Influence of drying procedure on glass transition temperature of PMMA based nanocomposites

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Abstract A literature review of poly(methyl methacrylate) (PMMA) nanocomposites shows inconsistent results regarding the influence of the addition of nanofillers on the mobility of the system. In academic research, solvent based preparation methods are often used to prepare nanocomposites with the aim to obtain a good and controlled dispersion. However, little attention is paid to the influence of the used solvent on the properties of the nanocomposites. We show that in PMMA nanocomposites prepared via solution casting from different solvents, the apparent decrease in glass transition temperature is caused by insufficient drying and that when an adequate drying procedure is used, an increase in glass transition temperature is always observed.

Keywords Nanocomposites, Polymer, Silica, Glass transition temperature, Solution casting, Processing

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Introduction

It is now generally accepted that the introduction of nanofillers alters the mobility of the polymer matrix and that, as a consequence, the dynamics of polymer nanocomposites are significantly different from the neat polymer. In summary, systems with strong polymer filler interactions show a decreased mobility while in systems where the interactions are weak or non-existing an increased mobility is observed. The glass transition temperature (Tg) is a relatively easy material property to measure and it is often used as a measure of changes of the dynamics in a particular system. For a polymer such as poly(2-vinylpyridine) with a pronounced polarity, large increases in the glass transition temperature were found in composites with silica as well as alumina nanoparticles.¹,² For apolar polymers such as poly(styrene) (PS) the absence of polar (side)groups implies a weak interaction with polar fillers and in these systems a decrease in glass transition temperature is normally observed with the introduction of nanofillers.¹⁻³ Following the reasoning presented above, a polymer such as poly(methyl methacrylate) (PMMA) is also expected to show an increase in glass transition temperature with the addition of a polar filler such as silica. However, contradictory results can be found in literature, where both increased, unchanged and decreased values of the glass transition temperature were reported. At this point, it is relevant to point out that solvent based methods are commonly employed to overcome dispersion issues in polymer nanocomposites. The polymer and the filler are dissolved/dispersed in a common solvent and the solvent is subsequently removed by solvent casting, spin coating or precipitation in a non-solvent. It is known that, similar to non-interacting fillers, also small diluents, molecules such as water or other solvents can significantly reduce the glass transition temperature of a polymer. However, even though solvent based methods are commonly applied to prepare nanocomposites, the literature is scarce on the potential effects of solvent retention on the properties of the obtained nanocomposites. The objective of this article is to discuss the influence of solvent retention on the glass transition temperature of PMMA based nanocomposites. First, relevant results from literature are presented. This is followed by a discussion on results from recent experiments from our group.
Literature review

Glass transition temperature in PMMA/silica nanocomposites

Many groups reported an increase of the glass transition temperature in PMMA/silica nanocomposites\(^4\)-\(^11\) and the general explanation given is that strong interactions between the hydroxyl groups at the silica surface and oxygen of the acrylate groups reduce the mobility of the polymer chains, thereby increasing the \(T_g\). Some groups, however, reported an unchanged value, or even a decrease in \(T_g\) with increased filler loading.\(^2\),\(^12\),\(^13\) The explanations are varying. Ash et al.\(^14\) attributed the decrease to residual solvent after the \textit{in situ} polymerization, Fu et al.\(^13\) stated that the polymer was in a non-equilibrium state after drying and that entrapped air increased the free volume in the polymer, thereby increasing the mobility and lowering the \(T_g\). They showed that after annealing at elevated temperatures, a \(T_g\) similar to the one of the pure polymer was found. Rittigstein and Torkelson\(^2\) observed a decrease in \(T_g\) when the samples were prepared by solvent casting in acetic acid and attributed this decrease to the screening of the interaction between the silica and the polymer by the acid molecules. When the samples were prepared in methyl ethyl ketone (MEK), no such screening took place, and an increase in \(T_g\) was found.

Glass transition temperature in other PMMA based nanocomposites

Several other nanosized particles have also been used in PMMA based nanocomposites. Ash et al.\(^14\),\(^15\) prepared PMMA/alumina composites \textit{via in situ} polymerization of MMA in the presence of alumina particles. At low filler loadings, the glass transition temperature remained unchanged, but upon increasing the loading, a decrease in \(T_g\) was found. The onset of the decrease was found to be dependent on the size of the filler, but when \(T_g\) was plotted as a function of the surface to volume ratio the curves overlapped. The same group also showed that if the particles are coated, the reduction disappears. A decrease of the glass transition temperature in alumina based PMMA nanocomposites was also confirmed by Rittigstein and Torkelson.\(^2\) Also gold particles have been used as filler material in PMMA composites. Srivastava and Basu\(^15\) prepared different sizes of gold particles \textit{via in situ} preparation of gold particles in the presence of PMMA. These PMMA capped particles were then mixed with PMMA homopolymer by using both good and bad solvents. Both increase and decrease in \(T_g\) were observed and were found to depend on the width of the interface region between the polymer matrix and the filler as calculated from SAXS data. This behavior was explained in terms of sharpness of the interface. A thin interfacial region gives a very sharp interface and the mean chain segment relaxation is dominated by the relaxation in the surface layer, which in this case is increased due to the non-interacting filler, and an overall decrease in \(T_g\) is observed. If, on the other hand, the interface is very diffuse, the relaxation is dominated by chain segments further away from the filler, which due to the presence of the filler have a lower mobility and an increase in \(T_g\) compared to an unfilled system is therefore observed.

In general, the changes in glass transition temperature in composites based on spherical or near spherical fillers are not so large, even at high filler loadings. In the case of anisotropic fillers, the situation is quite different. In nanocomposites made from PMMA and graphite prepared by Ramanathan et al.\(^17\) increases in the glass transition temperature of up to almost 40°C were observed. Also in PMMA/clay nanocomposites, large increases were found.\(^18\),\(^19\)

In Table 1, an overview of PMMA based nanocomposites and their corresponding glass transition temperatures can be found. As stated before, an increase in the glass transition temperature is observed in most cases. There are, however, some systems where a decrease was observed. Most notable are the samples spin coated in acidic acid which showed a decrease of almost 20°C.\(^5\) In the table, the drying procedures applied before the analysis are also listed. It is observed that for samples showing large \(T_g\) reductions, no or very short drying procedures were applied and it can therefore be hypothesized that the observed decreases could also be due to remaining solvent. Therefore, also the influence of solvent retention in polymer films is included in the literature review.

Related research on glass transition temperature in thin films

Another research area where the effect of confinement on the glass transition temperature has been discussed thoroughly is the area of thin and ultrathin films. For more details, the reviews of the topic by Forrest and Dalnoki-Veress\(^25\) and Alcoutlabi and McKenna\(^26\) are recommended as only the main findings are cited here below. It was shown by several groups that the glass transition temperature in a free standing thin film decreases with decreasing film thickness.\(^27\)-\(^31\) Most of the research focused on thin films of PS, but a decrease in glass transition temperature was also observed in free standing PMMA films, even though the reduction is small compared to PS films.\(^29\),\(^30\) The decrease in the glass transition temperature was attributed to an enhanced mobility at the surface of the film, and as the thickness of the film is decreased, the effect on the mobility of the whole sample is naturally increased. For supported films, the situation is different. It was shown that the glass transition temperature can increase,\(^32\)-\(^36\) decrease\(^33\)-\(^42\) or remain unaltered\(^29\),\(^32\) depending on the interaction between the film and the substrate upon which the film was cast.\(^43\) The magnitude of the shift was shown to depend not only on the thickness of the film, but also on the type of polymer and substrate. These results are in analogy with findings in nanocomposite research that show that the magnitude of the shift in glass transition temperature depends on the strength of the polymer–filler interaction. Supported thin films have therefore been successfully used as a simplified model for nanocomposites where the thickness of the film between supports can be assumed to represent the interparticle distance in the composite.\(^1\),\(^3\) By varying the thickness of the film, different filler loadings can be simulated. For PMMA films, an increase in glass transition temperature with decreased film thickness is generally observed, even though a decrease was occasionally observed.
<table>
<thead>
<tr>
<th>Group</th>
<th>Composite</th>
<th>Filler content (wt-%)</th>
<th>ΔT&lt;sub&gt;G&lt;/sub&gt; (°C)</th>
<th>Preparation method</th>
<th>Solvent</th>
<th>Drying time and temperature</th>
<th>Analysis method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Garcia et al.4</td>
<td>PMMA/silica</td>
<td>0–35</td>
<td>10 (max.)</td>
<td>Solution mixing</td>
<td>Toluene</td>
<td>12 h at 140°C</td>
<td>DSC</td>
</tr>
<tr>
<td>Moll and Kumar11</td>
<td>PMMA/silica</td>
<td>0–62.5</td>
<td>7 (max.)</td>
<td>Solution mixing</td>
<td>MEK</td>
<td>48 h at 150°C</td>
<td>DSC</td>
</tr>
<tr>
<td>Jouault et al.20</td>
<td>PMMA/silica</td>
<td>10 vol.-%</td>
<td>1 (at 5 vol.-%)</td>
<td>Solution mixing</td>
<td>DMAc</td>
<td>8 days at 130°C</td>
<td>DSC</td>
</tr>
<tr>
<td>Hub et al.12</td>
<td>PMMA/silica</td>
<td>4</td>
<td>7* 2**</td>
<td>Solution mixing</td>
<td>MEK</td>
<td>*Dried for 72 h at 140°C</td>
<td>DSC</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8</td>
<td>1* 0**</td>
<td></td>
<td></td>
<td>**Annealed for 72 h more at 140°C</td>
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<tr>
<td></td>
<td></td>
<td>12</td>
<td>−2* 1**</td>
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<td></td>
<td></td>
<td>10</td>
<td>0* 2**</td>
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<tr>
<td>Chinthamani-peta et al.9</td>
<td>PMMA/silica</td>
<td>0–23</td>
<td>~15 (max.)</td>
<td>In situ polymerization</td>
<td>THF</td>
<td>12 h at 80°C</td>
<td>DSC/DMTA</td>
</tr>
<tr>
<td>Zhang et al.10</td>
<td>PMMA/silica (vinyl functionalized)</td>
<td>0–10</td>
<td>13 (max.)</td>
<td>In situ polymerization</td>
<td>Water</td>
<td>24 h at 60°C</td>
<td>DSC</td>
</tr>
<tr>
<td>Hu et al.6</td>
<td>PMMA/fumed silica</td>
<td>0–4</td>
<td>~15 (max.)</td>
<td>In situ polymerization</td>
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<td></td>
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<td></td>
<td></td>
<td>1 h at 120°C</td>
<td>DSC</td>
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<tr>
<td>Sargsyan et al.8</td>
<td>PMMA/silica</td>
<td>0–65</td>
<td>6 (max.)</td>
<td>In situ preparation of silica</td>
<td>Water</td>
<td>8 h at 150°C</td>
<td>DSC/DMA</td>
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<td>Li et al.5</td>
<td>PMMA/silica</td>
<td>0–15, 37</td>
<td>DSC: no change</td>
<td>DSC: no change</td>
<td></td>
<td>12 h at 60°C + 12 h</td>
<td>DSC/DMTA</td>
</tr>
<tr>
<td></td>
<td>PMMA/silica</td>
<td>0–28</td>
<td>18 (max.)</td>
<td></td>
<td></td>
<td>110°C</td>
<td></td>
</tr>
<tr>
<td>Ferguson61</td>
<td>PMMA/silica</td>
<td>0–2</td>
<td>±2</td>
<td>DSC: 6 (max.)</td>
<td>THF/chloroform</td>
<td>5 days at 65°C</td>
<td>DMA</td>
</tr>
<tr>
<td>Fu et al.13</td>
<td>PMMA/silica</td>
<td>0–21.9</td>
<td>DSC: 6 (max.)</td>
<td></td>
<td>THF</td>
<td>1 day at RT</td>
<td>DSC</td>
</tr>
<tr>
<td>Kyriakos et al.21</td>
<td>PMMA/silica</td>
<td>0–5</td>
<td>DSC: ~14 (max.)</td>
<td></td>
<td>THF</td>
<td>6 h at 40°C + 8 h at</td>
<td>DSC/TSDC</td>
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<td></td>
<td></td>
<td></td>
<td>Fluorescence: ~10 (average)</td>
<td></td>
<td></td>
<td>140°C + 2 h at 120°C</td>
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<tr>
<td>Parker et al.22</td>
<td>PMMA/silica</td>
<td>0–5</td>
<td>DSC: ~14 (max.)</td>
<td>Solution mixing of grafted silica particles followed by precipitation</td>
<td>DMAc</td>
<td>Drying at 80°C</td>
<td>DSC/fluorescence</td>
</tr>
<tr>
<td>Rittigstein and Torkelsson7</td>
<td>PMMA/silica (10–15 nm)</td>
<td>0–0.6 vol.-%</td>
<td>−18 (max.)</td>
<td>Spin coating in acetic acid</td>
<td>Acetic acid</td>
<td>&gt;21 days in fumehood</td>
<td>Fluorescence</td>
</tr>
<tr>
<td></td>
<td>PMMA/silica (10–15 nm)</td>
<td>0–0.6 vol.-%</td>
<td>+6 (max.)</td>
<td>Spin coating in MEK</td>
<td>MEK</td>
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<tr>
<td></td>
<td>PMMA/aluinas (47 nm)</td>
<td>1–10 vol.-%</td>
<td>−5 (max)</td>
<td>Spin coating in MEK</td>
<td>MEK</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ash et al.14,15</td>
<td>PMMA/aluinas (39 nm)</td>
<td>1–5</td>
<td>−24 (max.)</td>
<td>In situ polymerization</td>
<td></td>
<td>2 h at 115°C</td>
<td>DSC/DMTA</td>
</tr>
<tr>
<td></td>
<td>PMMA/aluinas (39 nm)</td>
<td>1–5</td>
<td>0</td>
<td></td>
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</tr>
<tr>
<td>Pandis et al.23</td>
<td>PMMA/silver</td>
<td>0–0.5</td>
<td>−9 (max.)</td>
<td>In situ polymerization</td>
<td>Acetone, toluene, acetone/water</td>
<td>n.a.</td>
<td>DSC/DMA</td>
</tr>
<tr>
<td>Srivastava and Basu16</td>
<td>PMMA/gold</td>
<td>0–8</td>
<td>+6 (42 Å grafts)</td>
<td>In situ polymerization of the particles in presence of PMMA and redistribution of grafted particles in PMMA matrix via solvent mixing</td>
<td>Deionized water</td>
<td>n.a.</td>
<td>DSC/DMA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>−22 (1.4 Å grafts)</td>
<td></td>
<td></td>
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<tr>
<td>Meneghetti and Qutubuddin18</td>
<td>PMMA/MMT</td>
<td>10</td>
<td>18/16</td>
<td>Emulsion polymerization (exfoliated)</td>
<td>Deionized water</td>
<td>n.a.</td>
<td>DSC/DMTA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>8/8</td>
<td>In situ polymerization (intercalated)</td>
<td></td>
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<tr>
<td>Yeh et al.19</td>
<td>PMMA/MMT</td>
<td>0–5</td>
<td>22 (max.)</td>
<td>In situ emulsion polymerization</td>
<td>Water</td>
<td>24 h at 50°C</td>
<td>DSC</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0–5</td>
<td>16 (max.)</td>
<td>Solution mixing</td>
<td></td>
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</tbody>
</table>

*ΔT<sub>G</sub> is the change in glass transition temperature relative to PMMA bulk polymer.*
Influence of solvent on glass transition temperature in thin films

In thin film research, the films are almost exclusively prepared by spin casting where centrifugal forces contribute to a fast solvent evaporation and enables formation of homogeneous thin films down to the thickness of a few nanometres. However, since vitrification of the film generally occurs before solvent removal, complete solvent removal is not obtained in the spin casting process. For an amorphous polymer such as PMMA, with a high glass transition temperature, it was shown that a glassy material is obtained once the solvent fraction in the film is less than 0.19, and the formation of the glass will considerably decrease the evaporation rate of the solvent.44,45

The amount of retained solvent in different cast films was studied by several groups.44,45,47–49 García-Turiel and Jérôme used gas chromatography to study solvent retention in PS films spin cast from toluene. They concluded that while in thick films, there are only a few percent of solvents left after annealing at a temperature above the glass transition temperature, the amount of retained solvent can be much higher in thin films. Moreover, they found that the solvent molecules are mainly located at the interface between polymer and substrate. Their findings were supported by the observations of Perlich et al.47 who used neutron reflectometry to assess the amount of retained toluene in spin cast PS films annealed at different temperatures, both above and below the glass transition temperature. They found that solvent retention was molecular weight dependent and increased with increasing molecular weight. Even though annealing at temperatures above the glass transition temperature reduced the amount of solvent in the samples, there was always residual solvent present in the samples, also after annealing.

Zhang et al.48 also used neutron reflectometry to study the amount of toluene in spin coated films of both PS and PMMA. They observed that, while the PS films appeared solvent free already after drying at room temperature, PMMA films of a thickness of 121 nm contained 0.8 vol.% of toluene even after two annealing steps. They also found that the toluene content in the PMMA films was thickness dependent, with a larger amount of toluene retained in the thinner films. This was attributed to strong interactions between the polymer, the solvent and the substrate upon which the polymer was cast. Strong interactions decrease the mobility of the PMMA and thus, the diffusivity of the solvent out of the polymer.

While many groups focused on the quantification of the amount of solvent in the films, less researchers reported on the influence of the solvent retention on the properties of cast films. In two different papers, Patra et al. studied the thermal and mechanical properties of PMMA films prepared from different solvents.49,50 Their samples were dried for 4 or 15 days respectively at room temperature before tested with DSC. When the films were cast from toluene, THF or chloroform the glass transition temperatures were 20–35 °C lower than bulk values, while it was 8 °C higher in films cast from DMF. They explained the increase in the latter case with the ability of the solvent to form strong bonds with the carbonyl groups of the polymer thereby strengthening it. Bistac and Schultz studied the mobility in solution cast films
of PMMA using DSC and dielectric spectroscopy.\textsuperscript{51} They also used different solvents and concluded that the type of solvent largely influences the $\alpha$ and $\beta$ relaxation temperatures of samples dried at room temperature for 48 h. In contradiction to Patra et al. who found similar values of the glass transition temperature for samples cast from toluene or chloroform, Bistac and Schultz found values differing by almost 20°C. Glass transition temperatures were 12 and 33°C lower than in bulk PMMA respectively. The difference was explained by the difference in strength of the acid base interaction between the PMMA and the different solvent molecules. These results were confirmed by Serghei and Kremer, who found a 37°C decrease in the dynamic glass transition temperature in films solvent cast from chloroform when no annealing was performed. However, after annealing at 127°C for 12 h under nitrogen atmosphere, the bulk PMMA dynamics were recovered.\textsuperscript{52}

Another study of interest was made by Ellison et al.\textsuperscript{53} and concentrated on the effect of small molecular diluents on the thickness dependence of the glass transition temperature in different films. They showed that the confinement effect in spin coated thin films could be reduced. This was shown both for non-interacting PS films which would normally show a decrease in glass transition temperature and for poly(2-vinylpyridine), a polymer that is very strongly interacting with the substrate, which displayed an increase in glass transition temperature. In the former, a thickness independent glass transition temperature equal to that of the bulk polymer was found and in the latter only a very modest increase was found compared to an undiluted system. Yet another study on the water sorption of Poly(vinyl acetate) thin films shows that the water uptake suppresses the confinement effect noted in dry films (decrease in glass transition temperature with decreasing film thickness), and that the wet samples have a glass transition temperature that is actually higher than for dry samples.\textsuperscript{54} It was also shown that annealing at elevated temperatures for more than 300 min was necessary to obtain dry samples.

In addition to the solvent retention effects, it is well known that the fast solvent evaporation used in the spin casting process can result in non-equilibrium conformations of the polymer chains and cause residual stresses which might contribute to altered dynamics.\textsuperscript{55,56} The amount of residual stresses and the annealing time required to remove them depends on the solvent quality and the relaxation time towards an fully unperturbed state is very long.\textsuperscript{57}

**Influence of solvent on glass transition temperature in nanocomposites**

Solvent based methods are also commonly applied in the preparation of nanocomposites. In order to improve the dispersion, the filler and the polymer are dispersed in a common solvent and thereafter the solvent is evaporated. Even though literature on nanocomposites is abundant, there is little information on how sample preparation affects the properties of the obtained nanocomposites. Sen et al. prepared PS samples by solvent casting and a fast evaporating method, and they concluded that the traces of solvent (around 0.2 wt-%) left in the samples after annealing were not responsible for the decrease in the glass transition temperature found in the solvent cast samples. The explanation was that the samples prepared via their fast evaporation route contained similar amounts of residual solvent, but showed no glass transition temperature reduction.\textsuperscript{58} For a very different system, i.e. a fluororubberomer filled with carbon black and swollen in methyl ethyl ketone, it was shown that even at very high filler loadings (up to 35 wt-%), the filler did not influence the glass transition temperature of the system, which was solely dependent on the solvent fraction.\textsuperscript{59} Ferguson worked on a more relevant system for our research.\textsuperscript{60} He prepared PMMA films by solvent casting from different solvents where, in order to account for ethanol formation during the sol–gel process used to form silica from TEOS, also ethanol was added to the mixture. The influence of the drying procedure on properties such as the glass transition temperature was thereafter studied. Samples were dried in an oven at 65°C for several days and he concluded that it was impossible to remove all the solvent at this temperature. After 6 days of drying, about 4 wt-% of solvent was still present. The obtained nanocomposites showed an increase in glass transition temperature with increasing filler content, in accordance with most trends in literature, but it has to be mentioned that all the obtained values were lower than those found for reference PMMA films prepared from a solution without added ethanol.

In conclusion, it has been shown for both nanocomposites and thin films, that when an interacting filler or surface is present, a moderate increase in glass transition temperature in PMMA based systems can be expected. If the polarity of the matrix is increased, a larger increase in glass transition temperature is observed and if the polarity is decreased, the opposite is observed. There are, however, some examples where a decrease in glass transition temperature was found in PMMA composites. With the reasoning provided above, these findings are rather surprising. On the other hand, it was shown that solvents used in sample preparation are generally difficult to remove and a lower glass transition temperature as compared to the bulk polymer is often observed. It is therefore hypothesized that solvent retention is responsible for many of the observed reductions in glass transition temperature. In order to investigate the influence of the fillers on the properties of the prepared composite, a proper drying procedure is therefore needed. In the following section, experimental evidence for this hypothesis is put forward and it is shown that extensive drying is needed in order to observe the true influence of filler addition.

**Experimental**

**Materials**

PMMA V82S from Arkema, France, and the colloidal silica suspension from Nissan Chemicals, Japan in different solvents (MEK, toluene) were used as received. MEK, toluene, chloroform and acetone, all from Biosolve, Valkenswaard, the Netherlands, were used as received.

**Sample preparation**

The polymer was dissolved in the chosen solvent and for the nanocomposite samples colloidal silica in the same solvent.
was added to the dissolution. The samples were left on a shaker for two nights in order to fully dissolve and mix. Samples were subsequently poured into Petri dishes and left to evaporate at room temperature. Subsequently, they were dried in a vacuum oven under nitrogen flow at different temperatures and for varying periods of time.

**Characterization techniques**

A Q500 TGA from TA Instruments was used to confirm the filler loading in the samples and to assess how much solvent was present in the films. 10–15 mg of sample was heated to 600°C at a rate of 10°C min⁻¹ under nitrogen atmosphere. For the determination of the solvent content after drying, the samples were heated to 150°C at a rate of 10°C min⁻¹ and thereafter kept isothermally for 90 min. Thereafter, the samples were heated up to 450°C. The solvent content was set to be equal to the weight loss at 300°C. The molecular weight distributions both before and after drying experiments were determined using a size exclusion chromatography set-up from Waters with a Waters 510 pump and a Water 712 WISP chromatograph with an injection volume of 50 μL. The state of dispersion of the silica particles in the polymer matrix was studied with transmission electron microscopy. The measurements were performed using a FEI Tecnai 20 microscope, operated at 200 kV. Ultrathin sections were microtomed at room temperature and put on a copper grid with a carbon support layer. For the determination of the glass transition temperature via DSC measurements, a Q1000 DSC from TA Instruments was used. The samples were heated from room temperature to 200°C at a rate of 10°C min⁻¹ and held at that temperature for 5 min. Thereafter, they were cooled to room temperature, also at a rate of 10°C min⁻¹. The cycle was repeated once. The glass transition temperature was determined from the second heating run. In addition, a Q800 DMA, also from TA Instruments, was used to determine the glass transition temperature. The samples were undergoing a sinusoidal temperature at the maximum of the storage modulus (E’') peak.

**Results and discussion**

First, the influence of residual solvent on PMMA films will be discussed and in a second step, the corresponding nanocomposites will be considered. Some characteristics for the different solvents used in the sample preparation are listed in Table 2.

The samples were solvent cast into Petri dishes, left to evaporate in a fume hood for 1 week and thereafter dried in a vacuum oven at 120 or 140°C for one to five nights. Directly after solvent evaporation in the open air, DMA measurements were performed on the as cast films. The temperature at the maximum of tan δ and E'' are reported in Fig. 1 together with the solvent content as measured from TGA experiments. Even though the maximum of tan δ often is used as an equivalence to the glass transition temperature, E'' is corresponding better to the values obtained in DSC measurements and will hereafter be used as a measure of the glass transition temperature.

In Fig. 1, it is observed that all the samples still contain more than 10 wt-% solvent after 1 week evaporation at room temperature, and that in chloroform, there is as much as 20 wt-% solvent left after the evaporation step. Moreover, the glass transition temperatures in the as cast films are far below the temperature measured for neat PMMA (~117°C) and it decreases below 50°C in samples prepared from chloroform. Bistac and Shultz attributed the higher solvent retention in PMMA films prepared in chloroform compared to films prepared in toluene or acetone to the strong acid base interactions between the basic PMMA and the acidic chloroform. Acetone and toluene belong to a group of lightly basic solvents and do therefore only present weak interactions with PMMA. Similar results were obtained by Patra et al., who attributed the difference between toluene and chloroform to a weaker interaction with the PMMA molecules in the former. From these results, it is evident that the drying of samples at elevated temperatures before measurements is important, and that the drying procedure needs to be carefully reviewed when the solvent is changed.

Figure 2a shows the TGA traces measured on films prepared using MEK as solvent. Directly after solvent evaporation in air the samples contain a visible amount of solvent, but drying at 120°C for one night reduces this amount significantly and further drying does bring modest improvement. When the drying is performed at 140°C, the sample already appears dry after one night in the oven.

### Table 2 Presentation of different materials used in drying experiment

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Glass transition temperature (°C)</th>
<th>Density (g cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEK</td>
<td>80</td>
<td>0.81</td>
</tr>
<tr>
<td>Toluene</td>
<td>110</td>
<td>0.87</td>
</tr>
<tr>
<td>Acetone</td>
<td>56</td>
<td>0.79</td>
</tr>
<tr>
<td>Chloroform</td>
<td>61</td>
<td>1.48</td>
</tr>
<tr>
<td>PMMA</td>
<td>118</td>
<td>1.18</td>
</tr>
</tbody>
</table>
Fig. 2b, TGA results for the samples prepared in toluene are presented. After solvent evaporation, there is still a considerable amount of solvent present in the samples. Drying at 120 °C for one night removes some of the solvent and further drying at 120 °C does decrease the solvent content further but this is still not to an acceptable level. Drying overnight at 140 °C is more efficient than drying for five nights at 120 °C and further drying will reduce the solvent content, but only after three nights at 140 °C the sample contains less than 1 wt-% solvent.

In Fig. 3a, the solvent content after various times of drying and in Fig. 3b, the corresponding glass transition temperatures for samples prepared with different solvents are presented. When drying is carried out at elevated temperatures, the mobility of the solvent becomes important. Toluene has a high boiling point and is therefore less mobile than the other solvents at the drying temperature and the complete solvent removal is only possible when the drying temperature is increased to 140 °C. Solvents with low boiling points such as acetone and chloroform are easily removed at both drying temperatures. In Fig. 4, the glass transition temperature is plotted as a function of solvent content for the different solvents. The type of solvent determines how easily the residual solvent can be removed from the sample, but all the data can be collapsed onto a curve showing a linear dependence of the glass transition temperature on the solvent content. Only when the samples contain less than 1 wt-% of solvent, the glass transition temperature of the neat polymer is recovered.

Influence of silica on glass transition temperature of polymer nanocomposite films

Samples with 5 wt-% of silica was prepared using either MEK or toluene as a solvent. In Fig. 5, the transmission electron microscopy pictures of the as prepared systems can be found. The use of these two solvents results in a very different state of dispersion. The samples prepared in MEK show a good dispersion with individually dispersed particles, while the silica particles in the samples prepared using toluene are highly agglomerated. In the same figure, samples dried for 5 days at 140 °C are also presented. The state of dispersion is similar to the samples measured before drying, indicating that
the drying procedure has no influence on the state of the dispersion to the samples and that changes in glass transition temperature upon drying have a different origin.

The glass transition temperature as measured by DMTA and the solvent content in the as cast samples of samples containing 5 wt-% of silica can be seen in Fig. 6. The data of the unfilled samples are added as reference. The filled and unfilled samples contain similar amounts of solvent, and the samples prepared in toluene contain more solvent than the samples cast in MEK. All the samples do again show a lower glass transition temperature than the neat PMMA (117 °C) and there is no significant effect of filler addition on the glass transition temperature, as measured from the maximum of the $E'$. The glass transition as determined from the maximum of the tan δ is also added as a reference. It is noted that the tan δ of the unfilled MEK sample is much higher than the tan δ of the filled samples, and that a large decrease upon filler addition would be measured if this peak would be used to quantify the glass transition temperature. This result shows that not only the sample preparation but also the analysis method and the interpretation of the data are important issues to consider in order assessing the real effect of filler addition.

In Fig. 7a, the difference in glass transition temperature between the neat film and the nanocomposite prepared in the same solvent is presented as a function of the drying time. For samples prepared in MEK, a modest increase in glass transition temperature with the increase in drying time is observed, which is similar for both drying temperatures. However, for the sample dried in toluene, a decrease in glass transition temperature upon filler addition is initially observed, whereas a large increase is observed in samples dried at the higher temperature. After 3 days of drying at either temperature, a similar trend as in the MEK samples is observed. This is in line with the results presented by Fu et al. who showed that an initial decrease in the glass transition temperature disappeared after the samples was annealed for an additional time at 140 °C.13 The glass transition temperature as a function of solvent fraction is presented in Fig. 7b. The difference in glass transition temperature is increased with decreasing amount of residual solvent and that for both the solvents used, an increase in glass transition temperature upon filler addition is found when the samples are dry, consistent with the majority of the results in literature (Table 1).

Finally, in Fig. 8, the differences in glass transition temperature between PMMA/silica nanocomposites with different filler contents and neat PMMA are presented. The samples prepared in MEK (dried for two nights at 120 °C) show a good dispersion and a modest increase in glass transition temperature with increasing filler content. The
samples prepared in toluene (dried for two nights at 120 °C and an additional two nights at 140 °C) do also show a modest increase in glass transition temperature as compared to the neat polymer. However, as shown in Fig. 5, samples prepared from a toluene solution are prone to agglomeration and, as a consequence, the glass transition temperature is decreasing again upon increased filler content.

Conclusions

In this paper, we show that solvent retention in nanocomposites containing PMMA and silica nanoparticles can lead to a decrease in the glass transition temperature. This effect counteracts the effect of the filler addition and might lead to misinterpretations of the real influence of the filler addition. The drying step in a process method including the use of solvents has a major influence on the properties of the prepared nanocomposites and has to be carefully adapted to the employed polymer–filler–solvent system. It is concluded that improper matching of the drying time and temperature with the investigated polymer–filler system can partly explain the scattered results of the influence of filler addition on the glass transition temperature reported in the literature.

Conflicts of interest

The authors have no conflicts of interest to declare.

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References

Influence of drying procedure on PMMA based nanocomposites


