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Transparent Epoxy/Silica Nanocomposites with Increased Glass Transition Temperatures

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Abstract

Epoxy/silica nanocomposites were obtained by curing 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate in the presence of silica nanoparticles modified by (3-triethoxysilyl)propylsuccinic acid anhydride. Optimum conditions for the preparation of optically transparent polymer nanocomposites with increased glass transition temperatures are determined. The glass transition temperatures of the above nanocomposites are 30-40 °C higher than those of the neat epoxy resin synthesized under the same conditions (130 °C).

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Keywords: Epoxy resin; silica nanoparticles; nanocomposites.

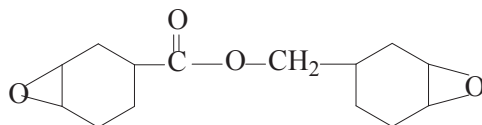
1. Introduction

For various technological applications, mechanical and thermal characteristics of polymer systems are traditionally improved by addition of inorganic fillers. When the size of filler particles is in the nanometer scale, the produced materials are called polymer nanocomposites (PNCs). Uniformly dispersed nanosized filler particles provide an exclusively high interfacial surface area between nanoparticles and a polymer matrix. This extensive interfacial surface area and nanoscale distances between nanoparticles fundamentally differentiate PNCs from traditional composites and filled plastics [1,2]. Due to the nanoscale structure of PNCs, a new combination of properties offers new advantages for the development of advanced materials, including polymer materials with high transparency, thermal resistance, and dimensional stability. These materials seem to be promising candidates for such practical areas as optics and electronics. In particular, the introduction of nanoparticles into polymer matrices used in LC displays makes it possible to utilize low-cost epoxy polymers with useful technological characteristics (excellent

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adhesion to various surfaces, chemical resistance, and transparency) but with moderate thermal characteristics (for example, a low glass transition temperature T_g and a high coefficient of thermal expansion). According to the literature data, the thermal characteristics of epoxy polymers can be improved by the addition of SiO_2 nanoparticles with a modified surface into the polymer matrix [3-10]. However, in most cases, the improvement was insignificant. For example, the cure of cycloaliphatic and/or aromatic epoxy resins in the presence of 10-70 wt% SiO_2 nanoparticles with surface-grafted phenyl groups promoting dipole-dipole interaction between nanoparticles and polymer matrix allows preparation of nanocomposites which preserve high transparency but their T_g values do not increase markedly [3-8]. When the SiO_2 nanoparticles are modified by surface-grafted functional groups that are capable of chemical interaction with the components of epoxy matrix, including epoxy, amine, or isocyanate groups, T_g increases by 10-20 °C as compared with the T_g of the unfilled polymer [9,10]. Nanoparticles of inorganic filler can increase T_g of polymer matrix by hindering the segmental mobility of a polymer as a result of the interaction with polymer chains, and the interaction between organic and inorganic components is the strongest when the filler is covalently bonded to the polymer matrix. However, no studies were performed with nanoparticles modified by anhydride groups, which are also able to covalently bind to epoxy matrix. The objective of this work consists in the preparation of a transparent nanocomposite material with increased glass transition temperatures as compared to that of unfilled polymer material. The nanocomposite will be based on epoxy resin (3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate) (EEC)

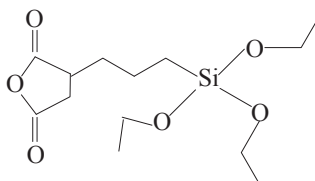


filled with SiO_2 nanoparticles modified by surface-grafted anhydride groups. Actually, such modified SiO_2 nanoparticles will serve as a multifunctional epoxy resin hardener. This approach should provide the preparation of highly cross-linked polymers.

2. Experiment

2.1. Preparation of epoxy/silica nanocomposites

EEC was purchased from Sigma-Aldrich. Silica nanoparticles used as 30% colloidal dispersions in isopropanol (IPA-ST) were obtained from Nissan Chemicals. According to the manufacturer, the particle dimensions are 10-15 nm. The surface of nanoparticles was modified with (3-triethoxysilyl) propylsuccinic acid anhydride (TESPSA) (94%; ABCR GmbH & Co. KG) which was used without any preliminary purification.



Silica nanoparticles modification was performed by the interaction of surface silanol Si-OH groups in SiO_2 nanoparticles with ethoxy groups of TESPSA according to the procedure described by us in [11]. The amount of TESPSA grafted on nanosilica was found to be about 0.23 mmol per gram of silica [11].

The epoxy resin was synthesized by curing of EEC and hexahydro-4-methylphthalic anhydride (HMPA) (98%, Acros Organics) without any preliminary purification.

Films of epoxy/silica nanocomposites were prepared by casting EEC mixtures containing different amounts of the modified SiO₂ nanoparticles onto a 70 × 70 mm glass support with a hydrophobic surface; this glass support was mounted onto a horizontal sheet in a Binder vacuum drying oven. The temperature was gradually increased (5–6 °C/min) to 80 °C, and the sample was allowed to stay at this temperature for 2 h until all solvent was evaporated. The prepared films were cured at 150 or 180 °C for 2, 4, and 11 h.

For the epoxy component, its cure conversion was quantitatively estimated via extraction with boiling acetone in the Soxhlet apparatus for no less than 72 h.

2.2. Characterization

The composition of the prepared composites was studied by IR spectroscopy. The IR spectra were recorded on a Nicolet Magna-75 spectrometer (USA) with a resolution of 2 cm⁻¹; the number of scans was 128. For the IR studies, dry samples were prepared as pellets with KBr powder; liquid samples were sandwiched between NaCl plates.

Glass transition temperatures were measured by a thermal mechanical analyzer (NETZSCH TMA 202) at a constant applied load of 100 g between 20 and 350 °C with a heating rate of 5 °C/min.

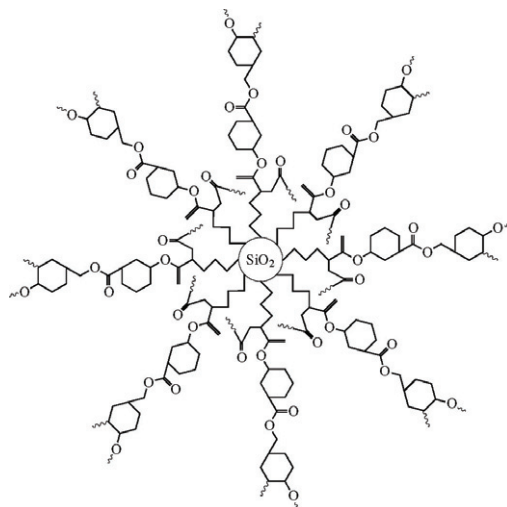
The morphology of the nanocomposites was studied by transmission electron microscopy (TEM) on a LEO912 AB OMEGA microscope. Ultrathin sections with a thickness of 100 nm were sectioned by using a diamond knife on a Ultracut ultramicrotome (Austria) at a cutting speed of 1 mm/s. Ultrathin sections of films with linear dimensions of about 0.1 mm were placed onto a carbon-coated copper grid (200 mesh).

The transparency of films based on epoxy/silica nanocomposites was measured on a Hewlett Packard HP 8452A UV spectrophotometer at the wavelength interval of 400–800 nm.

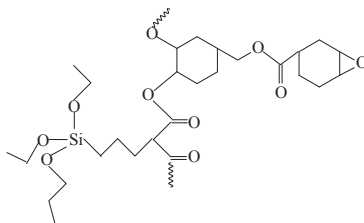
3. Results and Discussion

3.1. Preparation of epoxy/silica nanocomposites

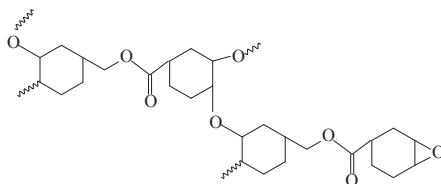
Nanocomposites based on the tetrafunctional epoxy resin EEC and the multifunctional hardener (modified SiO₂ nanoparticles) were synthesized via copolycondensation in the absence of any catalyst. The modified SiO₂ nanoparticles were used without their preliminary separation from the reaction mixture. This approach without separation of the modified nanoparticles from the reaction mixture allows one to prevent irreversible agglomeration of nanoparticles, which takes place during their coagulation as a dry powder. Taking into account the fact that 45.7% (or 0.23 mmol/g) of TESPSA is grafted onto the surface of nanosilica and that the initial mixtures contain not only the nanoparticles with surface-grafted anhydride groups but also approximately 50% of the unreacted bifunctional TESPSA, the thermal treatment of the mixture based on bifunctional and multifunctional epoxy hardeners with EEC can be accompanied by the occurrence of three competing cure reactions: the interaction of epoxy cycles with the surface-grafted anhydride groups on the surface of SiO₂ nanoparticles; the interaction of epoxy groups with the unreacted TESPSA, and the ring-opening polymerization with the opening of epoxy cycles of excessive EEC. The reaction between EEC and surface-grafted anhydride groups on nanoparticles leads to the development of a three-dimensional network (complex cycles) of the following structure:



When the epoxy resin is cured by the unreacted TESPSA, the resultant chemical structure of branched cyclic molecules can be presented as



An analysis of the IR spectra of the initial reaction mixtures based on EEC with the multifunctional hardener and the formed nanocomposites shows that, as a result of cure at 150 °C for 2 h, the intensity of the IR peak at 799 cm^{-1} (Figure 1) (C–H stretching vibrations of the oxirane cycle) decreases [12–14]. This observation indicates the occurrence of homopolymerization with the opening of oxirane cycles of the epoxy monomer and formation of linear chains of the EEC homopolymer:



As a result, the whole polymer system is transformed into an organo–inorganic nanocomposite material that contains linear chains and trivial cycles composed only of bifunctional and tetrafunctional units and complex cycles containing multifunctional units.

To define the cure conditions allowing the preparation of epoxy/silica nanocomposites with the maximum T_g , the degree of conversion of monomers and the thermal characteristics of the formed nanocomposites were studied as a function of the composition of the initial EEC-multifunctional hardener mixture and cure conditions. Cure was performed under isothermal conditions at 150 and 180 °C. The degree of conversion was estimated from the results of the extraction of soluble phase and its analysis by using the IR spectroscopic data.

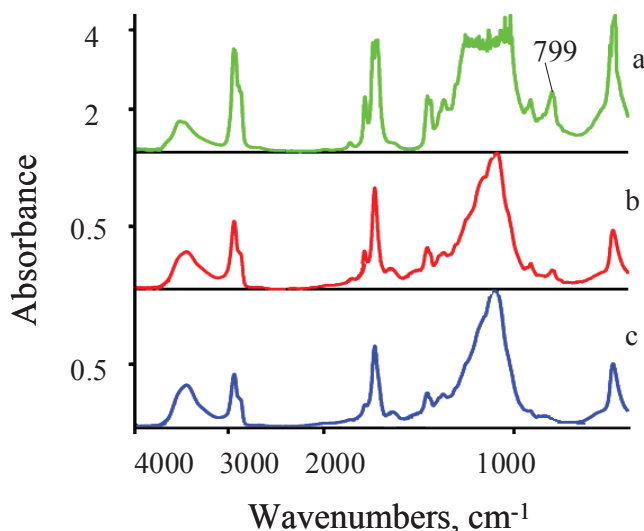


Fig. 1. FT-IR spectra of the reaction mixture containing epoxy resin and silica nanoparticles before (a) and after heating for 1 (b) and 2 (c) hs at 150 °C

Table 1 lists the T_g values for the nanocomposites prepared at different contents of the multifunctional hardener. It is seen that initially T_g markedly increases with increasing content of the multifunctional hardener from 10 to 20 wt%; then, T_g is seen to decrease as the content of the hardener increases up to 30 wt%. The initial increase in T_g is associated with an increase in the number of junctions in the cross-linked polymer. A further decrease in T_g with increasing concentration of nanoparticles can be explained by marked increase of the viscosity of the reaction system resulting in both the hindrance of curing process and the microphase separation. Therefore, to prepare the cross-linked polymer with a maximum T_g , the optimum content of filler particles is 20 wt%.

Table 1. Curing conditions and T_g for epoxy-silica nanocomposites prepared from the colloidal dispersion of 10-15-nm SiO_2 nanoparticles in isopropanol

Composition of initial mixture		Cure conditions		T_g , °C
$[\text{SiO}_2]$, wt%	EEC/TESPSA, mol. %	time, h	T , °C	
10	1 : 0.07	2	150	50±5
10	1 : 0.07	4	150	70±5
10	1 : 0.07	6	150	50±5
20	1 : 0.12	2	150	120±5
20	1 : 0.12	4	150	100±5
20	1 : 0.12	11	150	168±9
20	1 : 0.12	2	180	120±5
30	1 : 0.18	4	150	70±10

Figure 2 shows the thermomechanical curve for the nanocomposite with highest T_g value obtained in this study -168 °C.

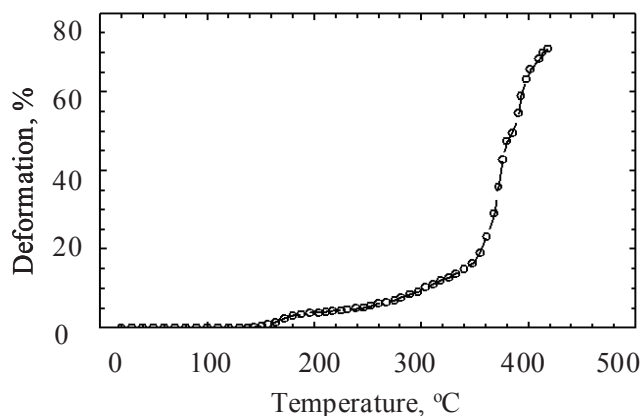


Fig. 2. Thermomechanical curve of nanocomposite prepared by curing of EEC with 20 wt% of modified SiO₂ nanoparticles at 150 °C for 11 h

It is worth mentioning that, in the course of cure at 150 °C, the reaction system composed of EEC and 20 wt% of nanosilica is transformed into the glassy state ($T_g = 160\text{--}170$ °C), and the conversion of functional groups virtually achieves 100%. According to the IR spectroscopic data, the selected reaction conditions provide a complete depletion of anhydride groups and opening of oxirane cycles of the epoxy component. One can expect that the reaction rate should markedly increase with the increasing reaction temperature above T_g (160–170 °C) [15]. Therefore, the composition containing EEC and 20 wt% of the multifunctional hardener is cured at 180 °C, when no degradation of the material occurs. However, T_g of the nanocomposite prepared under the above conditions appears to be lower and equal to 120 °C. Hence, the maximum depth of cure for EEC and 20 wt% multifunctional hardener can be achieved when the cure temperature is lower than the T_g of the formed nanocomposite. Since, at 150 °C, the reaction takes place in the glassy state, the whole process appears to be controlled by diffusion [15]. In the diffusion-controlled process, the reaction between neighboring functional groups has no serious limitations, whereas the interaction between distant groups is hindered or even prohibited. In this case, the process is directed toward the formation of small cycles and, hence, increases the connectedness of the structure [15]; as a result, T_g of nanocomposite increases. Therefore, with a decrease in the reaction temperature, the mean dimensions of the cycle decrease, and the ability of the system to form structures with higher T_g increases.

The morphology of the nanocomposites prepared from the mixtures containing different amounts of multifunctional hardener was characterized by TEM. It was shown that in all cases the nanoparticles are uniformly distributed within the epoxy matrix, and their dimensions in the matrix are similar to the initial dimensions of nanoparticles (about 10–15 nm) in the suspension, Figure 3. This observation evidences that, during formation of nanocomposites, no aggregation of nanoparticles takes place.

The transmittance spectra remain virtually unchanged when modified SiO₂ nanoparticles are introduced into epoxy matrix and their content is increased up to 30 wt%. Therefore, the introduction of 10–30 wt% of modified SiO₂ nanoparticles into the epoxy matrix does not entail any deterioration in the optical characteristics of the epoxy-based nanocomposites. These results agree with the data of TEM observations, which demonstrate a homogeneous distribution of nanoparticles in the volume of the epoxy matrix and indicate the absence of any aggregation.

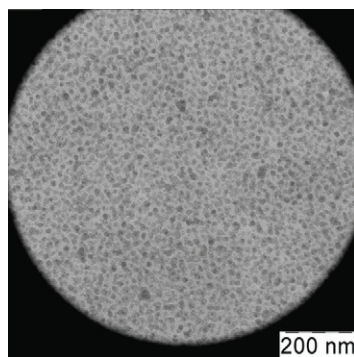


Fig. 3. TEM images of the epoxy/silica nanocomposites with 30 wt% of SiO₂ nanoparticles

To investigate the effect of the cure time on T_g , the experiments were performed under the following conditions: the reaction mixture containing EEC and 10 or 20 wt% of functionalized nanoparticles was heated for 2, 4, 6 or 11 h at 150 °C, Table 1 and 2. As follows from Table 1, in the case of 10 wt% of the nanoparticles, with an increase in the cure time from 2 to 4 h, the T_g of the nanocomposites increases. This increase is likely provided by an increased content of the gel fraction in the nanocomposite material (this content increases from 94 to 100 wt%) and by a reduced content of the sol fraction, which exerts the plasticizing effect on the formed polymer. When the cure time is further increased to 6 h, T_g of the nanocomposite, containing 10 wt% of SiO₂ nanoparticles decreases, Table 1. This tendency can be explained by degradation of the polymer matrix.

Table 2. Density of the nanocomposites after cure at 150 °C. The concentration of modified SiO₂ nanoparticles IPA-ST is 20 wt%

EEC/TESPSA, mol/mol	Cure time, h	Density, g/cm ³
1 : 0.12	2	1.303
1 : 0.12	4	1.308
1 : 0.12	11	1.312

In the case of the reaction mixture containing 20 wt% of the nanoparticles, T_g slightly decreases when the heating time is increased from 2 to 4 h, Table 1. In the both cases, the content of the gel fraction amounts to 100 wt%. These results can be explained by the plasticizing effect of the epoxy homopolymer. At the early stages of cure, the polycondensation reaction between EEC and the multifunctional epoxy hardener is accompanied by the concomitant homopolymerization of EEC and opening of oxirane cycle. Evidently, homopolymerization leads not only to the successive addition of EEC units to SiO₂ nanoparticles, but also to the formation of free epoxy resin homopolymers between network junctions that are not connected to SiO₂ particles. These “free” homopolymers can exert the plasticizing effect on the epoxy network: as a result T_g decreases due to weakening of intramolecular and intermolecular bonds [16]. As the cure time was increased from 2 to 4 h and the concentration of “free” epoxy homopolymers increases, T_g lowers. When the cure time is further increased from 4 to 11 h, T_g becomes higher. This behavior may be apparently explained by the fact that, with the increasing molecular mass of the epoxy homopolymer, its plasticizing effect decreases [16]. Table 2 illustrates the effect of the cure time on the density of nanocomposites. It is seen that the density slightly increases with an increasing cure time as expected.

Therefore, conditions providing preparation of networks with a stable and perfect structure depend on the composition of the reaction mixture. Higher concentration of the multifunctional hardener and longer curing time are required for the preparation of the network polymer with the highest glass transition temperature.

4. Conclusion

The optimum regime providing the preparation of nanocomposites based on the epoxy resin and the polyfunctional epoxy hardener (modified SiO₂ nanoparticles) with the best thermal characteristics is proposed. These nanocomposites are transparent and possess higher glass transition temperatures ($T_g = 160$ – 170 °C) as compared to that of the unfilled epoxy resin prepared under the same conditions ($T_g = 130$ °C).

Acknowledgement

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