

Reinforcement of crosslinked rubbery epoxies by in-situ formed silica

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Received 1 January 1999; received in revised form 9 April 1999; accepted 21 April 1999

Abstract

Rubbery crosslinked epoxide was reinforced with silica–siloxane structures formed in situ by sol–gel process from tetraethoxysilane. The increase in modulus by two orders of magnitudes was achieved at a low silica content (<10 vol%). Various polymerization procedures including simultaneous or sequential formation of the epoxide network and silica resulted in different structures of the microphase-separated organic–inorganic hybrid composite. Structure and morphology of the heterogeneous system were analyzed by electron microscopy and small-angle X-ray scattering. Temperature dependences of storage modulus and loss factor were used to evaluate phase structure of the hybrids and the interaction between epoxy and silica phases. Efficiency of the reinforcement depends on the reaction conditions; a crucial effect of an interphase formation is shown. Acid catalysis of the sol–gel process probably promotes grafting between epoxide and silica phases and leads to a more uniform and finer structure with smaller silica domains. Comparison of the mechanical data with the theoretical models reveals that studied composites correspond to the morphological model of the hybrid consisting of co-continuous epoxy and silica structures. © 1999 Elsevier Science Ltd. All rights reserved.

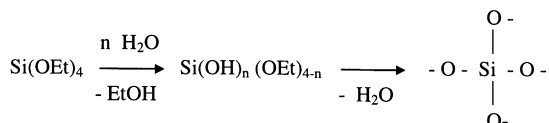
Keywords: Organic–inorganic hybrids; Dynamic mechanical properties; Sol–gel process

1. Introduction

For various technological applications, mechanical and thermal properties of polymer systems are commonly improved by addition of an inorganic filler. Material properties of the composites are determined by the respective properties of both physically mixed components and thus depend on the content of filler, its adhesion to polymer matrix, uniformity of dispersion, etc. In the last decade, a variety of elastomers, thermoplastics, linear or crosslinked systems, have been reinforced with inorganic fillers formed in situ [1–8]. These in-situ formed organic–inorganic (O–I) systems form a new class of composites, frequently described as O–I hybrids. These hybrids are also called as nanocomposites because of the small size of formed inorganic structures; usually of the nanometer size, resulting often in an optically transparent system.

In the hybrids, the inorganic phase is formed within an organic polymer matrix by sol–gel process consisting in hydrolysis and condensation of alkoxy derivatives of metals like Si, Ti, Al [9]. The most common precursor is tetraethoxysilane (TEOS) yielding a glassy silica network

which acts as a hard reinforcement in a soft polymer.



Procedures of the O–I hybrid synthesis involve either sequential type, i.e. inorganic phase formation within a polymer matrix, or a simultaneous polymerization of both organic and inorganic monomers. The hybrids with or without a covalent bond of the inorganic component to the polymer matrix may be formed. Organic monomers or polymers modified by alkoxy silane groups are used to provide bonding to the in situ formed inorganic structure. Strong interaction between phases was found [3,10–12] to improve the mechanical properties of the hybrid.

As a consequence of the molecular mixing of reacting components in the sol–gel process, the inorganic phase can be dispersed very finely in the organic matrix which is difficult to reach by mechanical mixing in the case of classical composites. The generally accepted Wilkes' morphological model of O–I hybrids [13] is based on the small-angle X-ray scattering (SAXS) analysis of the system poly(tetramethyleneoxide)-TEOS. According to this model, the hybrid is composed of silica-rich domains dispersed in the organic polymer-rich matrix. Besides, an interphase

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Table 1
Composition and moduli of the hybrid systems (v_{Eb} —volume fraction of the bound epoxide)

Sample	DGEBA:D2000:TEOS ^a	TEOS:IP ^b	SiO ₂		v_{Eb}/v_E	v_{Ebg}/v_{cb}	v_{eff}	$G_C \times 10^6$ (Pa)
			wt.%	vol%				
Simultaneous, one-stage (ET-1)								
1	1:1:3		6.2	3.8	0.14	0	0.038	2.1
2	1:1:4.75		7.7	4.7	0.16	0	0.047	2.6
3	1:1:9.5		15.7	9.5	0.48	0.10	0.14	6.9
Simultaneous, two-stage (ET-2)								
4	1:1:3		6.1	3.7	0.42	0.10	0.077	3.6
5	1:1:4.75		11.0	6.5	0.61	0.25	0.21	9.8
6	1:1:9.5		21.8	13.2	0.83	0.50	0.49	160
7	1:1:9.5 DBTDL		14.7	8.9	0.51	0.15	0.16	10.7
Sequential, epoxide network preformed (E1-T2)								
8	1:1	10:90	7.0	4.2	0.75	0.25	0.22	29
9	1:1	30:70	11.3	6.8	0.85	0.50	0.46	200
10	1:1	40:60	11.4	6.9	0.87	0.65	0.60	274
11	1:1	30:70 DBTDL	7.8	4.7	0.48	0.05	0.071	7.8
Composite DGEBA-D2000-Aerosil 200 (EAe)								
12	1:1		10	4.5	0.16	0	0.045	3.0
13	1:1		15	6.8	0.23	0	0.068	3.7
14	1:1		25	11.4	0.25	0	0.114	6.1

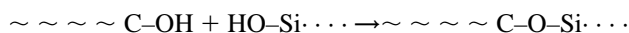
^a Ratio of functionalities.

^b Volume ratio.

v_{Ebg} —volume fraction of the bound epoxide in glassy state; $v_{eff} = v_{Si} + v_{Ebg}$ —effective volume fraction of the hard phase.

(intermixed layer) is present as a result of interpenetration of partly condensed siloxane–silica clusters and organic polymer. However, it is well known [9] that there is a possibility of controlling the structure and morphology by reaction conditions of the sol–gel process, which affects the final hybrid properties.

In previous papers [14,15], we have reported O–I hybrid systems composed of organic rubbery network and inorganic silica structure formed by the sol–gel process from TEOS. The organic part was represented by epoxide–amine network from diglycidyl ether of Bisphenol A (DGEBA) and poly(oxypropylene)diamine, Jeffamine® D2000. Simultaneous and sequential hybrid interpenetrating networks (IPN), DGEBA-D2000-TEOS, were prepared and their formation and structure were studied. The epoxide–silica IPNs were recently investigated by Bauer et al. [7]. During the hybrid network formation, the microphase separation takes place and resulting structure as well as final morphology were shown to be dependent on the synthesis procedure—one-stage or two-stage, the type of catalysis and concentration of the catalyst [7,14,15]. The sol–gel reactions were catalyzed by acid, neutral pH and basic catalysts. Grafting between the epoxide and silica networks is also an important factor controlling the hybrid morphology as it promotes miscibility and affects phase separation [7]. The covalent bonds between both networks are formed by the reaction of SiOH groups of hydrolyzed silica–siloxane clusters and C–OH group of the organic network resulting from the epoxide–amine reaction.



where $\sim \sim \sim \sim$ is an epoxide network and \dots is a silica structure.

In this paper, we dealt with the synthesis, phase structure analysis and elastic and thermal properties of the hybrid DGEBA-D2000-TEOS. Reinforcement of the rubbery epoxide–amine network by in situ formed hard silica structure was investigated as a function of factors influencing growth and morphology of the inorganic phase. Different ways of the O–I hybrid synthesis were used and the effects of the network formation, structure, morphology and interphase interaction on mechanical properties were studied. The structure and morphology were analyzed by SAXS and electron microscopy. The interphase interaction between the epoxide network and the silica phase was evaluated by means of dynamic mechanical analysis (DMA). In situ formed hybrid systems were compared with a classical composite, epoxide network filled with a pyrolyzed silica—Aerosil 200.

2. Experimental

2.1. Materials

2.1.1. Organic phase

A rubbery epoxide material was prepared by curing the diglycidyl ether of Bisphenol A (DGEBA) with poly(oxypropylene)diamine, Jeffamine® D2000 (Huntsman Int. Trading) ($M_w = 1970$). Long flexible polyether chain makes the cured material rubbery and moreover, it solubilizes siloxane structures formed in the sol–gel process and

makes a hybrid transparent. The equivalent of functional groups for the epoxy groups in DGEBA and NH groups in D2000 were respectively, $E_E = 171$ g/mol $E_{NH} = 492$ g/mol.

2.1.2. Inorganic phase components

Tetraethoxysilane (TEOS) (Fluka, 99.3%, GC analysis), the filler Aerosil 200 (specific surface 200 m²/g) (Degussa) and catalyst dibutyltin dilaurate (DBTDL) were used as received. Catalyst *p*-toluenesulfonic acid monohydrate (TSA) was purified by multiple recrystallization from methanol and the diluent isopropyl alcohol (IP) was distilled at 82°C.

2.2. Synthesis of epoxy–silica hybrid networks

The hybrid network DGEBA-D2000-TEOS consists of stoichiometric epoxide–amine network DGEBA-D2000 and a silica network formed from TEOS.

Sol–gel process: Hydrolysis and condensation of TEOS was performed in IP solutions at a molar ratio TEOS:H₂O = 1:3. The reaction was catalyzed with acid TSA and by the polymer base catalyst D2000 used as a curing agent of the epoxide. 2 mol% of TSA relative to TEOS was employed. The catalytic conditions were given by the relative concentration of TSA and D2000. In addition, pH-neutral catalyst DBTDL was used.

Simultaneous, as well as sequential, IPNs were prepared by three different procedures. Composition of the systems and the content of SiO₂ in the cured samples are given in Table 1. The hybrid systems were transparent.

2.2.1. One-stage process

All reaction components including water were mixed and reacted simultaneously. The hybrid networks with various contents of silica were prepared by varying ratio of functional groups of the components DGEBA:D2000:TEOS from 1:1:3 up to 1:1:9.5. The hybrid with the highest amount of TEOS corresponds to the mass ratio D2000:TEOS = 1:1. Concentration of catalytically active NH₂ groups in the D2000 catalyst ranged from 2.5 to 21 mol% relative to TEOS [14]. Hence, the sol–gel process was in fact catalyzed by D2000 because of its molar excess over the acid catalyst TSA (2 mol%). The volume ratio TEOS:IP = 45:55 was used. The curing schedule was as follows: 2 h at room temperature, 48 h at 90°C in teflon molds and 48 h at 130°C in an oven under vacuum. This one-step procedure of the hybrid formation from the epoxide and TEOS is denoted as ET-1.

2.2.2. Two-stage “simultaneous” process

1. TEOS was hydrolyzed under acid catalysis in the mixture TEOS–H₂O–IP–TSA at room temperature for 1 h.
2. In the second stage the prehydrolyzed TEOS was mixed with the organic components DGEBA-D2000 to start the “simultaneous” formation of both organic and inorganic

polymer phases. In fact the sol–gel process is faster and silica structures are formed prior to the epoxy system.

The first stage of the sol–gel process was catalyzed by the acid and the second one by the polymer base which was in excess. Also pH-neutral DBTDL was used as a catalyst in the first stage (sample 7 in Table 1). The hybrid network composition and curing schedule were the same as in the one-stage procedure. The two-stage polymerization is denoted as ET-2. Higher content of silica in ET-2 systems with respect to ET-1 can be caused by acidic prehydrolysis of TEOS and acceleration of polycondensation. During the base catalysis in ET-1 hybrid, the hydrolysis is rather slow [14] and a high amount of monomers remains in a reaction system even at a high conversion. This unhydrolyzed monomer can evaporate which results in a lower silica content in the product. DBTDL is not as efficient in catalysis of hydrolysis as TSA; therefore, the ET-2 sample using DBTDL (sample 7) shows low SiO₂ content.

2.2.3. Two-stage sequential process with preformed epoxide network

1. The stoichiometric epoxide–amine network was prepared first by curing DGEBA with D2000 at an equivalent ratio of functional groups for 16 h at 90°C and 2 h at 130°C.
2. The epoxide–amine network was swollen for 24 h at room temperature in the mixture TEOS–H₂O–IP–TSA. Equilibrium degree of swelling increases with the content of TEOS and reaches the value $w_{swollen}/w_{dry} = 1.95–2.35$ according to the volume ratio of the swelling mixture TEOS:IP ranging from 10:90 to 40:60. The content of SiO₂ in the system was controlled by this ratio (see Table 1). A higher amount of TEOS resulted in phase separation. The swollen sample was placed in a polyethylene sack and heated to 90°C for 5 days to form a silica–siloxane polymer phase by sol–gel process within the epoxide network. Drying of samples was performed in an oven under vacuum at 130°C for 3 days.

The sol–gel process is catalyzed by the acid because the D2000 agent incorporated in the epoxide–amine network is not efficient as a base catalyst [14]. Also DBTDL was used to catalyse the sol–gel process (sample 11 in Table 1). The sequential procedure with the epoxide network formed first is denoted as E1-T2.

2.2.4. Ordinary particulate composite

The reference classical composite DGEBA-D2000-Aerosil 200 was prepared by mechanical blending the silica Aerosil 200 with the reaction mixture of the epoxide system and subsequent curing for 16 h at 90°C and 2 h at 130°C. The composite is indicated as EAe.

2.3. Analysis

Dynamic mechanical analysis (DMA): Apparatus

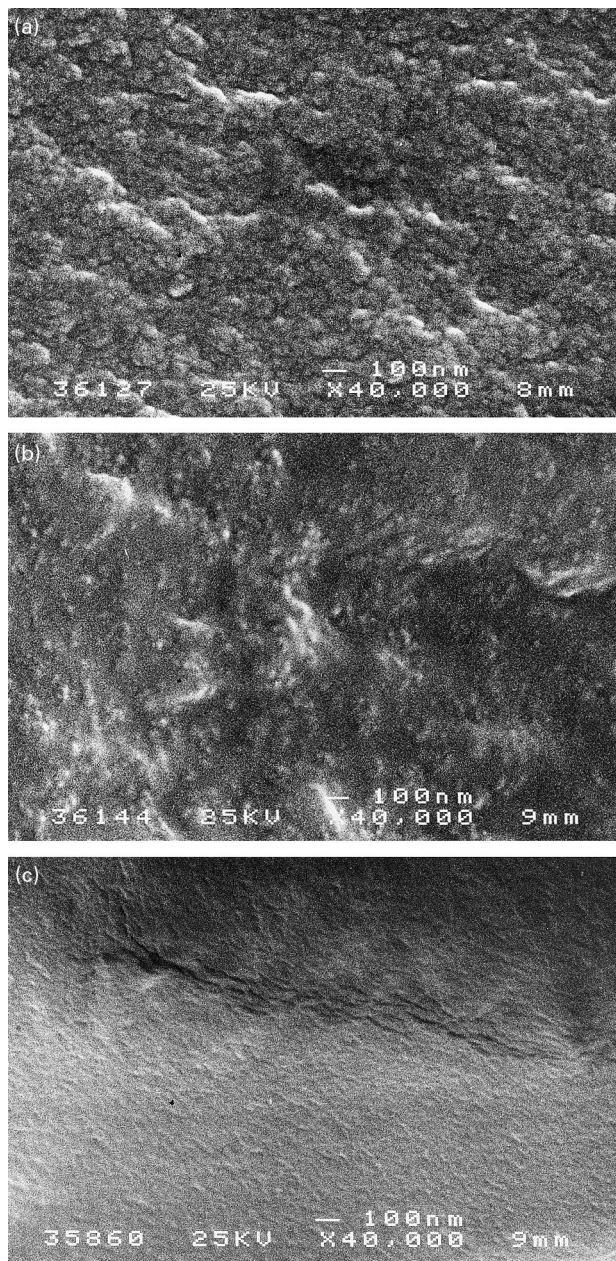


Fig. 1. SEM micrograph of the DGEBA-D2000-TEOS hybrid prepared for different polymerization procedures (a) ET-1, (b) ET-2, (c) E1-T2.

Rheometrics System Four was used to follow dynamic mechanical behavior of the hybrid networks. Temperature dependence of the complex shear modulus of rectangular samples ($5 \times 1 \times 0.1 \text{ cm}^3$) was measured by oscillatory shear deformation at a frequency of 1 Hz.

Silica content: SiO_2 (wt.%), in hybrid networks was determined by a standard analytical method by treatment of the sample with sulfuric acid followed by combustion to constant weight. The volume fraction of the silica phase was calculated using the density value, $\rho = 2.2 \text{ g/cm}^3$, for the pyrolyzed Aerosil (in the case of the classical composite). The bulk density of silica xerogels $\rho = 1.65 \text{ g/cm}^3$ [16]

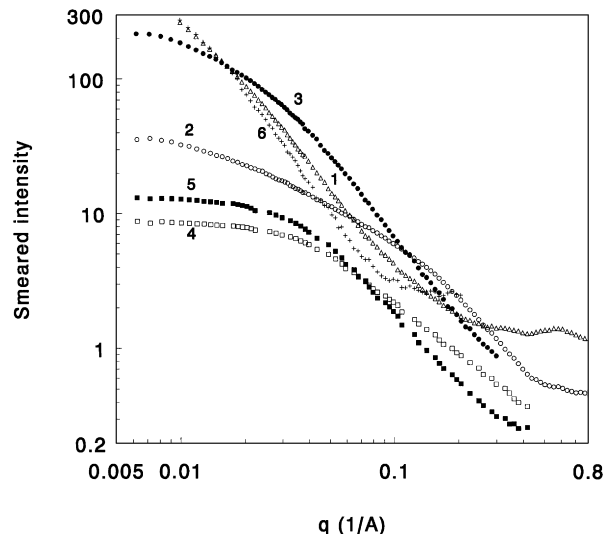


Fig. 2. SAXS profile of the DGEBA-D2000-TEOS hybrid prepared for different polymerization procedures and of the composite DGEBA-D2000-Aerosil. 1 (Δ) ET-1, 2 (\circ) ET-2, 3 (\bullet) ET-2, DBTDL prehydrolysis, 4 (\square) E1-T2, 5 (\blacksquare) E1-T2, DBTDL catalysis, 6 (+) EAe.

(prepared under similar conditions) was used for the in situ formed, incompletely condensed silica clusters.

SAXS experiments were performed using a Kratky camera (Paar KG, Graz) with a slit collimation [14]. The samples fractured in tension and coated with a platinum layer were micrographed using a JEOL JSM 6400 scanning electron microscope (SEM) [14].

3. Results

3.1. Network structure and morphology

The three polymerization procedures lead to different structures and morphologies of the O–I hybrids [14] as shown in micrographs in Fig. 1 and SAXS graphs in Fig. 2. The morphology ranges from silica domains of various sizes dispersed within an organic matrix to co-continuous epoxy–silica phases. Siloxane–silica clusters are incompletely reacted and the condensation conversion α determined by ^{29}Si CP/MAS NMR reaches the value $\alpha = 0.79\text{--}0.85$. Nevertheless, the silica regions are in glassy state as the glass transition temperature of the silica phase was found to be $T_g = 340^\circ\text{C}$. (T_g was determined by DSC using a model TEOS system polymerized under the same conditions as in the hybrid up to the same conversion). The inner structure of the silica domains was characterized by fractal dimension D_m evaluated from the slope in the Porod region of the SAXS profiles (see Fig. 2). The detailed description of the silica structure evolution and of the morphology of epoxide–silica hybrids are given in previous papers [14,15]. The fraction of the sol is about 3% after extraction of the samples with dioxane. The sol involves both an uncrosslinked epoxide system and silica structures.

Grafting between epoxide and silica structures taking place in the hybrid was proved in a model system. Branched uncrosslinked epoxide DGEBA-D2000 was prepared using nonstoichiometric ratio of functional groups $[2\text{NH}_2]/[\text{epoxy}] = 3.0$. The critical ratio for network formation was found to be 2.45 and hence the reaction mixture did not gel [17]. Polymerization of TEOS was carried out in the medium of this branched epoxide and a specimen containing formed silica network was extracted with dioxane and dimethylformamide. Very low sol fraction, $w_s = 4\text{--}7\%$, reveals grafting of the uncrosslinked epoxide onto the silica network.

The one-stage polymerization, ET-1, is base-catalyzed with D2000 as explained in Section 2.2.1. The SEM micrographs show large siloxane–silica aggregates of the size $\sim 100\text{--}300$ nm composed of smaller silica particles. The SAXS graph shows a steep slope of the scattering curve 1 in Fig. 2 revealing quite compact silica structures with a high value of the fractal dimension, $D_m = 2.7$.

The two-stage polymerization procedure with an acid prehydrolysis of TEOS, ET-2, results in the formation of smaller silica structures reaching $\sim 50\text{--}100$ nm in diameter. These silica domains seem to span continuously throughout the organic matrix. Two linear parts in the SAXS profile of the curve 2 in Fig. 2 were interpreted by two size scales of fractal behavior—compact small particles with fractal dimension $D_m = 2.7$ aggregated in large, more open silica clusters with lower fractal dimension, $D_m = 2.0$. Acid catalysis in the first stage is of crucial importance because of the acceleration of the hydrolysis and formation of a high content of silanols affecting the structure as shown below. Compact clusters, similar to those observed in one-stage process ET-1, were formed if neutral DBTDL catalyst was used instead of TSA in the first step (see curve 3) due to low efficiency of DBTDL to catalyze the hydrolysis.

The structure and final morphology of the in situ formed hybrids is to a great extent determined by relative rates of the reaction and microphase separation during polymerization. Significant acceleration of the polycondensation was observed in ET-2 system because of an acid prehydrolysis of TEOS compared to the one-stage procedure, ET-1 [14]. Very fast polymerization and gelation of siloxane phase in the two-stage ET-2 hybrid results partly in chemical quenching of the system, slowing down the diffusion and preventing a more extensive phase separation. The course of the polymerization was followed by SAXS [15]. Fractal dimension of the formed structures in ET-2 is rather low, $D_m = 1.7$ near the gel point, which corresponds to the model of diffusion-limited cluster–cluster reaction mechanism [9] and agrees with the slow diffusion in the process. On the contrary, microphase separation is allowed to proceed during slow polymerization of the ET-1 system and a more heterogeneous morphology is formed.

In the sequential IPN, E1-T2, the silica structures grow within the preformed epoxide network. During swelling of the network with a TEOS–H₂O–IP mixture at room temperature, the hydrolysis of TEOS takes place, increasing

the degree of swelling up to an equilibrium value (cf. Ref. [7]). No grafting to the epoxide network does occur in this stage as all Si components could be extracted from the network with dioxane. After curing at a higher temperature, the sol fraction decreases to 2–4% as a result of the silica network formation and grafting between silica and epoxide networks. The content of SiO₂ in the hybrids increases with the fraction of TEOS in the TEOS–IP mixture (see Table 1). The distribution of the inorganic phase, however, is not homogeneous throughout the sample due to a nonhomogeneous swelling of the epoxide network. The results reveal a surface skin with a higher SiO₂ concentration compared with that in the inner part. Figs. 1 and 2 show that the resulting structure is finer and the formed silica clusters are smaller compared with the simultaneous IPNs. Silica domains of size ~ 10 nm in diameter are detected in a SEM micrograph (Fig. 1(c)). All the sol–gel process is catalyzed by the acid (samples 8–10) promoting the formation of the open fine structure. SAXS analysis gives the fractal dimension $D_m = 1.9\text{--}2.2$ (see smaller slope of curve 4 in Fig. 2). In the case of DBTDL catalysis (sample 11) instead of TSA, the formed silica clusters are more compact, $D_m = 2.7$ (see curve 5). In addition to the effect of catalysis, the morphology is influenced in this case by the fact that the silica clusters grow within the epoxide network. Steric hindrance inside the solid organic matrix—in contrast to “simultaneous” IPNs—prevents the formation of large silica aggregates (cf. Ref. [18]) and morphology is more homogeneous.

Our results seem to contradict those of Bauer et al. [7] who found a strong phase separation manifested by a high value of the slope of SAXS curves in sequentially prepared IPN. On the contrary, a finer morphology was observed in “simultaneous” IPNs as a consequence of a good miscibility of two phases due to grafting between networks. The difference between our and Bauer’s experiments consists in conditions of postcuring of the sequential IPNs. No heat treatment was applied by Bauer et al. in an uncatalyzed sol–gel process in the swollen epoxide network. In such a case, the grafting is unlikely. On the contrary, acid catalysis, postcuring and drying at 130°C were used in our experiments which made the grafting possible.

The mechanically blended composite DGEBA-D2000-Aerosil shows the largest and most compact (colloidal) silica structures. The steep slope of the intensity SAXS profile of curve 6 in Fig. 2 reveals compact surface fractal particles indicating a sharp phase separation in epoxy network–silica.

4. Dynamic mechanical properties and interphase formation

Valuable information on morphology and mainly on interface of the microphase-separated hybrid systems was obtained from DMA.

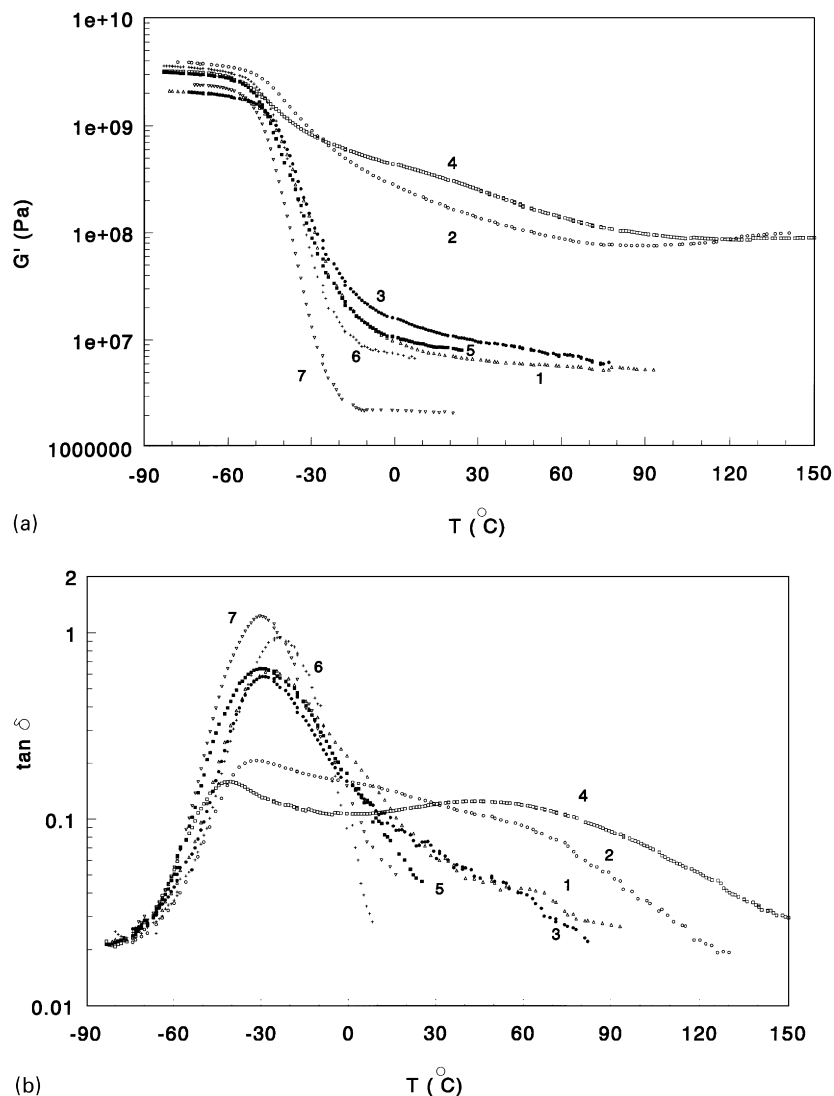


Fig. 3. Dynamic shear modulus (a) and loss factor $\tan \delta$ (b) of the DGEBA-D2000-TEOS hybrid networks and the composite DGEBA-D2000-Aerosil as a function of temperature. 5–13 vol% SiO_2 . 1(Δ) ET-1 (sample 3), 2(\circ) ET-2 (6), 3(\bullet) ET-2 DBTDL prehydrolysis (7), 4(\square) E1-T2 (10), 5(\blacksquare) E1-T2 DBTDL catalysis (11), 6(+) EAe (13), 7(∇) DGEBA-D2000.

Fig. 3 shows shear storage modulus $G'(T)$ and loss factor $\tan \delta (= G''/G')$ of studied systems as functions of temperature. One can see a significant reinforcement of some “in situ” prepared hybrid networks (Fig. 3(a)) with respect to neat DGEBA-D2000 network (curve 7). Storage modulus of the hybrids rises with increasing content of the inorganic component and this reinforcing effect is strongly dependent on the way of the hybrid preparation and the silica phase formation (see Fig. 4). Significant reinforcement can be seen mainly in the case of the sequential E1-T2 hybrid network (curve 4 in Figs. 3(a) and 4). The figures reveal an important effect of the acid prehydrolysis of TEOS with TSA resulting in a higher modulus of the hybrid ET-2 (curve 2) compared with the ET-1 system prepared without prehydrolysis (curve 1). Much lower moduli were found if the pH neutral DBTDL catalyst instead of TSA was used for hydrolysis in ET-2 (curve 3 in Fig. 3, point 3 in Fig. 4) or in E1-T2

(curve 5 in Fig. 3 or point 5 in Fig. 4). The reinforcement achieved with Aerosil in the classical composite EAe is much lower (curve 6). The drop of the modulus in the simultaneous IPNs at low SiO_2 contents in Fig. 4 is caused by the fact that the hybrid network systems ET-1 and ET-2 were prepared in IP solutions. (In contrast, the composite EAe and the epoxide network in the E1-T2 hybrid were synthesized in bulk.) Obviously, the presence of a diluent in polymerization leads to a network with a lower cross-linking density and elastic modulus of the dry system.

The increase in the storage modulus of the hybrid networks (Fig. 3(a)) is accompanied by changes in the loss factor $\tan \delta$ (Fig. 3(b)). The peak of $\tan \delta$ located at about -30°C , which corresponds to the glass transition of the neat DGEBA-D2000 network (curve 7), decreases and broadens in the epoxy-silica hybrids, which is typical of most composite systems [19]. The decrease in the loss

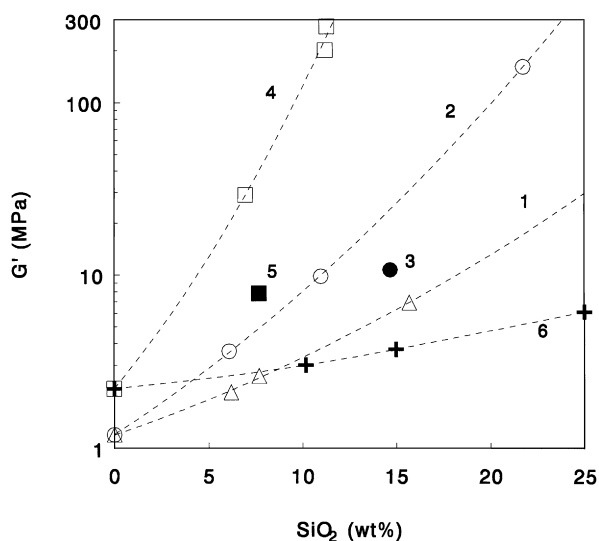


Fig. 4. Dynamic shear modulus of the DGEBA-D2000-TEOS hybrid networks and the composite DGEBA-D2000-Aerosil at 25°C as a function of the SiO₂ content. 1(Δ) ET-1, 2(○) ET-2, 3(●) ET-2 DBTDL prehydrolysis, 4(□) E1-T2, 5(■) E1-T2 DBTDL catalysis, 6(+) EAe.

maximum height is proportional to SiO₂ concentrations and depends on the synthesis procedure of the hybrid network. The most striking drop in the $\tan \delta$ maximum is observed in the sequential IPN, E1-T2, while the composite with Aerosil, EAe, shows only a mild lowering. Some of our hybrid composites display a new damping peak at a higher temperature (Fig. 3(b)), which gives evidence of the phase separation in the epoxy–silica system. The temperatures scanned in DMA are too low to detect the transition in the highly condensed silica phase in the epoxy–silica hybrid. (The silica–siloxane domains show $T_g = 340^\circ\text{C}$ as discussed above.) In conformity with previous papers [11,20–23], the new loss peak located above 0°C can be attributed to glass transition of organic network chains with reduced mobility due to their interaction with glassy silica domains. This interaction is very strong owing to grafting between silica and epoxide networks [7] and possible hydrogen bonding. Formation of the immobilized interphase layer of the epoxide–amine network which is in contact with the silica phase leads to a decrease in the volume fraction of the “free” nonhindered chains of the organic network. Consequently, the loss factor peak at about -30°C diminishes as the fraction of these unrestricted chains decreases. Wilkes et al. [20], Pascault et al. [22] and others assigned the peak at higher temperatures often observed in hybrid systems to the organo-silica mixed phase of the Wilkes’ morphological model.

The absence of the high-temperature peak in the composite with Aerosil, EAe, and only a slight decrease in the $\tan \delta$ amplitude of the -30°C peak give a proof of the absence of an immobilized layer, obviously due to a weak interaction between epoxide and silica phases. It is well known that microphase separation is detectable by DMA only if domains exceed a critical size of about 5–10 nm;

hence, a minimum interfacial area and thickness of a bound polymer layer are necessary in order to be seen as a new phase [19,23]. The position of the new damping peak on temperature scale is governed by the strength of the interphase interaction. Broadening of the damping peak observed for the one-stage hybrid system ET-1 evidences broadening of the spectrum of relaxation times typical of composite materials; a likely reason of the latter effect is widening distribution of the lengths of immobilized epoxide–amine chains.

The hybrid systems are composed of three phases: the flexible free epoxide–amine network (matrix), the immobilized (bound) chains of the organic network and the inorganic phase with the corresponding volume fractions, v_{Ef} , v_{Eb} and v_{Si} , respectively. (The two former phases are detected by the DMA damping peaks and the silica phase is observed by SAXS and SEM.) Thus,

$$v_{\text{Ef}} + v_{\text{Eb}} + v_{\text{Si}} = v_{\text{E}} + v_{\text{Si}} = 1 \quad (1)$$

The decrease in v_{Ef} was roughly estimated from the reduction of the corresponding loss factor maximum at -30°C . It has been empirically found [19,24,25] that the loss factor of a composite is approximately given as a sum of the contributions of constituting phases. In notation for our composites we obtain

$$\tan \delta_c(T) = \tan \delta_{\text{Ef}}(T)v_{\text{Ef}} + \tan \delta_{\text{Eb}}(T)v_{\text{Eb}} + \tan \delta_{\text{Si}}(T)v_{\text{Si}} \quad (2)$$

New damping mechanisms arising at the interfaces are quite unlikely because of interfacial adhesion between polar organic and inorganic components. Obviously, the loss factor of the silica phase is negligible in the scanned temperature interval. Moreover, we will assume that the loss factor at -30°C is mainly given by the free chains while the contribution of bound chains is much smaller and could be neglected. Then,

$$v_{\text{Ef}} = \tan \delta_c(-30^\circ\text{C}) / \tan \delta_{\text{Ef}}(-30^\circ\text{C}) \quad (3)$$

The value of $\tan \delta_{\text{Ef}}(-30^\circ\text{C})$ was determined for the neat epoxide network. The estimate of v_{Ef} and $v_{\text{Eb}} = 1 - v_{\text{Si}} - v_{\text{Ef}}$ in various hybrid systems are given in Table 1.

The fraction of interphase v_{Eb} is controlled by the reaction mechanism and procedure of the O–I hybrid formation. Acid catalysis with TSA promotes a faster and more extensive hydrolysis of TEOS compared with the catalysis by basic (D2000) and pH-neutral (DBTDL) catalysts leading to higher concentration of Si–OH groups in the siloxane–silica clusters. Therefore, grafting to the epoxide network is more promoted in the acid-catalyzed ET-2 and E1-T2 systems than in the networks prepared under catalysis with D2000 (ET-1) or with DBTDL catalysts (samples 7,11), which agrees with the DMA results (see Table 1). Strong interaction of the components in the ET-2 hybrid network proved by an appearance of the high-temperature $\tan \delta$ peak (Fig. 3(b)) leads to the formation of a finer morphology with small silica domains (Fig. 1). In contrast, a weak interaction in the one-stage ET-1 hybrid results in a

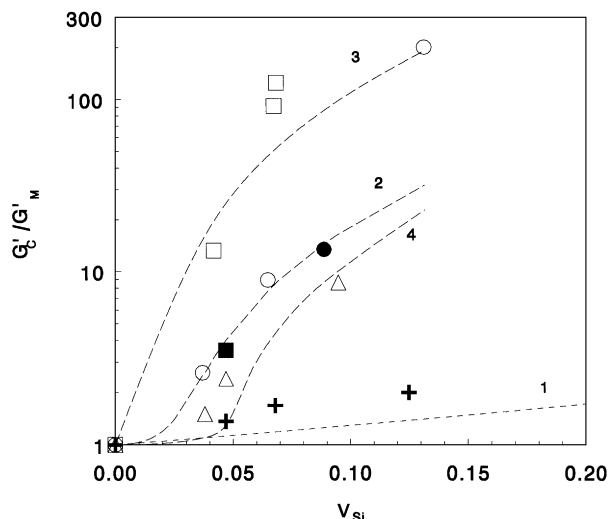


Fig. 5. Relative modulus of the composite as a function of the volume fraction of the silica phase. Curves—theoretical models, $G_{Si} = 4 \times 10^9$ Pa, $G_E = 2.2 \times 10^6$ Pa, $G_{EG} = 2 \times 10^9$ Pa; curves 1–4 theory; curve 1 Kerner–Nielsen model (Eq. (4)): $\nu_M = 0.5$, $\nu_{max} = 0.6$; curve 2 Equivalent box model (Eq. (6c), see also Eq. (7), $K = 0$, $\nu_{cr} = 0$, $t = 2.0$; curve 3 EBM, $K = 10$, $t = 2.0$, $\nu_{cr} = 0$; curve 4 EBM, $K = 0$, $t = 2.0$, $\nu_{cr} = 0.02$; experimental results; Δ ET-1, \circ ET-2, \bullet ET-2 DBTDL prehydrolysis, \square E1-T2, \blacksquare E1-T2 DBTDL catalysis, +EAE Moduli of the rubbery and glassy epoxy network matrix $G_M (= G_E)$ and G_{EG} , respectively, were measured. Modulus of incompletely condensed siloxane–silica domains $G_f (= G_{Si})$ was taken from literature data [16] on xerogels prepared from TEOS under similar conditions. For experimental relative modulus G_c/G_M the values of $G_E (= G_M) = 2.2 \times 10^6$ Pa and 0.8×10^6 Pa for the epoxy network prepared in bulk and in 40% solution were taken, respectively.

more heterogeneous morphology and larger silica regions. Due to a very low content of Si–OH in pyrolyzed Aerosil, the reaction between matrix and filler is very limited, which accounts for a weak adhesion between phases in the composite EAE. A stronger interaction in the sol–gel formed epoxide–silica system with respect to the classical blended composite epoxide–silica Cabosil may also be deduced from a higher thermal stability of the former system determined by Bauer [7]. There is also a feedback morphology–interphase interaction observed in the E1-T2 hybrid network. Formation of the silica clusters is sterically hindered by the preformed epoxide network and very small silica domains are built up [14]. A large surface of the silica phase given by the small size and open structure of the domains promotes the interaction with the epoxide network.

The results reveal the effect of the interphase interaction on mechanical properties of the hybrid systems. Rising interaction results in a larger immobilized layer which is reflected in increased composite modulus. The efficiency of the reinforcement increases in the series EAE < ET-1 < ET-2 < E1-T2 (Figs. 3 and 4). For a given content of SiO₂, the sequential IPNs with a preformed epoxide network exhibit the highest modulus, the most significant decrease in magnitude of the low-temperature maximum of tan δ of the “free” epoxide chains and the

largest shift of the high-temperature peak of tan δ to higher temperature (Fig. 3(b)).

5. Discussion

Morphology of O–I hybrids is usually described by Wilkes’ model corresponding to a particulate composite with silica domains dispersed in an organic matrix. However, some authors [7,26–31] assume a co-continuous morphology. In order to understand the morphology of the O–I hybrid systems better, we will compare our experimental results on the moduli of studied hybrids with the prediction of existing models assuming either particulate or bicontinuous phase structure.

5.1. Model of a particulate composite with filler dispersed in matrix

Modulus of a heterogeneous two-phase system depend on the moduli and volume fractions of components as well as on morphology. Of existing models, the Kerner model modified by Nielsen [19] (Eq. (4)) is frequently used:

$$G_c/G_M = (1 + AB\nu_f)/(1 - B\Psi\nu_f) \quad (4)$$

$$A = (7 - 5\nu_M)/(8 - 10\nu_M)$$

$$B = ((G_f/G_M) - 1)/((G_f/G_M) - A)$$

$$\Psi = 1 + \nu_f(1 - \nu_{max})/\nu_{max}^2$$

where G_c , G_M , G_f are moduli of the composite, matrix and filler, respectively, ν_M the Poisson ratio of the matrix, ν_f the volume fraction of the filler and ν_{max} the maximum packing fraction of the filler.

Our experimental results show that reinforcement of the rubbery epoxy matrix by in situ formed silica is very effective even at low fractions. About 7 vol% of silica in the hybrid E1-T2 brings about an increase in the modulus at room temperature by two orders of magnitude. Such an increase in modulus is incompatible with the model of particulate composites (see also Ref. [26]) as shown in Fig. 5. Theoretical prediction of the Kerner–Nielsen model for a composite of rubbery matrix filled with hard particles (curve 1) anticipates much lower values of the relative modulus (Eq. (4)) than experimental data. Only moduli of the particulate composite EAE are close to the theory. Thus, the effect of morphology and interaction between phases in O–I hybrid composites must be considered in order to explain the experimentally observed reinforcement. Considering the above discussion on interphase interaction, we assume that the effective volume fraction of the filler, ν_{eff} , is higher than ν_{Si} owing to the adhering immobilized epoxide layer. However, only the bound epoxide regions which are in glassy state at room temperature could be comparatively efficient as a hard filler and contribute to the increase in modulus: $\nu_{eff} = \nu_{Si} + \nu_{Ebg}$, where ν_{Ebg} is the

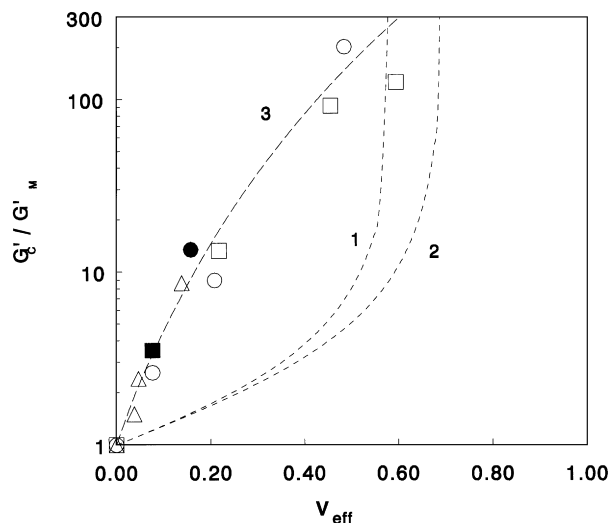


Fig. 6. Relative modulus of the composite as a function of the effective volume fraction of the hard phase, v_{eff} . Curves—theoretical models, $G_{\text{Si}} = 4 \times 10^9$ Pa, $G_{\text{E}} = 2.2 \times 10^6$ Pa, 1 Kerner–Nielsen model (Eq. (4)): $v_{\text{max}} = 0.6$, $v_{\text{M}} = 0.5$, 2 Kerner–Nielsen model: $v_{\text{max}} = 0.7$, $v_{\text{M}} = 0.5$, 3 Davies model (Eq. (9)): $v_{\text{eff}} = v_{\text{Si}} + v_{\text{Ebg}}$ (see Table 1) experimental results. Δ ET-1, \circ ET-2, \bullet ET-2 DBTDL prehydrolysis, \square E1-T2, \blacksquare E1-T2 DBTDL catalysis.

fraction of the bound epoxide in the glassy state. Fig. 3(b) shows that in the cases of very strong interaction, the major part of the bound epoxide layer is in glassy state at room temperature, i.e. the $\tan \delta$ peak appears above room temperature. On the contrary, in the hybrid ET-1, the organic network part bound by silica is almost completely in rubbery state at room temperature, v_{Ebg} is negligible and epoxide does not contribute to the filler effect. The fraction of the immobilized epoxide in glassy state, v_{Ebg} , was estimated (see Table 1) from the areas under the $\tan \delta$ damping curve above room temperature ($= T_{\text{lab}} + 20^\circ\text{C}$) (the fact that the maximum of $\tan \delta$ measured at a frequency of 1 Hz appears about 20°C above glass transition temperature must be taken into account). The relative modulus of the composite, $G_{\text{C}}/G_{\text{M}}$, calculated using the effective volume fraction of the hard phase, is shown in Fig. 6 (curves 1 and 2 for various values of the adjustable parameter v_{max} in Eq. (4)). Obviously, even increased fractions of the filler in a particulate composite cannot account for the observed reinforcement.

5.2. Bicontinuous model

We suppose that high moduli of the heterogeneous systems under study can be explained by assuming that the O–I hybrid consists of two co-continuous phases, i.e. of the organic and inorganic networks and of dispersed particles of the inorganic sol. Bicontinuous morphology of O–I hybrids was already evidenced by SAXS measurements [27,28]. On the basis of the simulation of SAXS models, Landry et al. [28] concluded that silica forms a continuous phase in the organic polymer matrix as a result of the phase

separation by spinodal decomposition. Also the light scattering [29] and electron microscopy [30] results are in conformity with this conclusion. Ductile to brittle transformation with increasing content of TEOS in mechanical tensile studies was used as an evidence of a continuous silica phase in a hybrid by Mauritz et al. [31]. Bauer et al. [7] assumed the continuous silica phase in the IPN epoxy–silica as the hybrid specimen kept the shape of the silica skeleton after combustion of the organic component during TGA.

The effect of phase continuity on dynamic mechanical properties can be treated in terms of combined parallel and series models. The equivalent box model (EBM) [32] assumes that each component is coupled partially in parallel (subscript p) (fraction continuous in the direction of acting force) and partially in series (subscript s) (discontinuous fraction). The modulus of a binary system can be expressed as [33]

$$G_{\text{C}} = (v_1)_p G_1 + (v_2)_p G_2 + v_s^2 / [(v_1)_s / G_1 + (v_2)_s / G_2]. \quad (5)$$

In our case the model involves three phases: silica phase (v_{Si}), glassy epoxide phase (v_{Ebg}) (i.e. fraction of the bound epoxide layer showing T_{g} above room temperature) and rubbery epoxide phase (v_{ER}). If several components are coupled in series, the resulting modulus of the assembly is mainly determined by the modulus of the softest component. As $G_{\text{ER}} (= 2.2 \times 10^6 \text{ Pa}) \ll G_{\text{Ebg}} (= 2 \times 10^9 \text{ Pa}) < G_{\text{Si}} (= 4 \times 10^9 \text{ Pa})$, it is obvious that the series branch of the EBM model can be neglected in comparison with parallel branch:

$$\begin{aligned} G_{\text{C}} &\cong (v_{\text{Si}})_p G_{\text{Si}} + (v_{\text{Ebg}})_p G_{\text{Eg}} + (v_{\text{ER}})_p G_{\text{E}} \\ &\cong (v_{\text{Si}})_p G_{\text{Si}} + (v_{\text{Ebg}})_p G_{\text{Eg}} \end{aligned} \quad (6a)$$

where $v_{\text{ER}} = v_{\text{Ef}} + v_{\text{Ebr}}$, $v_{\text{E}} = v_{\text{Ef}} + v_{\text{Ebr}} + v_{\text{Ebg}}$, G_{Ebg} is the glassy modulus of the epoxide which may approximate the modulus of the immobilized epoxide layer in glassy state; v_{Ebr} is the fraction of the bound epoxy layer in rubbery state. Obviously, the thickness of the glassy interphase layer in certain type of composites is proportional to the interphase interaction. The extent of the immobilization of the epoxy chains in the interphase can be characterized by $v_{\text{Ebg}}/v_{\text{Si}} = K$. Then

$$G_{\text{C}} \cong (v_{\text{Si}})_p (G_{\text{Si}} + K G_{\text{Eg}}) \quad (6b)$$

The percolation theory [34] can predict the modulus of two-phase systems where the contribution to the modulus of the second component is negligible. This approach was modified to calculate the volume fractions coupled either in parallel or in series for both components [33] in co-continuous systems. Thus for silica phase in the O–I hybrids we can write:

$$(v_{\text{Si}})_p = [(v_{\text{Si}} - v_{\text{Sicr}})/(1 - v_{\text{Sicr}})]^f \quad (7)$$

where v_{Sicr} is the critical volume fraction at which the

component assumes partial phase continuity and t is the critical exponent. For spherical particles dispersed in a matrix $v_{cr} = 0.156$ [35] was calculated. For chemical IPNs with covalent bonds we can expect that the critical fraction approaches zero ($v_{Sicr} \geq 0$). Then

$$G_C = [(v_{Si} - v_{Sicr})/(1 - v_{Sicr})]^t (G_{Si} + KG_{Eg}) \approx (v_{Si})^2 (G_{Si} + KG_{Eg}) \quad (6c)$$

The theoretical curves of the EBM model in Fig. 5 (curves 2–4) were calculated using $t = 2.0$ [36] and various values of parameter K , i.e. $K = 10$ (curve 3) and $K = 0$ (curve 2), corresponding to systems (i) with strong epoxy–silica interaction and (ii) without any interaction, respectively. The hybrids E1-T2 and ET-2 with a high silica content obviously fit the theoretical curve for strong interaction, while ET-2 with a small silica content corresponds to a weak interaction. The critical volume fraction $v_{Sicr} = 0.02$ was assumed to better fit the data of more heterogeneous one-stage systems with lower phase continuity (see curve 4). Note that the curves 1–4 are predicted by theoretical models. The fact that Eq. (6c) (curves 2–4) fits well with the experimental data in contrast to Kerner–Nielsen model (curve 1) proves that the O–I composites can be viewed as IPNs.

Also the model of Davies [37] was successfully used to predict the modulus of systems containing two continuous phases in IPNs [38].

$$G_C^{1/5} = v_1 G_1^{1/5} + v_2 G_2^{1/5} \quad (8)$$

The curve predicted by Davies' empirical equation (Eq. (9)) in Fig. 6 (curve 3) was calculated considering an effective volume fraction of the hard phase, v_{eff} , consisting of silica and glassy immobilized epoxide phase. Modulus of the hard phase was assumed to be equal to that of silica, G_{Si} .

$$G_C^{1/5} = v_{Ef} G_E^{1/5} + v_{eff} G_{Si}^{1/5} \quad (9)$$

Figs. 5 and 6 show a satisfactory agreement of bicontinuous models with the experimental data (curves 2–4 in Fig. 5 and curve 3 in Fig. 6). The models fit reinforced systems both with weak and strong interphase interaction assuming enhanced effective volume fraction of the hard phase. Thus, dynamic mechanical properties provide a direct experimental prove that the microphase-separated epoxy–silica hybrid forms a co-continuous IPN.

5.3. Crosslinking of the matrix with filler

Interphase crosslinking is sometimes considered [39,40] as alternative explanation of the excessive reinforcement. The filler dispersed in the matrix is believed to act as a giant multifunctional crosslink [41] if there is a good adhesion between phases or a covalent bond to the matrix exists. The plateau modulus above T_g in the linear PMMA–TEOS system [3] was interpreted as a result of crosslinking between the polymer matrix and silica clusters formed

from TEOS. Physical and chemical interaction between organic and inorganic phases were proved [3,12]. A significant increase in modulus with increasing crosslinking between silica phase and polymer was observed by Huang et al. [10] in the alkoxy silane-modified PTMO–TEOS system. Using the theory of rubber elasticity Miller et al. [40] interpreted high modulus in this system by crosslinking through silica junctions. The agreement with the experiment, however, is surprising because application of this theory to a heterogeneous system with glassy domains and approximation of the crosslink functionality are not fully justified.

6. Conclusions

The rubbery epoxide network DGEBA-D2000 was reinforced with silica formed in situ by sol–gel process. Increase in the modulus by two orders of magnitude at low contents of the silica phase (<10 vol%) was achieved. Three different polymerization procedures were used to prepare microphase-separated simultaneous and sequential IPNs of the epoxy–silica hybrid DGEBA-D2000-TEOS. The results show very close relations among polymerization mechanism, interphase interaction, morphology and dynamic mechanical properties.

- The way of a hybrid synthesis and catalytic conditions (acid, base, pH neutral) determine the reaction mechanism, final structure and morphology. In contrast to the base and pH neutral catalysis of the sol–gel process, the acid catalysis promotes fast hydrolysis of the siloxane structures which results in the high contents of Si–OH groups and an extensive grafting to the epoxide network.
- Grafting between the rubbery epoxide and glassy silica networks results in the formation of the interphase epoxide layer with reduced mobility and increased T_g . The increase in T_g above the room temperature then brings about vitrification of a part of this organic layer which contributes to the reinforcement.
- Because of the strong interphase interaction, more uniform morphology of the O–I hybrids is developed in corresponding systems (see Fig. 1).
- Modulus of the hybrid networks rises with growing content of SiO₂ and increasing interphase interaction.
- The results prove that DGEBA-D2000-TEOS system does not correspond to the morphological model of a particulate composite consisting of rubbery epoxide matrix and in situ formed, dispersed glassy silica particles. Dynamic mechanical properties fit the model assuming the co-continuous morphology of the epoxy matrix and of the silica phase or the silica-glassy epoxide phase continuously extending through the macroscopic sample.

Acknowledgements

The authors wish to thank the Grant Agency of the Czech Republic for support of the work (project no. 203/98/0884). The third author J.K. is greatly indebted to the Grant Agency of the Academy of Sciences of the Czech Republic for financial support of this work (project no. A4050706).

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