Influence of Sample Preparation and Processing on Observed Glass Transition Temperatures of Polymer Nanocomposites

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ABSTRACT: Polymer composites composed of poly(methyl methacrylate) (PMMA) and silica (14 nm diameter) have been investigated. The influences of sample preparation and processing have been probed. Two types of sample preparation methods were investigated: (i) solution mixture of PMMA and silica in methyl ethyl ketone and (ii) in situ synthesis of PMMA in the presence of silica. After removing all solvent or monomer, as confirmed using thermogravimetric analysis, and after compression molding, drops in $T_g$ of 5–15 °C were observed for all composites (2–12% w/w silica) and even pure polymer reference samples. However, after additional annealing for 72 h at 140 °C, all previously observed drops in $T_g$ disappeared, and the intrinsic $T_g$ of bulk, pure PMMA was again observed. This is indicative of nonequilibrium trapped voids being present in the as-molded samples. Field-emission scanning electron microscopy was used to show well-dispersed particles, and dynamic mechanical analysis was used to probe the mechanical properties (i.e., storage modulus) of the fully equilibrated composites. Even though no equilibrium $T_g$ changes were observed, the addition of silica to the PMMA matrices was observed to improve the mechanical properties of the glassy polymer host.

Keywords: electron microscopy; glass transition; mechanical properties; nanocomposites

INTRODUCTION

The inclusion of nanoparticles into polymeric materials is well-known to increase mechanical and impact strength,4 to provide tunable optical and electrical properties,2 or to improve thermal and photo-oxidative resistance of the host polymer matrix.3 However, it is difficult to disperse the nanoparticles within polymer matrices because of the high-energy interface that is often created in many polymer/nanoparticle nanocomposites,4,5 thereby significantly minimizing property enhancements. Because of the technologically relevant applications of nanocomposites, as well as fundamental curiosity, the nanoparticle/
polymer interface has been the subject of numerous investigations in recent years. Results have shown significant, and sometimes anomalous, changes in observed properties, such as reductions in the glass transition temperature \( T_g \) and viscosity \( \eta \) even with small concentrations of filler (1–2% v/v). However, recent work has shown that these may not be true equilibrium property changes, but rather non-equilibrium observations due to phenomena such as trapped voids between the nanoparticles and surrounding matrix. This assumption is encouraged by results of earlier investigations of colloidal suspensions, where the influence of air inclusion on the rheological properties has been reported. Free surfaces in many polymer films are known to have reduced \( T_g \) and hence, reduced viscosities, and therefore the inclusion of trapped voids within polymers is expected to yield similar property changes. It is therefore extremely important that we understand the roles of sample preparation and processing on the equilibrium material properties of polymer nanocomposites.

Here, we probe the mechanical and thermal properties of nanocomposites composed of poly (methyl methacrylate) (PMMA) with fumed silica (ca. 14 nm diameter). The influence of sample preparation methods and sample processing has been analyzed. Results show initial drops in \( T_g \) of approximately 5–15 °C for PMMA/silica (4–12 wt % silica) after initial sample preparation, solvent/monomer removal, and compression molding, even though \( T_g \) increases would be expected from previous investigations of PMMA thin films on silica substrates. However, after annealing further for 3 days above the intrinsic \( T_g \) for pure PMMA \( (T_g,0 \approx 110 \, ^\circ C) \), these \( T_g \) drops all disappeared and \( T_g,0 \) was observed for all samples. Field-emission scanning electron microscopy (FE-SEM) shows excellent dispersion of the silica particles, which can be attributed to the highly favorable PMMA/silica interaction. Subsequent examination of the storage modulus \( (E') \) below \( T_g,0 \) using dynamic mechanical analysis (DMA) reveals improvements in the mechanical properties of the glassy polymer for the PMMA/silica nanocomposites. Therefore, equilibrium inclusion of nanoparticles within polymer matrices can have a significant impact on the mechanical properties of the host polymer, even though it may not be accompanied by changes in other properties such as \( T_g \).

**EXPERIMENTAL**

**Materials**

Atactic PMMA was purchased from Scientific Polymer Products (PMMA-100; \( M_w \approx 100 \, kDa; M_w/M_n \approx 2 \)). Differential scanning calorimetry (DSC) was used to measure \( T_g,0 = 108 \, ^\circ C \), while proton nuclear magnetic resonance spectroscopy was used to determine the tacticity triad distributions \( (m = 0.14; mr = 0.36; rr = 0.50) \). Methyl methacrylate (MMA; Fluka), methyl ethyl ketone (MEK; Acros), activated basic alumina (Brockmann I; Sigma-Aldrich), 2,2-azobis(isobutyronitrile) (AIBN; Sigma-Aldrich), and fumed silica particles (14 nm diameter as reported by manufacturer; Sigma-Aldrich) were used as received.

**Differential Scanning Calorimetry**

\( T_g \)s were measured using a TA Q1000 DSC. Data were collected for 10 mg (approximate) samples in aluminium pans over two runs (each run consisted of a cooling and a heating cycle) from 30 to 180 °C at a controlled heating/cooling rate of 10 °C/min. The glass transition temperatures of the nanocomposites were characterized as the inflection point of the change in specific heat from the second cooling run in all cases. To minimize inaccuracies in the presented glass transition temperatures the mean value of at least five different specimens was used.

**Dynamic Mechanical Analysis**

\( E' \) was measured using a TA 983 DMA in flexural mode. The arms of the DMA move back and forth in the horizontal plane to flex the specimens at the specified frequency. The analysis was done at constant frequency (sinusoidal oscillation, 2 Hz) with amplitude (strain) of 0.5 mm. After equilibrating the sample at 30 °C a controlled temperature program with a heating rate of 5 °C min \(^{-1} \) was carried out. Storage moduli \( (E') \) were obtained over a temperature range of 30–130 °C. The samples were compression molded at 170 °C into uniform samples with dimensions of approximately 11 mm in length and 5 mm in width with a thickness of 0.5 mm and further annealed for 72 h at 140 °C.
Field-Emission Scanning Electron Microscopy
FE-SEM of the resulting nanocomposites was performed on a JSM-6400F cold field-emission scanning electron microscope from JEOL. The cross-sections of the samples were prepared by freeze fracture. The freshly prepared surfaces were sputtered with a 10 nm (nominal) palladium–gold film. In general, an accelerating voltage of 5 kV was used to obtain high quality images to observe the dispersion of the fillers within the polymer matrix.

Nanocomposite Preparation
PMMA nanocomposites with 4–12% (w/w) silica (Composites A–D, see Table 1) were prepared. A 5% (w/w) stock suspension of the silica nanoparticles in MEK was prepared by bath sonication. For further stabilization approximately 0.5% (w/w) of PMMA-100 was added to the filler suspension. No sedimentation of the silica particles could be observed, even after several weeks, and the suspension was observably stable during preparation of the samples. A volume of stock suspension, dependent on the concentration of nanoparticles desired in the nanocomposite, was mixed with a 10% (w/w) solution of PMMA-100 in MEK. The resulting mixture was sonicated for 2 min to ensure a good dispersion of the fillers within the polymer solution. Using dilute solution viscometry of PMMA-100 in MEK (20 g/dL), negligible change in PMMA-100 was observed with sonication times up to 10 min. The product was poured into a PTFE Petri dish and dried at room temperature. To remove residual solvent the glassy composites were annealed for 72 h at 140 °C in vacuo and compression molded at 170 °C into 0.5 mm films. TGA was used to confirm complete removal of monomer. The mass of the recovered composite and known mass of nanoparticle addition were used to approximate the weight fraction of nanoparticles for the composites synthesized in situ.

In Situ Nanocomposite Synthesis
Atactic PMMA was synthesized via free radical polymerization in presence of silica nanoparticles, resulting in a 10% (w/w) nanocomposite (Composite E). The procedure is similar to a previously reported method. MMA (monomer) was put through an activated basic alumina column immediately prior to polymerization to remove inhibitor. Silica nanoparticles were added to 50 mL inhibitor-free MMA in a 125 mL round-bottom flask. After the addition of 42 mg AIBN (initiator), the flask was briefly purged and subsequently bubbled with dry nitrogen for 30 min to remove dissolved oxygen from the solution. To ensure uniform dispersion of the nanoparticles, the resulting mixture was sonicated for 10 min. Under a constant nitrogen purge the suspension was allowed to polymerize at 60 °C in an oil bath until a viscous liquid was observed (ca. 2 h). Identical solutions, except without nanoparticles, were synthesized in parallel for comparison (PMMA-200). Under these conditions, $M_w \approx 200$ kDa, with $M_w/M_n \approx 2$ and $mm = 0.16$, $mr = 0.31$, and $rr = 0.53$. The product was poured into a PTFE Petri dish and dried at room temperature. To remove the residual monomer the composites were annealed for 72 h at 140 °C in vacuo and compression molded at 170 °C into 0.5 mm films. TGA was used to confirm complete removal of monomer. The mass of the recovered composite and known mass of nanoparticle addition were used to approximate the weight fraction of nanoparticles for the composites synthesized in situ.

RESULTS AND DISCUSSION
Using DSC, the $T_g$s of Composites A, C, and D were analyzed after compression molding, as shown in Figure 1. In each case, the $T_g$ was observed to decrease by approximately 5–15 °C. Previous investigations of PMMA films on silica have shown dramatic increases in $T_g$ and therefore, these results appear inconsistent with these prior results. In fact, the observed $T_g$ drops are more consistent with previously reported $T_g$ changes in thin, free-standing PMMA films. However, upon annealing these compo-

Table 1. List of Composites Investigated

<table>
<thead>
<tr>
<th>Composite</th>
<th>Polymer</th>
<th>Nanoparticle</th>
<th>% Filler (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>PMMA-100</td>
<td>Silica</td>
<td>4</td>
</tr>
<tr>
<td>B</td>
<td>PMMA-100</td>
<td>Silica</td>
<td>6</td>
</tr>
<tr>
<td>C</td>
<td>PMMA-100</td>
<td>Silica</td>
<td>8</td>
</tr>
<tr>
<td>D</td>
<td>PMMA-100</td>
<td>Silica</td>
<td>12</td>
</tr>
<tr>
<td>E</td>
<td>PMMA-200</td>
<td>Silica</td>
<td>10</td>
</tr>
</tbody>
</table>
sites at 140 °C for an additional 72 h (in vacuo), the \( T_g \) drops disappeared. This implies that the compression molded samples were not at equilibrium, and that relatively long times (much, much greater than terminal relaxation time\(^{41} \)) are necessary to reach equilibrium.\(^{7,12} \) This is further confirmed with pure PMMA-100 samples prepared identically to the composites, as shown in Figure 2. To test the variability of sample preparation methods on these observations,\(^ {14,17} \) in situ prepared composites (Composite E) were prepared and analyzed using DSC along with pure reference samples (PMMA-200). Again, a drop in \( T_g \) was observed for the compression molded samples, but after additional annealing at 140 °C for 72 h (in vacuo) the drops in \( T_g \) again disappeared. Observing essentially identical behavior for both the composites and the pure homopolymer reference samples implies that attaining equilibrium is not directly tied to attaining equilibrium at the polymer/particle interface. The length scales associated with these changes in \( T_g \) is most likely significantly larger than the individual polymer chains, consistent with the formation of microvoids.

Figure 3 shows FE-SEM images of Composites D and E after further annealing (140 °C for 72 h after compression molding). Dispersion is clearly very good for the PMMA/silica nanocomposites investigated here because of the favorable PMMA/silica interaction (\( \sim 4 \) kT attractive).\(^ {28} \) However, identical thermal behavior is observed for all composites and pure reference samples (see Table 2) regardless of silica loading. This is quite different from previously reported results by Rittigstein and Torkelson,\(^ {14} \) who showed 5–6 °C increases in \( T_g \) with PMMA/silica nanocomposites prepared using MEK as a solvent and very low silica loadings (< 2% w/w 10–15 nm particles), although it should be noted that they used a molecular probe to determine \( T_g \)\(^ {20,21} \) rather than calorimetry. The DSC results presented here may indeed explain the contradictory results previously reported\(^ {8,11,14,17} \) as well as the absence of any trend in the observed \( T_g \) of the as-pressed samples (\( T_{g,AM} \)) as a function of silica loading. Observed \( T_g \)s may be strongly dependent on a combination of variables such as solvent, particle inclusion methods, polymer molecular weight, nanoparticle/polymer interaction, compression molding (void formation), thermal annealing history, and the experimental method used to measure \( T_g \).

Finally, even though the relatively high silica loadings used here yielded no changes in \( T_g \) after proper equilibration was established after long annealing times, the inclusion of silica was observed to provide enhanced mechanical properties (i.e., increased \( E' \)) of the glassy host polymer. Results of the DMA for Composites A–C...
are shown in Figure 4. A trend in $E'$ with increased silica loading is observed in Figure 4 and the results for $E'$ at 30 °C for the composite ($E'_{C,30}$) relative to $E'$ at 30 °C for pure PMMA-100 ($E'_{m,30}$) are shown in Table 3. According to the Halpin-Tsai relationship,\(^1\)

$$\frac{E'_{C}}{E'_{m}} = \frac{1 + \xi \kappa \varphi_p}{1 - \kappa \varphi_p}, \quad (1)$$

where $\varphi_p$ is the volume fraction of particles (fillers), $\xi = 2$ for spheres\(^1\) and

$$\kappa = \frac{E'_{f} / E'_{m} - 1}{E'_{f} / E'_{m} + \xi}, \quad (2)$$

where $E'_{f}$ is the modulus of the filler ($\sim 10^5$ MPa for silica\(^2\)). Because $E'_{f} \gg E'_{m}$, $\kappa \approx 1$ over the range of filler loadings used here for “ideal” mechanical reinforcement. Figure 5 shows a plot of the results in Table 3 as compared to eq 1. The “ideal” value of $\kappa = 1$ does not represent the data well. This is because the Halpin-Tsai model\(^1\) does not account for the strong interaction between the PMMA and silica,\(^2\) which can lead to bridging between the particles (i.e., connection of the particles by polymer chains),\(^3\) thereby causing an increase in the effective $E'_{m}$. This regime is important to note as sample preparation and processing techniques are extremely important in this regime with the highly diminished polymer chain mobility due to confinement.\(^2\)

**Table 2.** $T_g$ measured using DSC (second cooling cycle) for as-molded samples ($T_g^{AM}$) and molded samples annealed for 72 h at 140 °C ($T_g^{140}$)

<table>
<thead>
<tr>
<th>Polymer/Composite</th>
<th>$T_g^{AM}$ (°C)</th>
<th>$T_g^{140}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA-100</td>
<td>103</td>
<td>109</td>
</tr>
<tr>
<td>Composite A</td>
<td>96</td>
<td>111</td>
</tr>
<tr>
<td>Composite C</td>
<td>104</td>
<td>109</td>
</tr>
<tr>
<td>Composite D</td>
<td>101</td>
<td>108</td>
</tr>
<tr>
<td>PMMA-200</td>
<td>105</td>
<td>113</td>
</tr>
<tr>
<td>Composite E</td>
<td>105</td>
<td>115</td>
</tr>
</tbody>
</table>

Figure 3. FE-SEM images depicting (a, b) Composite D and (c, d) Composite E. Clearly, the 14 nm silica particles are well-dispersed for both preparation methods because of the attractive interaction between the PMMA and silica. Interparticle spacings have been approximated to be 169 ± 81 nm and 178 ± 71 nm for Composites D and E, respectively, using image analysis.
CONCLUSIONS

We have probed the influence of sample preparation and processing on the observed \( T_g \) changes in polymer nanocomposites, namely those formed from PMMA and 14 nm fumed silica. Two types of sample preparation were investigated: (i) solution mixture of PMMA and silica in MEK and (ii) \textit{in situ} synthesis of PMMA in the presence of silica. After removing all solvent or monomer, as confirmed using TGA, and after compression molding, drops in \( T_g \) of 5–15 °C were observed for all composites (2–12% w/w silica) and even pure polymer reference samples (PMMA-100 and PMMA-200). However, after additional annealing for 72 h at 140 °C, all \( T_g \) drops disappeared, and the intrinsic \( T_g \) of bulk, pure PMMA was again observed. This is in agreement with previous investigations, where non-equilibrium trapped voids were attributed to such observations.\(^8,14,16\) This is proof that full equilibration of the composites must be achieved for true changes in the thermal properties to be probed. Finally, the mechanical properties (i.e., \( E' \)) of the PMMA composites were probed using DMA. Results of the composites containing PMMA-100 show mechanical reinforcement upon addition of filler, even though no \( T_g \) changes were observed. Therefore, the addition of filler to polymer matrices can indeed influence the mechanical properties of the glassy polymer host, even though changes in other material properties, such as \( T_g \),\(^1\) could not be observed. The sample preparation history and the methods used to probe changes strongly influence the conclusions drawn about the influence of the nanoparticles on the materials properties.

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### REFERENCES AND NOTES