Toughening of epoxy resin with poly(methyl methacrylate) grafted silica core-shell particles

Peng Yang, Liyuan Zhu, Xue Xia, Haitao Wang,* Qiangguo Du and Wei Zhong*

The key laboratory of Molecular Engineering of Polymers, Ministry of Education and Department of Macromolecular Science, Fudan University, Shanghai 200433, China. fax: +86-21-65640293. e-mail: weizhong@fudan.edu.cn; wanght@fudan.edu.cn.

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Abstract: Structurally well-defined core-shell particles were prepared by modifying the surface of silica with initiators for atom transfer radical polymerization (ATRP), and followed by using these initiator-modified particles as ATRP macro-initiators for methyl methacrylate. These particles were characterized with Fourier-transform infrared spectroscopy (FT-IR), thermo-gravimetric analysis (TGA) and scanning electron microscopy (SEM). The tethered polymer chains on the grafted silica particles were cleaved with hydrofluoric acid and measured with gel permeation chromatography (GPC). The results showed that poly(methyl methacrylate) (PMMA) chains grew from the particle surfaces in form of individual particles comprising of a hard silica core and a well-defined, densely grafted outer polymer layer. Diglycidyl ether of bisphenol-A (DGEBA) based epoxy resin was toughened with various doses of the synthesized PMMA-grafted silica particles. Resulting composite materials were characterized by tensile testing, SEM, dynamic mechanical analysis (DMA) and TGA. The results indicated that the incorporation of the core-shell particles improved the toughness of the composites without any significant deterioration of its thermal properties.

Introduction

For thermsetting polymers such as epoxy resins, which are normally used as matrices in composite materials for a wide range of electric, electronic, automotive and aerospace applications, toughness is a very important issue. Highly cross-linked epoxy matrices, however, often behave undesirably brittle because plastic deformation is constrained. Moreover, the local stress concentration may initiate cracks which lead to spontaneous failure. It is therefore a primary aim of many researchers to provide epoxy with higher toughness.

Toughening of the resin either by admixing suitable toughening agents or chemical modification usually improves the energy absorption capacity. Such toughening agents are, for example, rubber [1], thermoplastics [2], core-shell particles [3], liquid crystals [4], hyperbranched polymers [5, 6], inorganic nanoparticles [7, 8], and their combinations. In recent years, some toughening mechanisms were proposed to explain the improvement in toughness of epoxy resins after application of various toughening agents. Some of the essentials mechanisms can be summarized as microcracking mechanism [9], crack pinning mechanism [10, 11], crack deflection mechanism [12], and crack bridging mechanism [13, 14]. However, the commonly applied traditional toughening agents often have to compromise other properties such as storage modulus and thermal properties. Application of the core-shell particles offers several advantages [15, 16], such as an increase in the toughness of
epoxy resins without significant deterioration in their thermo-mechanical properties, better dispersion of the particles, and reduction of the internal stress of the resins.

There are several methods for grafting polymer chains onto particle surface in order to produce core-shell particles. They involve grafting a polymer chain through either covalent linkage to the surface [17], or from a particle surface modified with polymerization initiators [18-20]. The “grafting from” route, which consists of immobilizing initiator molecules onto the surface of the particles and performing the polymerization at the particle surface, provides maximum structural control. A controlled radical polymerization method such as atom transfer radical polymerization (ATRP) [21] is preferred, because such methods control the molecular weight, molecular weight distribution, and structure of the resulting polymer. This technique has been proven [22, 23] to be effective in production of polymers of precise dimension and functionality.

This paper presents preparation of core-shell particles comprised of a silica core and a well-defined, densely grafted PMMA layer and their application for toughening epoxy resin without any significant deterioration of its thermal properties. Effects of these particles on the tensile strength, tensile energy absorption, thermo-mechanical properties, and thermal stability of the composites were investigated in terms of their size, grafted PMMA amount, and their content in epoxy resin.

Results and discussion

Characterization of PMMA-grafted silica

FT-IR spectra of the silica after MMA polymerization gave clear evidence for polymer grafting (Fig. 1). The band of the hydroxyl stretching modes at 3417cm⁻¹ and Si-O stretching modes at 1105cm⁻¹ belonged to silica. The appearance of the carbonyl vibration band at 1735cm⁻¹ was observed after the polymerization. It originated from grafted PMMA. Meanwhile, the intensity of the carbonyl vibration band enhanced with the increased content of grafted PMMA.

![FTIR spectra of pure silica and PMMA grafted silica particles](image)

**Fig. 1.** FTIR spectra of pure silica and PMMA grafted silica particles.

TGA results shown in Fig. 2 indicated the weight loss at 600 °C of the PMMA-grafted silica samples. From these data, the initiator grafting density on silica particles could
be calculated according to equation (4). The initiator grafting density of 30 and 400 nm silica particles was calculated to be 0.1 and 0.06 mmol/g, respectively. Silica particles with a mean diameter of 30 nm had higher specific surface area and more reactive hydroxyl groups, thus one might achieve higher grafting density, compared with larger silica particles.

Fig. 2. TGA curves of SiO$_2$, SiO$_2$ modified with BIBAPTES and PMMA-g-SiO$_2$.

Fig. 3 shows the scanning electron micrographs of silica particles before and after the surface-initiated ATRP of MMA. The original silica particles were spherical and near-monodispersed with a smooth, featureless surface morphology. Surface grafting of PMMA led to well-separated silica particles, suggesting that each silica particle was coated with a layer of PMMA, and the spacing between the particles increased with increasing molecular weight of the grafted polymer.

Fig. 3. SEM micrographs of pure 400nm silica and PMMA-grafted silica particles.

To confirm the ATRP grafting of PMMA onto the silica particles, the tethered polymer chains on the grafted silica particles were cleaved with hydrofluoric acid and measured with GPC. PMMA samples of various molar masses ($M_n$=13,862–116,190 g/mol) and low polydispersity ($M_w/M_n$<1.6) were obtained after the ATRP of MMA.
from BIBAPTES modified silica particles (Fig. 4). With the increase of molecular weight of PMMA, termination between chains on the particles became faster, that might be the reason of the larger polydispersity of the sample 400 nm-20% compared with sample 400 nm-10%.

![Graph showing GPC results of PMMA grafted from silica particles.](image)

**Fig. 4.** The GPC results of PMMA grafted from silica particles.

Thus, structurally well-defined core-shell particles were prepared by means of modification of the surface of silica with ATRP initiators and then using these initiator-modified-particles as macro-initiators for the ATRP of MMA. Well-defined PMMA chains were developed from the particle surfaces to yield individual particles comprised of a silica core and a well-defined, densely grafted outer polymer shell.

**Toughness of epoxy resin with PMMA-g-SiO₂**

The results of the stretching test are shown in Tab. 1. Before and after the slash of the sample code the particles used in the composites and the weight content of the particles, were separately measured. The results indicated that the tensile strength and tensile energy absorption of epoxy-based composites made with neat silica particles were higher than pure epoxy resin. Key toughening mechanisms, such as crack pinning, crack deflection, and plastic deformation well explained the results. PMMA grafted silica particles showed even better effect for the toughening of epoxy than neat silica particles. In addition to the load-partaking effect of neat silica particles, the grafted silica particles might act as bridging particles that applied compressive traction in the crack wake and deformed plastically in the material surrounding the crack tip, providing further crack shielding. As the crack propagate through the composite matrix, the crack front bowed out between the filler particles and was pinned by the particles. The 30 nm silica particles did not show better toughening performance because of their high specific surface area. It could improve the interfacial interaction but it also could produce agglomerates and stress concentration.
Tab. 1. Mechanical properties of epoxy and EP/SiO$_2$ composites.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Tensile energy absorption ($\times 10^3$kJ/m$^2$)</th>
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<tr>
<td>Pure</td>
<td>47.34</td>
<td>5.57</td>
<td>1.02</td>
</tr>
<tr>
<td>400nm/1%</td>
<td>46.61</td>
<td>5.26</td>
<td>0.95</td>
</tr>
<tr>
<td>400nm/2%</td>
<td>56.31</td>
<td>5.59</td>
<td>1.41</td>
</tr>
<tr>
<td>400nm/3%</td>
<td>57.21</td>
<td>5.33</td>
<td>1.30</td>
</tr>
<tr>
<td>400nm-20%/1%</td>
<td>57.31</td>
<td>5.84</td>
<td>1.43</td>
</tr>
<tr>
<td>400nm-20%/2%</td>
<td>66.97</td>
<td>5.79</td>
<td>1.62</td>
</tr>
<tr>
<td>400nm-20%/3%</td>
<td>72.58</td>
<td>5.57</td>
<td>1.59</td>
</tr>
<tr>
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<td>48.91</td>
<td>5.37</td>
<td>1.01</td>
</tr>
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<td>400nm-10%/2%</td>
<td>60.42</td>
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<td>1.46</td>
</tr>
<tr>
<td>400nm-10%/3%</td>
<td>61.84</td>
<td>5.68</td>
<td>1.19</td>
</tr>
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<td>30nm/1%</td>
<td>53.38</td>
<td>6.03</td>
<td>1.05</td>
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<td>30nm/2%</td>
<td>56.57</td>
<td>6.51</td>
<td>1.40</td>
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<tr>
<td>30nm/3%</td>
<td>59.65</td>
<td>5.95</td>
<td>1.31</td>
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<tr>
<td>30nm-30%/1%</td>
<td>54.35</td>
<td>5.98</td>
<td>1.49</td>
</tr>
<tr>
<td>30nm-30%/2%</td>
<td>62.56</td>
<td>6.32</td>
<td>1.55</td>
</tr>
<tr>
<td>30nm-30%/3%</td>
<td>70.43</td>
<td>5.86</td>
<td>1.49</td>
</tr>
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</table>

The fracture surfaces of pure epoxy and the composite samples loaded with neat or grafted particles were comparatively examined using SEM (Fig. 5). Pure epoxy resin (Fig. 5.a) exhibited a relatively smooth fracture surface with cracks almost parallel to the crack-propagation direction. This indicated typical brittle fracture behaviour, and showed that no large-scale plastic deformation occurred during fracture, thus accounting for the low tensile energy absorption of the unfilled epoxy samples. Compared to the pure epoxy sample, the roughness of the composites fracture surfaces considerably increased with the increasing of both the particles and the grafted PMMA content. Sample of 400 nm-20%/3% (Fig. 5.h) accepted as the reference showed a much more rough fracture surface and a typical tensile morphology. The increased surface roughness implied that the path of the crack tip was distorted because of the core-shell silica particles in the epoxy matrix, making crack propagation more difficult, thus altering the path of the propagating crack. Therefore, the tensile energy absorption was then improved by incorporating core-shell particles into the epoxy composites. The micrographs proved the intervention of the crack pinning toughening mechanism in inorganic particles filling thermosetting resins. The microscopic studies delivered evidence for de-bonding of the silica particles and subsequent plastic void growth in the epoxy polymer (Fig. 5.i). These voids were also observed in the fracture surfaces of samples with different content of core-shell particles. De-bonding of particles, reducing the constraint at the crack tip and hence allowing the matrix to deform plastically via a void growth mechanism, was a source of considerable energy dissipation. Generally, a good dispersion was achieved for the PMMA-grafted particles, while the non-grafted particles showed small agglomerates (Fig. 5.f), which acted as stress concentration sites for crack initiation and led to toughness descend of composites. The PMMA-grafted silica with a mean diameter of 30nm showed obvious agglomerates (Fig. 5.j & k) even with 1% weight content, which proved the results of mechanical properties in Tab. 1.
Fig. 5. SEM micrographs of fractured surfaces of epoxy/silica composites: (a) pure epoxy, (b) 400 nm/1%, (c) 400 nm/3%, (d) 400 nm-10%/1%, (e) 400 nm-10%/3%, (f) partial enlarged view of (c), (g) 400 nm-20%/1%, (h) 400 nm-20%/3%, (i) partial enlarged view of (h), (j) 30 nm-30%/1%, (k) partial enlarged view of (j).

Thermal properties of the composites

Given proof of improvements in tensile strength and tensile energy absorption, the effects of PMMA-grafted silica particles on other properties of the composites were
assessed. Dynamic mechanical analysis (DMA) was used to determine the glass transition temperature and the storage modulus of the composites, as shown in Fig. 6. A $T_g$ of 167 °C was observed for the pure epoxy sample. Addition of all kinds of the silica particles did not significantly affect the glass transition temperature of the composites, and their $T_g$ values all lay within the range between 168-170 °C.

**Fig. 6.** Dynamic mechanical properties of epoxy and epoxy/silica composites.

From the DMA results, the modulus vs. temperature curves of the composites with both neat silica and core-shell particles showed similar patterns to that for the pure epoxy sample. Likely, the introduction of PMMA soft shell did not deteriorate the thermo-mechanical properties of the composites.

**Fig. 7.** TGA curves of epoxy/silica composite materials.
Thermal stability of the samples was recognized with TGA (Fig. 7). First, both 5% mass loss temperature and the char yield increased with the increased loading of both neat silica and PMMA grafted silica particles much more than thermal stable neat silica particles could improve the thermal stability of the composite. However, the grafted silica particles with a less thermal stable PMMA soft shell also improved the thermal stability of the composite. Thus, the core-shell particles retained the positive effects of the hard silica particles on the thermal properties of the composite; improved its toughness; while not compromising the thermo-properties. High surface coverage as well as a tiny amount of the PMMA soft shell could rationalize that effect.

Conclusions

In this work, polymer chains were grafted from silica particles by ATRP, via the “grafting from” method. Structurally well-defined core-shell particles were prepared by modification of the surface of silica with initiators for ATRP and the use this initiator as macro-initiators. The testing results showed that PMMA chains grew from the particle surfaces to yield individual particles comprised of a silica core and a well-defined, densely grafted outer polymer layer. DGEBA based epoxy resin was toughened with various amounts of the synthetic PMMA-grafted silica particles. The incorporation of silica particles improved the toughness of the composites because of silica perturbing the crack front, thus altering the path of the propagating crack. silica with a mean diameter of 30 nm did not show better toughening competence for the reason that its high specific surface area led to agglomerates and stress concentration. Silica particles grafted with PMMA had better effect in toughening of epoxy than the neat or less grafted one. Besides the effect of the neat silica particles, the grafted PMMA acted as a bridging particle that applies compressive traction in the crack wake and deformed plastically in the material surrounding the crack tip, which provided additional crack shielding. Furthermore, the DMA and TGA results showed that the addition of silica particles slightly enhanced the thermal properties of the composites, such as glass transition temperature and thermal stability.

Experimental part

Materials

Commercial grade diglycidyl ether of bisphenol-A (DEGBA) of epoxide equivalent weight of 184-210g/ep was purchased from Shanghai Resin Factory (Shanghai, China). Silica particles of 400 nm in diameter (a mean value) were prepared according to Stöber method [24], and 30 nm silica nanoparticles were supplied by Zhoushan Mingri nanomaterial Co. Ltd. (Zhejiang, China). 3-Aminopropyltriethoxysilane (APTES), 4,4′-diaminodiphenyl methane (DDM), copper(I) bromide and triethylamine were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Ethyl 2-bromoisobutyrate (E2Br-iB) was obtained from Tokyo Kasei Kogyo Co. Ltd. 2-Bromoisobutyryl bromide (BIBB) and N,N,N′,N′,N′-pentamethyldiethylenetriamine (PMDETA) were purchased from Aldrich. All of them were used as received. Methyl methacrylate (MMA) was purchased from Shanghai chemical reagents company (Shanghai, China) and was distilled under reduced pressure before use.
**Preparation of 3-(2-bromoisoobutyramido) propyl triethoxy silane**

3-(2-Bromoisoobutyramido) propyl triethoxysilane (BIBAPTES), was synthesized according to the following procedure [25] as shown in equation (1): APTES (1.79 g, 10 mmol) was mixed with triethylamine (1.01g, 10mmol) in dry THF (50mL). On continuous agitation under nitrogen, BIBB (3.45g, 15mmol) was then added dropwise within 30 min and agitation was maintained for 12 h. The precipitate was filtered off through a frit funnel. Evacuation of the solvent under reduced pressure left a yellowish oil which was re-dissolved in CH2Cl2 (20 mL) and washed with 0.01M hydrochloric acid (2×20mL) and then cold water (2×20mL). The organic phase was dried over anhydrous CaCl2. After the removal of the solvent, the final colorless oil was left (90.5% yield).

\[ \text{OSiO}_2\text{NH}_2 + \text{BrO} \text{Et}_3\text{N} \xrightarrow{\text{THF, RT, 12hr}} \text{OSiO}_2\text{O} \text{OSiO}_2\text{NH} \text{O} \text{Br} \]

(1)

**Binding of ATRP initiator to silica particles**

BIBAPTES was grafted onto the silica surface according to the procedure illustrated in equation (2). Silica particles (4g) were dispersed in ethanol (36 mL) on 20 min sonication followed by addition of BIBAPTES (1.32 g) on stirring. The reaction mixture was continuously stirred for 12h at 80°C and the particles were centrifuged. Non-grafted coupling agent was removed from the particles on three consecutive cycles of re-suspending in ethanol and centrifugation. Finally, the initiator-coated silica particles were suspended in DMF.

\[ \text{SiO}_2 \xrightarrow{\text{C}_2\text{H}_5\text{OH, 80°C}} \text{SiO}_2 \]

(2)

**Polymerization from silica particle surfaces**

Shown as equation (3), the suspension of modified silica particles in DMF (40 mL) was added to a mixture of CuBr (0.1148 g, 0.8 mmol), PMDETA (0.4152 g, 2.4 mmol), prescribed amount of MMA and free initiator [20] ethyl 2-bromoisoobutyrate (E2Br-iB) (0.078g, 0.4mmol) into a 250 mL three neck flask under nitrogen. All liquids were deoxygenated by 30 min. purging nitrogen. The reaction mixture was agitated until homogenized. Then, the reaction flask was heated for 48 h at 80 °C under continuous nitrogen purge. After the reaction was over, the particles were washed with three cycles of consecutive centrifugation and re-suspension in THF in order to remove non-grafted PMMA. The remarks of synthesized particles were shown in Tab. 2.
Tab. 2. Remarks of different PMMA grafted silica particles.

<table>
<thead>
<tr>
<th>Code</th>
<th>diameter of SiO₂ (nm)</th>
<th>[M]₀:[I]₀:[Cu(I)]₀ :[PMDETA]₀</th>
<th>Weight loss at 600°C (%)</th>
<th>Mₙ of grafted PMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>400nm-20%</td>
<td>400</td>
<td>500:1:1:3</td>
<td>20.51</td>
<td>1.16×10⁵</td>
</tr>
<tr>
<td>30nm-30%</td>
<td>30</td>
<td>500:1:1:3</td>
<td>34.42</td>
<td>7.41×10⁴</td>
</tr>
<tr>
<td>400nm-10%</td>
<td>400</td>
<td>100:1:1:3</td>
<td>10.82</td>
<td>1.39×10⁴</td>
</tr>
</tbody>
</table>

Preparation of epoxy/silica composites

A certain amount of either neat silica or PMMA-grafted silica particles were dispersed in THF by 30 min sonication. Then, epoxy resin DGEBA was added; the mixture was heated to 80 °C for 6 h in order to evaporate THF. Then the curing agent, DDM (27 phr), was added at 80 °C. Finally, the mixture was poured into a mould and curing was performed at 80, 120 and 150 °C for 4 h during each curing step. Non-modified silica of mean diameters of both 30 and 400 nm, and three samples of PMMA-grafted silica particles as above were tested. Composites contained 0, 1, 2 or 3 w/w% of such particles.

Measurements

FT-IR spectra of PMMA-grafted silica particles were obtained from KBr pressed pellets with a Nicolet Magna 550 FTIR spectrometer.

Thermogravimetric analysis of PMMA-grafted silica particles was performed with a Perkin-Elmer PYRIS 1 instrument. The scans were performed at 10 °C/min in air in the temperature range from 50 to 600 °C. The residual weight of all specimens kept a constant value after heating over 500 °C. Therefore, the values of the weight loss were used as the actual PMMA content of PMMA-grafted silica. Thermal stability of the epoxy/silica composites was also characterized by TGA and the scans were performed at 20 °C/min in air in the temperature range from 50 to 800 °C.

The initiator grafting density (Gᵢ) was determined by equation (4):

\[
Gᵢ = \frac{W_{%_{SiBr}} - W_{%_{Si}}}{100 - W_{%_{SiBr}} - 100 - W_{%_{Si}}} \frac{W_{%_{SiBr}}}{M}
\]

where \( W_{%_{SiBr}} \), \( W_{%_{Si}} \) and \( M \) (253g/mol) were the weight loss after initiator grafting, the weight loss of the neat silica particles; and the molar mass of the initiator calculated by subtracting the molar mass of the Si and Br atoms, respectively.

Number average molecular weights (\( M_n \)), weight average molecular weight (\( M_w \)), and molecular weight distribution (\( M_w/M_n \)) were determined using GPC at 30 °C with THF as the eluent at flow rate of 1 mL/min. Aqueous HF (5%) and Aliquat 336 (phase
transfer catalyst) were stirred with a toluene suspension of the PMMA-grafted silica particles. The polymer, cleaved from silica particles, could then be isolated by precipitation and analyzed using an Agilent 1100 GPC instrument which was calibrated with a series of low dispersity polystyrene standards.

The microstructure of PMMA-grafted silica particles and the fractured surface morphology of the epoxy/silica composites were examined by SEM. A TESCAN 5136 MM instrument was used. Samples were gold sputtered.

All the specimens for tensile testing were cast into the dumb-bell shaped type. Gauge length, width of narrow section and thickness of the specimens were 50, 3 and 3mm respectively. Overall length and width were 75 and 15mm. Tests for tensile strength, elongation at break and tensile energy absorption were performed with a universal testing machine (SANS CMT5504) at ambient temperature using a constant crosshead speed of 10 mm/min. Minimum 5 specimens were tested in each case. Tensile energy absorption was calculated from equation (5):

\[
E = \int_{0}^{\text{Tensile stress at break}} \int_{0}^{\text{Elongation at break}} d(\text{Tensile stress}) \times d(\text{Tensile strain})
\]  

Dynamic mechanical tests were carried out on a Netzsch DMA 242 instrument set for compression mode. The tests were performed in the temperature range from 50 to 300 °C, at a heating rate of 3 °C/min and oscillating frequency of 10 Hz. The amplitude of the vibration was adjusted to 60 μm.

References