussion**

Typical stress-strain curves for the nanoparticle-filled polymer and neat PMMA are shown in Figure 1. In this graph, a 5 wt% uncoated alumina nanocomposite sample displays an increase in strain-to-failure of over 800%. This ductile behavior was typical of coated or uncoated alumina-filled samples. In addition to the dramatic increase in strain-to-failure, the appearance of the samples was altered. A neck occurred coincident with a drop in engineering stress in the region beyond the yield point. The translucent samples also became almost transparent in the necked regions. Figure 2 shows the percentage of the samples in each weight percent that exhibit the yield point behavior. As can be seen in Figure 2, there appears to be a critical weight percent where the majority of the specimens fail in a typically ductile fashion.

In PMMA, the primary mode of failure in the temperature and strain rate regime of the

![Figure 1](image1.png)

**Figure 1.** Typical stress-strain curves for neat and filled PMMA showing yielding vs. non-yielding behavior (4% min$^{-1}$ strain rate). The nanoparticle-filled PMMA clearly shows a yield point.

![Figure 2](image2.png)

**Figure 2.** Percentage of tensile tests resulting in failures past the yield point. The greatest percentage of ductile failures occurred at 5 wt%, where 73% of the failures were ductile in nature.
present experiments is by crazing that leads to brittle failure [13]. The failure surface of the neat PMMA shown in Figure 3a shows the typical craze failure morphology. The fracture surfaces presented in Figures 3b and 4 do not show any attributes of crazing. This observation coupled with the ductile behavior shown in Figure 1 implies that the mode of failure has been altered from crazing to homogeneous yield.

The $T_g$ of a filled polymer system typically increases, or is at least constant, with the addition of high modulus fillers [14]. As shown in Table I, a very large decrease ($20^\circ$C) in the $T_g$ was recorded by both DMA and DSC for both coated and uncoated systems. The varying $T_g$ does fall well within the range of that reported in the literature for varying tacticities [15]. However, as shown in Table I, there were no dramatic changes in the tacticity. Glass transition temperature drops have also been shown for varying molecular weights [13], but as can also be seen from Table I, the molecular weights do not show much variation. In addition, retained monomer can also cause a significant decrease in $T_g$, but liquid NMR data show less than 1% by volume of retained monomer in any sample. Decreases in $T_g$, of the same order as reported here,

![Figure 3](image)

**Figure 3.** (a) Typical fracture surface of PMMA – uniaxial tension. (b) Low resolution SEM micrograph of heavily yielded (40% elongation) PMMA/alumina nanocomposite (5 wt%) showing fast fracture behavior initiating at a defect.

![Figure 4](image)

**Figure 4.** Fracture surfaces of PMMA nanocomposites containing (a) uncoated and (b) coated alumina particles at 5 wt% showing good dispersion. Note the appreciable agglomeration in image (a) and the cavities surrounding each particle or agglomerate in both images.
have recently been observed in thin films as a function of film thickness and interfacial properties, and in polymer systems with large void concentrations in which the chain mobility in the vicinity of the voids has been shown to increase by NMR [16,17]. This may be related to the change in $T_g$ observed in the nanocomposites. If the polymer were not bound to the particles, a matrix with many voids would result with a very high internal surface area. This could be viewed as having the same characteristics as a thin polymer film with a large surface to volume ratio. Because the free volume of the polymer is higher near a surface, the large surface area could cause a decrease in $T_g$. If simple cubic packing is assumed, and the particles are well dispersed, the typical interparticle distance for 39 nm particles is 83 nm. This spacing supports a $T_g$ drop of this magnitude, as seen in the higher molecular weight polystyrene results of Mattsson et al [18] and the hypothesis that the bulk composite is behaving as a thin film. The voids that are present around each particle in Figure 4 seem to support this model of a large surface area of “free-standing” polymer that is present within the matrix.

The modulus data presented in Figure 5 show a sharp drop, followed by a slow increase with filler weight percent. The modulus of PMMA typically drops as temperature increases, therefore this drop could be entirely due to the drop in $T_g$ that raises the relative testing temperature ($T_g$-$T_{test}$) of the samples. As the weight percentage of the particles increases, the polymer becomes stiffer due to the higher volume percent of high modulus filler particles. The brittle to ductile yield transition of a glassy polymer is normally seen at elevated temperatures (within 30°C of $T_g$), but it can also be achieved with very low strain rates in uniaxial tension [13]. In these cases, the transition is due to the ability of the polymer chains to change their local conformation and relieve applied stress before crazing can occur. In the alumina/PMMA system an increase of 20°C in the relative testing temperature does not account for the phenomenal strain-to-failure exhibited by the nanocomposite or the complete lack of crazing. Ductility can also occur if the stress state in the polymer is changed in such a way that the shear-yielding criterion is reached prior to the formation of crazes, such as by the application of a hydrostatic stress [9]. As stated in the introduction, the presence of nanoparticles can lead to a change in stress state. If, in fact, the nanoparticles exist with minimal bonding to the surrounding matrix, the application of a tensile stress, would cause the voids to expand, relieving the resulting triaxial stress and preventing craze void formation and premature failure. In effect, this process of matrix yielding between each nanoparticle would distribute the yield process throughout the composite, leading to delocalized yielding and the observed strain-to-failure behavior. On the other hand, significant agglomeration of the particles in the 10 wt% runs would cause the composites to fail prior to yielding due to the more conventional propagation of cracks initiated from large agglomerates that lead to premature brittle fracture of the composite.

In conclusion, we have found that the addition of nanoparticles to a brittle matrix (PMMA) can lead to a ductile-type behavior in which the nanocomposite yields by shear through

<table>
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<th>Molecular Weight (Mn)</th>
<th>Neat PMMA</th>
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<th>PMMA/Uncoated Al₂O₃</th>
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<td>65.3%</td>
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Table I. Chemical and Transition Temperature Data PMMA/Alumina Nanocomposites.
the suppression of craze formation or through the delocalization of homogeneous yielding throughout the matrix.

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References