

High-Performance Epoxy Hybrid Nanocomposites Containing Organophilic Layered Silicates and Compatibilized Liquid Rubber

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ABSTRACT: A mixture of two epoxy resins, tetraglycidyl 4,4'-diaminodiphenyl methane and bisphenol-A diglycidylether, cured with 4,4'-diaminodiphenyl sulfone, was used as matrix material for high-performance epoxy hybrid nanocomposites containing organophilically modified synthetic fluorohectorite and compatibilized liquid six-arm star poly(propylene oxide-*block*-ethylene oxide) (abbreviated as PPO). The hydroxy end groups of the poly(propylene oxide-*block*-ethylene oxide) were modified, yielding a six-arm star PPO with an average of two pendant stearate chains, two phenol groups, and two hydroxy end groups. The alkyl chains of the stearate end groups played an important role in tailoring the polarity of the polymer. Its phenol end groups ensured covalent bonding between liquid polymer and epoxy resin. Two different organophilic fluorohectorites were used in combination with the functionalized PPO. The morphology of the materials was examined by transmission

electron microscopy. The hybrid nanocomposites were composed of intercalated clay particles as well as separated PPO spheres in the epoxy matrix. As determined by dynamic mechanical analysis, the prepared composites possessed glass-transition temperatures around 220°C. Although the tensile moduli remain unaltered, the tensile strengths of the hybrid materials were significantly improved. The relatively high fracture toughness of the neat resin, though, was not preserved for the hybrid resins. Scanning electron microscopy of the fracture surfaces revealed extensive matrix shear yielding for the neat resin, whereas the predominant fracture mode of the hybrid nanocomposites was crack bifurcation and branching. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3088–3096, 2004

Key words: thermosets; nanocomposites; organoclay; compatibilization; liquid rubber

INTRODUCTION

High-performance epoxy resins based on multifunctional epoxy compounds, such as tetraglycidyl 4,4'-diaminodiphenyl methane (TGDDM) cured with aromatic diamines like 4,4'-diaminodiphenyl sulfone (DDS), are extensively used as matrices for fiber-reinforced composites in the aeronautics industry. Their high modulus and high temperature performance, however, are accompanied by inherent brittleness attributed to the high crosslink density of these materials.¹ Therefore, it is of interest to modify the epoxy matrix to improve the material properties and extend the range of applications of polymeric composites.

In recent years, the incorporation of elastomeric modifiers has been a successful way of enhancing fracture toughness.² For use in epoxy polymers the

toughening modifier should be initially miscible in the resin and is intended to phase-separate during cure to preserve easy processability and to yield enhanced mechanical properties.³ The phase-separated rubber particles are presumed to act as stress concentrators, thus initiating energy absorbing “toughening” processes attributed to multiple plastic deformation processes.^{4,5}

Since the early works of McGarry and the pioneering advances at B.F. Goodrich Company, the technology of rubber toughening has been applied to epoxy resins through the use of low molecular weight liquid butadiene acrylonitrile copolymers bearing carboxyl, amine, or epoxy reactive end groups.^{6,7} Liquid polyethers like poly(propylene oxide)^{8–10} or poly(tetrahydrofuran)^{11,12} have also been used as toughening agents. Modification of their end groups can be used to tailor the phase-separation behavior and the adhesion to the matrix by chemical bonds. The improvement in fracture toughness by the addition of liquid rubber modifiers, though, is often at the expense of bulk properties such as tensile modulus or thermal properties. This is not unexpected because modulus and glass-transition temperature of the

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modifier are usually much lower compared to those of the matrix.

Nanocomposite technology, using organophilic layered silicates (OLS) as nanoscale reinforcements, offers another general possibility for the modification of polymer matrix properties. Substantial improvements of mechanical and physical properties including modulus,¹³ barrier properties,¹⁴ flammability resistance,¹⁵ and ablation performance¹⁶ have been reported for this type of materials at low silicate content. Hence, this technique may offer an ideal combination of desired material properties when combined with liquid rubber toughening.

A general synthesis of the silicate nanocomposites involves dispersion of clay particles into single layers in a polymer matrix. Polymer/layered silicate nanocomposites were first developed by researchers from Toyota based on the thermoplastic polyamide 6¹⁷ and were later extended to thermosets like epoxies by Giannelis and Pinnavaia.^{18,19} Polymer/clay composites are usually divided into three general types: (1) conventional composite with the silicate acting as filler on the microscale; (2) intercalated nanocomposite based on the insertion of polymer between the clay layers, which remain in a long-range order; and (3) exfoliated nanocomposite in which individual layers are dispersed in the matrix.

Only few attempts have been made so far to combine liquid rubbers and OLS to achieve hybrid nanocomposites.^{20,21} Particulate inorganic fillers, however, have been extensively used in combination with liquid rubbers to enhance the mechanical properties of epoxy resins and other polymeric matrices in industry. Therefore, patents mainly deal with these organic/inorganic formulations.^{22–25}

In this work, a mixture of tetraglycidyl 4,4'-diaminodiphenyl methane (TGDDM) and bisphenol-A diglycidylether (BADGE), cured with 4,4'-diaminodiphenyl sulfone (DDS), was used as matrix material for high-performance hybrid nanocomposites containing organophilically modified synthetic fluorohectorite and compatibilized liquid six-arm star poly(propylene oxide-*block*-ethylene oxide) (abbreviated as PPO). Thermal properties, tensile properties, and fracture toughness were analyzed to clarify the influence of the different modifiers. The various morphologies of the materials were examined by transmission electron microscopy (TEM) and were correlated with the mechanical properties. Scanning electron microscopy (SEM) of the fracture surfaces revealed different fracture modes of the hybrid nanocomposites.

EXPERIMENTAL

Materials

Bisphenol-A diglycidyl ether [BADGE, epoxy equivalent weight (EEW) = 186 g/eq, Araldite GY250], tet-

raglycidyl 4,4'-diaminodiphenyl methane (TGDDM, EEW = 126 g/eq, Araldite MY720), and 4,4'-diaminodiphenyl sulfone (DDS, Hardener HT976) were received from Vantico AG (Basel, Switzerland). Synthetic fluorohectorite (Somasif ME-100), prepared by heating talcum in the presence of Na₂SiF₆, was supplied by UnicoopJapan Ltd. (Tokyo, Japan). Octadecylamine (ODA), purchased from Fluka (Buchs, Switzerland), was used to render the clay organophilic. For the preparation of an ODA adduct, a low molecular weight BADGE (EEW = 170 g/eq, Araldite MY790), provided by Vantico AG, was used. The liquid rubber used was a poly(propylene oxide-*block*-ethylene oxide) six-arm star polymer (PPO; Baygal VP.PU 99IK01 P.64, $M_n = 3300$ g/mol) from Bayer AG (Leverkusen, Germany). End-tipping with ethylene oxide provided primary hydroxy end groups for the PPO. Methyl stearate and methyl 4-hydroxy benzoate as well as dibutyltin dilaurate were purchased from Sigma-Aldrich (Seelze, Germany) and used as received.

Preparation of organophilic layered silicates and modification of liquid polymer

An adduct was prepared by the reaction of two equivalents of octadecylamine with the BADGE resin MY790. MY790 (65 g, 0.19 mol) was dissolved in 100 mL THF at 60°C. A solution of 103 g ODA (0.38 mol) in 80 mL THF was added dropwise and the reaction mixture was stirred for 3 h at 60°C under reflux. The solvent was removed, yielding the waxy adduct octadecylamine (AODA). The organophilic layered silicate Somasif/AODA used in this study was prepared by ion-exchange reaction of Somasif ME-100 with the protonated AODA as organic cation in aqueous phase as described by Kornmann et al.²⁶ The OLS Somasif/OODA was similarly prepared by using octadecylammonium chloride in the ion-exchange reaction as reported elsewhere.²⁷

To provide the liquid rubber with stearate moieties, 400 g poly(propylene oxide-*block*-ethylene oxide) (0.12 mol PPO, 0.73 mol OH groups) was first dried in a round-bottom flask for 2 h at 100°C and 0.1 hPa pressure. Then 73 g methyl stearate (0.24 mol, an equivalent of 33% with respect to hydroxy end groups of the PPO) and 2.2 mL dibutyltin dilaurate (2.4 g, 0.5 wt %) as a catalyst were added. The mixture was heated to 160°C and stirred for 45 h under continuous nitrogen flow. In the beginning, a cloudy emulsion was formed, which turned into a homogeneous solution after 30 min reaction time. After being cooled to room temperature, a vacuum of 0.1 hPa was applied for 1 h to degas the colorless product and remove traces of methanol that formed during the reaction. To introduce additional phenol end groups into the polymer, 289 g of the alkylated PPO (0.076 mol PPO, 0.30 mol OH groups) prepared in the first modification step

was reacted for 67 h together with 23.2 g methyl 4-hydroxy benzoate (0.16 mol, an equivalent of 50% with respect to hydroxy end groups of the PPO) at 160°C, similar to the first modification reaction. Dibutyltin dilaurate (1.6 mL, 1.7 g, 0.5 wt %) was added as a catalyst.

The resulting modified poly(propylene oxide-*block*-ethylene oxide)s were designated 4H4 and 2P4, respectively. Only 2P4, bearing pendant alkyl chains as well as phenol end groups, was used for the preparation of the hybrid nanocomposites.

Epoxy hybrid nanocomposite preparation

To prepare the epoxy hybrid nanocomposites, mixtures of equal amounts of BADGE (Araldite GY250) and TGDDM (Araldite MY720) were used as epoxy components. BADGE (130.5 g) and TGDDM (130.5 g) were mixed together with 20 g of the modified PPO 2P4 at 80°C and 8 hPa pressure over a period of 30 min with a Molteni Labmax high shear mixer (Rheinfelden, Switzerland) to reduce residual water. Somasif/ODA (10 g) was then added to the liquid prepolymers and dispersed therein by use of an IKA Ultra-Turrax T25 basic high-performance disperser (IKA-Werke, Staufen, Germany) for 6 min. Afterward, the organophilic layered silicate was swollen in the resin for 3 h at 90°C under reduced pressure with the Labmax mixer. Then 109 g DDS (Hardener HT976) was dissolved in the reaction mixture at 135°C over a period of 25 min of mixing at 8 hPa. The epoxy resin was then poured into a mold (200 × 200 × 4 mm³) and curing was performed at 140°C for 3 h and at 220°C for 7 h in a vented oven to produce high-performance epoxy hybrid nanocomposites containing 5 wt % of liquid polymer and 2.5 wt % of OLS. All of the different hybrid nanocomposites were produced according to this method. Additionally, composites containing only one additive component, either 2.5 or 5 wt % OLS or 10 wt % PPO, were also prepared for comparison.

Analysis and testing

GPC measurements were performed with a Knauer microgel set C11 (Berlin, Germany), using DMF as eluent at 45°C and a Polymer Laboratories evaporative mass detector EMD960 (Amherst, MA) operating at 110°C. The polymers were dissolved in DMF at a concentration of 5 mg/mL before analysis.

DSC measurements were carried out on a Perkin-Elmer 7 Series Thermal Analysis System (Perkin Elmer Cetus Instruments, Norwalk, CT) in the temperature range of -100 to 30°C at a heating rate of 10 K/min. The melting point of indium (156°C) was used for calibration.

Characterization by means of transmission electron microscopy (TEM) was conducted as reported elsewhere.²⁸

Dynamic mechanical analysis (DMA) was performed with specimens of 50 × 4 × 2.5 mm by means of temperature sweeps from 20 to 250°C in an RSA II dynamic mechanical analyzer (Rheometrics, Piscataway, NJ) equipped with dual-cantilever fixture at a frequency of 0.3 Hz, a strain of 0.08%, and a scanning rate of 2 K/min.

The linear coefficient of thermal expansion (CTE) was investigated by using a Mettler Toledo (Greifensee, Switzerland) TMA 40 thermal mechanical analysis at a heating rate of 5°C/min in the temperature range from 30 to 150°C.

Tensile tests were performed on a Zwick (type 1445) universal testing machine (Ulm, Germany). Tensile modulus, tensile strength, and elongation at break were measured on dumbbell-shape specimens (type 1A according to EN/ISO 527/2) machined from the cured sheets. For the determination of the tensile modulus incremental mechanical grips were positioned on the dumbbells.

Fracture toughness (K_{Ic}) was determined in accordance with the ESIS testing protocol.²⁹ The tests were done with a Zwick universal testing machine type 1445 on compact-tension (CT) specimens (dimensions: 35 × 35 × 4 mm³), which were notched by sawing. The notch root was sharpened by a razor blade before tensile loading (mode I) at room temperature with a crosshead speed of 1 mm/min.

To gain a deeper understanding on the effect of morphology on the fracture mechanical response, the surface of broken CT specimens was inspected in a scanning electron microscope (SEM; JSM-5400, JEOL, Tokyo, Japan). The fracture surface was coated with an alloy of Au/Pd before SEM investigations.

RESULTS AND DISCUSSION

Hybrid nanocomposite preparation

For the preparation of the hybrid nanocomposites, compatibilized liquid six-arm star poly(propylene oxide-*block*-ethylene oxide), abbreviated as PPO, and organophilic layered silicate were used as additives for an epoxy system cured with an aromatic diamine.

The liquid six-arm star PPO was modified before use in the epoxy resin to tailor its polarity and end-group reactivity, affecting phase separation and matrix adhesion. As depicted in Figure 1, the hydroxy groups of the PPO were modified with methyl stearate and methyl 4-hydroxy benzoate in two consecutive transesterification reactions. In the first step, a six-arm star polymer, bearing an average of two alkyl chains and four hydroxy end groups, was formed (designated 4H4). In the second step, two of the remaining

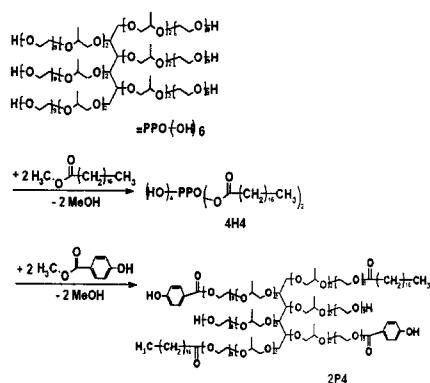


Figure 1 Reaction scheme for the transesterification reactions yielding the compatibilized liquid polymer for the modification of epoxy hybrid nanocomposites.

hydroxy groups were modified, yielding a liquid polymer with two pendant alkyl chains, two phenol groups, and two hydroxy end groups (designated 2P4). Just two end groups were converted in each transesterification, thus ensuring an excess of hydroxy groups and a complete consumption of the ester reactants. $^1\text{H-NMR}$ verified the complete introduction of the functional groups into the polymer by ester linkages. Thus, no purification of the modified PPOs was necessary. GPC measurements confirmed that the polydispersity of the polymers remained low (~ 1.2) throughout the whole modification process. The calculated molecular masses of the modified PPOs were based on the M_n of the unmodified PPO, taking into account the respective gain in molecular weight by the attachment of the functional esters. Table I lists the properties of the unmodified six-arm star PPO and the two modified liquid polymers. It should be noted that there is a statistical distribution of end-group functionality with theoretical values as average number.

Only lately, have Kornmann et al.²⁶ demonstrated that the use of novel intergallery cations enhances the

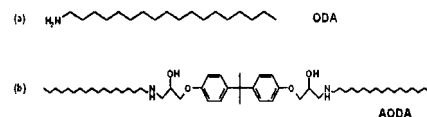


Figure 2 Chemical structures of the alkylamines used for the modification of the layered silicate Somasif ME-100: (a) octadecylamine (ODA) and (b) adduct of BADGE resin and octadecylamine (AODA).

compatibility between organophilic layered silicate and epoxy matrix, resulting in significantly enlarged interlayer distances. He used protonated adducts from BADGE resin and octadecylamine for the organophilic modification of layered silicates, which gave intercalated nanocomposites with enhanced tensile properties. In this study, we use layered silicates rendered organophilic by means of the conventional octadecylamine (ODA) as well as the novel adduct of bisphenol-A diglycidyl ether resin and two equivalents of octadecylamine (AODA). The adduct AODA was prepared and analyzed according to the procedures presented by Kornmann et al.²⁶ The chemical structures of both alkylamines are shown in Figure 2.

To prepare the high-performance epoxy hybrid nanocomposites, the modified liquid PPO 2P4 was first mixed with an epoxy system containing equal amounts BADGE (Araldite GY250) and TGDDM (Araldite MY720). Then, one of the organophilic layered silicates, Somasif/ODA or Somasif/AODA, was dispersed in this mixture. After swelling the OLS in the resin for 3 h, the nanocomposites were cured by the addition of DDS (Hardener HT976). A stepwise cure cycle was applied: first 3 h at 140°C followed by 7 h at 220°C .

Various hybrid nanocomposites containing different amounts of liquid polymer 2P4 and organophilic layered silicate, Somasif/ODA or Somasif/AODA, respectively, were prepared and designated according

TABLE I
Properties of the Six-Arm Star Poly(propylene oxide-*block*-ethylene oxide)s Used as Starting Material, Intermediate, and Compatibilized Product for the Modification of Epoxy Hybrid Nanocomposites

Property	Virgin PPO	4H4	2P4
M_n (g/mol) ^a	3270	3800	4040
M_w/M_n ^b	1.14	1.23	1.28
OH functionality	6	4	2
OH concentration (mmol/g)	1.83	1.05	0.49
Alkyl functionality	0	2	2
Alkyl concentration (mmol/g)	0	0.53	0.49
Phenol functionality	0	0	2
Phenol concentration (mmol/g)	0	0	0.49
T_g ($^\circ\text{C}$) ^c	-58	-50	-47

^a Determined by $^1\text{H-NMR}$ in DCCl_3 on a Bruker ARX300 operating at 300 MHz.

^b Determined by GPC in DMF.

^c Determined by DSC.

TABLE II
Compositions and Gel Times Recorded at 140°C of the Epoxy Hybrid Nanocomposites Containing Organophilic Layered Silicate Somasif/ODA or Somasif/AODA and Modified PPO Six-Arm Star Polymer 2P4

Sample	Content (wt %)					t_{gel} at 140°C (min)
	BADGE	TGDDM	DDS	PPO 2P4	OLS	
DDS-0	35	35	30	0	0	70
DDS-2P4/10	32	32	26	10	0	90
DDS-ODA/5	33	33	29	0	5	65
DDS-ODA/2.5	34.3	34.3	28.9	0	2.5	70
DDS-AODA/2.5	34.3	34.3	28.9	0	2.5	69
DDS-2P4/10-ODA/5	30	30	25	10	5	62
DDS-2P4/5-ODA/2,5	32	32	28.5	5	2.5	88
DDS-2P4/5-ODA/5	32	32	26	5	5	75
DDS-2P4/5-AODA/2.5	32.5	32.5	27.5	5	2.5	78

to their compositions. Composites with only one of the additives were synthesized for comparison. Compositions of all materials prepared are listed in Table II.

The gel time of each composite was recorded at 140°C with a Gelnorm gel timer from Gel Instrumente AG (Thalwil, Switzerland) according to DIN 16916 and 16945 (cf. Table II). The gel time of the neat epoxy resin is 70 min. When using only one additive, the gel time is slightly shortened by the addition of the OLS and significantly prolonged by the addition of modified PPO. The hybrid nanocomposites containing both additives require intermediate time spans to gel. As reported by other authors,³⁰ the amino groups of the organic cations in the OLS act as catalysts for the epoxy cure and thus shorten the gel time. The converse effect of the PPO on the gel time is attributed to the dilution of the reaction mixture by the liquid polymer. Gelation is also slowed down by the integration of the PPO as high molecular building block into the epoxy network by its reactive phenol end groups.

Morphology

The morphology on the microscale as well as on the nanoscale was observed by TEM. As shown in Figure 3, the epoxy hybrid nanocomposites exhibit two distinct features: spheres of phase-separated PPO and intercalated silicate particles [cf. Fig. 3(a), (b)]. The nanocomposites consisting of one of the organophilic layered silicates as single additive, on the other hand, exhibit the silicate particles alone [cf. Fig. 3(c), (d)].

The modified 2P4 is fully miscible in the uncured resin, allowing easy processability. Because of the nonpolar stearate chains attached to the star polymers, the liquid rubber phase-separates during cure. Small spheres with diameters of about 200 to 900 nm are formed in the epoxy matrix. Although the pendant alkyl chains tailor the polarity of the PPO, the phenol end groups of the modified PPO ensure the covalent bonding of the polymer to the epoxy network.

The organophilic layered silicates remain in their original form of particles of stacked sheets, called tactoids, when being incorporated into the epoxy resin [cf. Fig. 3(a), (c)]. These tactoids (dimensions: $1 \times 2 \times 4 \mu\text{m}^3$) are homogeneously dispersed in the matrix. The mean interlayer distance of the silicate sheets is increased by the interdiffusion of epoxy resin between the layers, resulting in intercalated nanocomposites. In the nanocomposite DDS-ODA/2.5, the interlayer distance measured by TEM is expanded from 1.9 nm for Somasif/ODA (measured by WAXS with Cu-K α) to 4 nm. In the hybrid nanocomposites with the compatibilizing PPO 2P4, the interlayer distances of the Somasif/ODA are further increased to 7 nm. When using the adduct AODA as intergallery cation, however, the initially higher interlayer distance of 3.3 nm for Somasif/AODA (measured by WAXS with Cu-K α) is further expanded to 7.5 nm in the epoxy nanocomposite DDS-AODA/2.5. For the hybrid nanocomposites

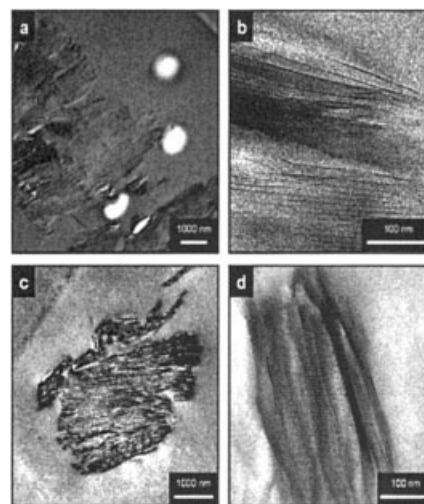


Figure 3 TEM micrographs of (a) and (b) epoxy hybrid nanocomposite DDS-2P4/10-ODA/5, as well as (c) and (d) nanocomposite DDS-ODA/5, at different magnifications.

TABLE III
Thermal and Mechanical Properties of the Epoxy Hybrid Nanocomposites Containing Organophilic Layered Silicate Somasif/ODA or Somasif/AODA and Modified PPO Six-Arm Star Polymer 2P4

Sample	T_g (°C)	CTE (ppm/K)	Modulus (MPa)	Strength (MPa)	Elongation at break (%)	K_{Ic} (MPa m ^{-1/2})
DDS-0	212	47.57	3470	46	3.1	1.34
DDS-2P4/10	226	76.03	3240	45	3.8	1.13
DDS-ODA/5	204	53.21	3840	59	3.0	1.36
DDS-ODA/2.5	242	56.97	3870	61	5.0	1.52
DDS-AODA/2.5	241	54.78	3860	51	4.0	1.37
DDS-2P4/10-ODA/5	213	79.28	3680	57	3.9	1.13
DDS-2P4/5-ODA/2.5	227	68.09	3750	53	2.8	1.18
DDS-2P4/5-ODA/5	223	57.08	3890	58	2.7	1.19
DDS-2P4/5-AODA/2.5	230	58.06	3760	55	4.8	1.17

consisting of Somasif/AODA, however, an even higher value of about 8 nm is found. Thus, the higher interlayer distance of the organophilic silicate prepared with the adduct AODA leads to a slightly enhanced intercalation when this OLS is incorporated into epoxy composites together with the modified PPO. The modified PPO helps to expand the interlayer distances of the organophilic silicates by diffusing between the sheets during the dispersion of the silicate in the reaction mixture. This diffusion is facilitated by the similar polarity of the long alkyl chains present in the interlayer cations and the liquid polymer-bearing alkyl chains. However, phase separation of the modified PPO between the silicate layers could not be observed. The ammonium cations are known to accelerate epoxy cure (cf. the shortened gel time). This effect is especially feasible between the silicate sheets where the ammonium concentration is the highest in the material. The accelerated cure, however, might prevent phase separation by fast buildup of a network structure, thus hindering coalescence of the liquid rubber particles inside the galleries. Furthermore, the single rubber molecules between the silicate layers cannot easily agglomerate to form distinct phases because of their restricted mobility in the confined geometry of the galleries.

Thermal properties

When analyzed by DMA, all hybrid nanocomposites exhibit glass-transition temperatures of about 220°C, whereas the T_g of the neat epoxy resin was 212°C. These high glass-transition temperatures render the studied high-performance epoxy resins suitable for applications in demanding environments. The exact values are given in Table III and are depicted in Figure 4. Referring to the composites with only one additive, the T_g is increased by the addition of modified PPO as well as the addition of small amounts of layered silicates. Adding 5 wt % of Somasif/ODA instead of 2.5 wt % Somasif/ODA, however, decreases the glass-

transition temperature of the corresponding nanocomposite from 242 to 204°C. An overall increase of the glass-transition temperatures is the result of hybrid composites containing small amounts of both additives. Nevertheless, the hybrid nanocomposite with high additive loading, DDS-2P4/10-ODA/5, shows a T_g similar to that of the neat resin.

The liquid PPO 2P4 is rendered immiscible with the epoxy resin by its pendant alkyl chains. After cure, it forms a separated phase that does not affect the glass transition of the matrix. Nanocomposites containing organophilic layered silicates are often reported to possess a higher thermal stability and a higher glass-transition temperature than those of unfilled resins because the silicate layers are said to restrain relaxational mobility of the polymer segments near the polymer/clay interface.^{18,31} The layered silicates added to the hybrid nanocomposites in this study, however, improved the T_g only when incorporated in small amounts, but lowered the T_g values of the materials when used in higher amounts. This can be attributed to a greater influence by the clay surface on the epoxy cure, leading to a reduced crosslink density at the polymer/clay interface at high loadings.²⁸ The

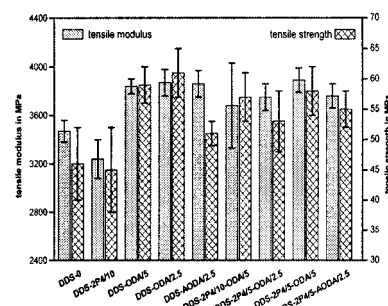


Figure 4 Glass-transition temperatures and coefficients of thermal expansion (CTE) of the epoxy hybrid nanocomposites containing organophilic layered silicate Somasif/ODA or Somasif/AODA and modified PPO six-arm star polymer 2P4.

amino groups present in the OLS may change the chemistry of the polymerization reaction because they are known to act as catalysts for epoxy homopolymerization.³⁰ It is unlikely, though, that a high crosslink density as in the epoxy-amine reaction is produced. As the stoichiometry is changed by the homopolymerization, unreacted resin remains in the matrix, further lowering the T_g by plasticizing the network.³²

The CTE values of the studied composites were examined by TMA and are displayed in Figure 4. The thermal expansion of the epoxy composites is generally increased by the single addition of either of the two additives used. For the hybrid nanocomposites, containing both additives, the CTE ranges from 50 to 80 ppm/K compared to 47 ppm/K for the neat resin. Table III lists the exact values. The nanocomposites containing one of the organophilic silicates as single filler show only a slightly increased thermal expansion compared to that of the neat resin. All composites containing PPO, however, exhibit significantly higher CTE values.

The higher CTE values of the composites with liquid PPO can be explained by the different thermal behavior of the PPO phase and the surrounding epoxy network. During the cooling process after cure, high stresses are built up at the interface, increasing the local free volume and thus increasing thermal expansion. When residual PPO, which has not completely phase-separated, is incorporated into the epoxy network by its reactive end groups, the CTE of the resin is further increased.³³ In our study, however, the OLS does not decrease the thermal expansion as reported by others.^{34,35} Probably additional free volume, which increases the CTE, is generated as a result of network inhomogeneities at the polymer/clay interface.

Tensile properties

The mechanical properties of the various hybrid nanocomposites were examined by tensile testing. The re-

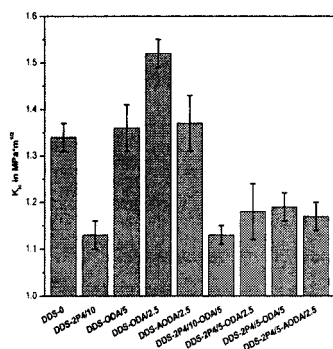


Figure 5 Tensile modulus and tensile strength of the epoxy hybrid nanocomposites containing organophilic layered silicate Somasif/ODA or Somasif/AODA and modified PPO six-arm star polymer 2P4.

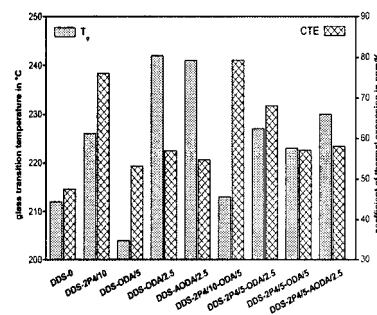


Figure 6 Fracture toughness of the epoxy hybrid nanocomposites containing organophilic layered silicate Somasif/ODA or Somasif/AODA and modified PPO six-arm star polymer 2P4.

sults for the hybrid materials and the composites with Somasif/ODA, Somasif/AODA, and PPO 2P4 alone are listed in Table III.

The tensile modulus of the neat resin is 3470 MPa. According to Figure 5, the tensile moduli of all hybrid composites are increased compared to that of the neat epoxy resin. The improvement of their stiffness is thereby solely based on the reinforcement by the silicate particles. When layered silicate was used as a single additive, the modulus of the nanocomposite was increased by about 10% to values around 3850 MPa. The reinforcement can be ascribed to stress transfer from the matrix to the rigid intercalated silicate particles.²⁸ However, DDS-ODA/5 does not possess a higher stiffness than that of DDS-ODA/2.5. As mentioned above in the discussion of the T_g of the materials, larger amounts of silicates may influence epoxy cure and ultimately network density. As a result for DDS-ODA/5, the potential improvement of stiffness by higher silicate loading is counterbalanced by a weaker matrix network. The stiffness of the epoxy composite containing the soft PPO alone is reduced by 7%. Obviously, the stiffening effect of the clay compensates for the softening effect of the liquid polymer, given that all hybrid nanocomposites possess similar tensile moduli of about 3700 MPa.

The slight increase in stiffness is accompanied by a significant increase in strength for all epoxy hybrid nanocomposites. The improvement, again, is based on the incorporation of the rigid silicate particles. As shown in Figure 5, the epoxy hybrids possess tensile strengths of nearly 60 MPa, which represents an improvement of 20% compared to 45 MPa for the neat resin. The modified PPO, however, leaves the tensile strength of the materials unaltered. Because of the formation of a separate phase bonded to the matrix, the addition of 2P4 does not reduce the composites' strengths as a miscible liquid polymer would do.

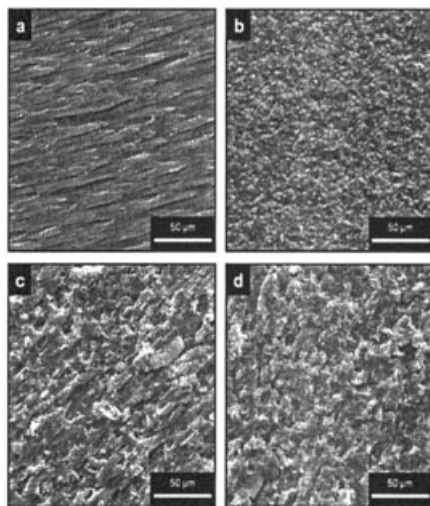


Figure 7 SEM micrographs of fracture surfaces of epoxy hybrid nanocomposites: (a) DDS-0, (b) DDS-2P4/10, (c) DDS-ODA/5, and (d) DDS-2P4/10-ODA/5 at the same magnification.

Fracture properties

Fracture toughness was elucidated in CT geometry in the form of the stress intensity factor K_{Ic} . The results are listed in Table III. Figure 6 presents the fracture toughness of the various epoxy hybrid nanocomposites. Unmodified multifunctional epoxy resins are usually brittle, exhibiting K_{Ic} values of 0.4 to 0.7 MPa $m^{-1/2}$.³² The neat resin in our work, however, shows a rather high fracture toughness of 1.34 MPa $m^{-1/2}$ because the additional use of BADGE lowers the high crosslink density of the TGDDM/DDS system, thus enabling extended matrix shear yielding. The addition of 2.5 wt % Somasif/AODA as a single additive increases the fracture toughness of the resulting nanocomposite. The use of Somasif/ODA, however, does not affect the toughness. Thus, the intercalated silicate particles with larger interlayer distances of Somasif/AODA (7.5 nm) compared to those of Somasif/ODA (4 nm) are more effective in toughening the composite materials. This effect was already found by Zilg et al.²⁸ in their examination of various epoxy nanocomposites with different intercalated layered silicates. If one of the organophilic layered silicates is used as a nanofiller in combination with the modified PPO 2P4, however, the K_{Ic} values of the resulting hybrid materials are reduced by 15% to about 1.15 MPa $m^{-1/2}$. The liquid polymer, originally applied as a toughener, is thus responsible for a decrease in toughness. This is also highlighted by the lowest toughness of the composite DDS-2P4/10 containing the liquid polymer as a single additive. Tightly bonded to the epoxy network, the 2P4 phases might also inhibit shear yielding, which is thought to be the most effective toughening mechanism in thermosets.⁵

Regarding the SEM micrographs in Figure 7, the neat epoxy resin presents a rough fracture surface with shear ribs and shear steps [cf. Fig. 7(a)]. These shear ribs are formed by matrix shear yielding and afford a relatively high K_{Ic} value of 1.34 MPa $m^{-1/2}$. For the PPO composite DDS-2P4/10 a smooth fracture surface containing cavitated PPO phases was recorded by SEM [cf. Fig. 7(b)]. Fine tails near the equator of the PPO spheres hint at crack pinning as the most prominent fracture mode. The composites containing one of the OLSs alone [e.g., Somasif/ODA in Fig. 7(c)] or in combination with the liquid polymer 2P4 [cf. Fig. 7(d)] show very rough fracture surfaces attributed to deflection of the crack path at the silicate particles. The individual tactoids, however, cannot be found in the SEM images. Crack bifurcation and crack branching are the dominating fracture mechanisms for the hybrid nanocomposites, given that no crack pinning can be resolved from the SEM micrographs. Probably, the PPO spheres in the hybrid composites even initiate cracks, thus lowering the K_{Ic} of these materials to values of about 1.15 MPa $m^{-1/2}$.

CONCLUSIONS

A mixture of two epoxy resins, tetraglycidyl 4,4'-diaminodiphenyl methane (TGDDM) and bisphenol-A diglycidylether (BADGE), cured with 4,4'-diaminodiphenyl sulfone (DDS), was used as matrix material for high-performance hybrid nanocomposites containing organophilic layered silicate and functional six-arm star PPO.

The poly(propylene oxide-*block*-ethylene oxide) could be easily modified by transesterification reactions at the hydroxy end groups. A six-arm star polymer with two pendant stearate chains, two phenol groups, and two hydroxy end groups was prepared. The alkyl chains tailor the polarity of the polymer in such a way that it phase-separates during epoxy cure, forming PPO spheres dispersed in the matrix. The phenol end groups of the modified PPO ensure a covalent bonding between the liquid polymer and the epoxy resin. Two different organophilic fluorohectorites, modified in one case with octadecylamine and in the second with an adduct of BADGE with two equivalents of octadecylamine, were used in combination with the functional PPO.

The prepared hybrid nanocomposites possessed high glass-transition temperatures of 220°C. The T_g values were even elevated compared to that of the neat resin by the addition of the modified PPO. However, the coefficient of thermal expansion of the composite materials was increased by the addition of the liquid polymer. Although the stiffness was only slightly increased, the strength of the hybrid composites was improved by 20%, mainly because of the addition of the layered silicate particles. The relatively

high toughness of the neat resin, though, could not be preserved for the hybrid materials. Their K_{Ic} was decreased by 15% to values of $1.15 \text{ MPa m}^{-1/2}$ compared to $1.35 \text{ MPa m}^{-1/2}$ for the neat resin. Hence, the extensive matrix yielding of the neat resin with the generation of shear ribs was the most effective failure mode. The predominant fracture mode of the hybrid nanocomposites initiated by the silicate particles, crack bifurcation and branching, was less effective. Crack pinning by the PPO spheres could be resolved only when the modified polymer was used as a single additive and afforded the lowest K_{Ic} values.

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