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Composites via heterogeneous crosslinking of concentrated emulsions

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Polymer composites based on an epoxy resin oligomer, an amine terminated oligomer or maleic anhydride, and one or several monomers among styrene, methyl methacrylate, butyl methacrylate, glycidyl methacrylate, and acrylonitrile have been prepared using the concentrated emulsion pathway. Each of the components of the composite was first transformed in a concentrated emulsion in which water with a low volume fraction was the continuous phase. The concentrated emulsions containing monomers were partially polymerized (to ensure their stability during the subsequent heating) before being mixed with one or two concentrated emulsions, each containing one of the above mentioned oligomers. The mixture of concentrated emulsions was subjected to heating for the complete polymerization of the monomer and for the reaction between the epoxy resin and the amine terminated oligomer or the maleic anhydride to occur. The reaction generates a crosslinking among the cells of the concentrated emulsions (heterogeneous crosslinking) and thus achieves compatibilization among various incompatible components. The composites were characterized using Fourier transform infra-red spectroscopy, differential scanning calorimetry, swelling, as well as solubility measurements. Tensile measurements showed that the components of the composites were compatibilized and that the latter possess excellent mechanical properties. Copyright © 1996 Elsevier Science Ltd.

(Keywords: composite; concentrated emulsion; compatibilization of polymers; heterogeneous crosslinking)

INTRODUCTION

Several methods have been developed in recent decades to prepare polymer composites. In addition to melt blending and graft copolymerization, the blending of two or more types of latexes by mechanical mixing was also suggested[1,2]. Because of the 'low viscosity' of the latex components, intimate dispersion could be achieved by employing a relatively low mechanical energy for mixing[3]. When the latexes were further crosslinked, a network or interpenetrating latex networks was (or were) obtained[4,5]. The mixing and crosslinking were so far exclusively conducted in a multi-step way, i.e. the latexes were sequentially formed, coagulated and crosslinked. In this paper, we propose a novel procedure, in which each of the polymers involved is first transformed as such, or as monomers in a concentrated emulsion in water. The concentrated emulsion of monomers is partially polymerized before it is mixed with one or two concentrated emulsions of polymer or oligomer. At least one of the concentrated emulsions contains a component which can react with the components of the other concentrated emulsions. During heating, the monomers polymerize completely and the above reaction occurs. The final result is a composite in which the various incompatible polymers are made compatible, due to the reaction.

To illustrate the procedure, we prepared two kinds of composites. One is based on an epoxy resin (poly[bisphenol A-*co*-epichlorohydrin], PBPAE), an amine terminated oligomer (poly[butadiene-*co*-acrylonitrile]), denoted PBAn, and at least two monomers out of styrene (St), methyl methacrylate (MMA), butyl methacrylate (BMA) and glycidyl methacrylate (GMA), one of them being glycidyl methacrylate. Concentrated emulsions in water were first prepared from each of the three components: PBPAE, PBAn and the monomers. After the concentrated emulsion containing monomers was partially polymerized (to ensure the stability of the concentrated emulsion in the subsequent heating), the three concentrated emulsions were mixed and subjected to heating. During heating, complete polymerization of the monomers takes place and the amine terminated oligomer reacts with the epoxy resin and the GMA. In what follows, the above composite will be called the epoxy/amine system. The other composite is based on PBPAE, maleic anhydride (MAn) and one or several monomers among St, BMA and acrylonitrile (An). Two concentrated emulsions in water were prepared, one from the epoxy resin, and the other from the mixture between the monomers and MAn. After the partial polymerization of the latter, the concentrated emulsions were mixed and subjected to heating. The MAn can react with the epoxy resin and can also copolymerize with the monomers. This provides the compatibilization between the epoxy resin and the

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formed polymer. This composite will be called the epoxy/anhydride system. In both composites, the components do not dissolve one in another. PBPAE and PBAn separate even in their common solvent chloroform. The best way to mix these components is via concentrated emulsions.

A concentrated emulsion has the appearance of a paste, and differs from the conventional emulsion in that the volume fraction, ϕ, of the dispersed phase is greater than 0.74 (which represents the volume fraction of the most compact arrangements of spheres of the same size), and may be as high as 0.99. At high volume fractions, the concentrated emulsions are composed of polyhedral cells less than 1 μm in size, separated by thin films of continuous phase. Its use in the preparation of latexes and composites has recently been suggested[6–8].

Since, in the mixture of concentrated emulsions suggested in the present paper, the components cannot dissolve one in another, the reactions between the functional groups are likely to take place at the interface of the cells. The compact packing of the cells in a concentrated emulsion provides the best opportunity for inter-cell surface reactions, i.e. heterogeneous crosslinking[9], to take place. Unlike the homogeneous crosslinking, the heterogeneous one involves particularly the surface region of the latexes. The use of the concentrated emulsion method has another advantage. To acquire toughness, the flexible component of the composite must be in the size range 0.5–2 μm[10,11]. In the other processing methods, strict conditions must be employed to achieve such a size range. By using the concentrated emulsion mixing method, the size of the cells just falls in that favoured range, and hence toughening can be easily ensured.

EXPERIMENTAL

Materials

Azobisisobutyronitrile (AIBN, Kodak) was recrystallized from methanol. All the other chemicals were purchased from Aldrich. St, BMA, MMA, An and GMA were filtered through an inhibitor removal column before use. MAn, PBPAE (epoxy resin, molecular weight = 4000, 1800, which are denoted as E4000 and E1800, respectively), PBAn (molecular weight = 4900, amine equivalence = 1200), dodecyl sulfate sodium salt (SDS, 70%), chloroform (99%), methanol (99%) were used as received.

Preparation of the epoxy/amine composites

Three concentrated emulsions in water were first prepared separately from a solution of PBPAE (0.5 g per g chloroform), a solution of PBAn (1 g per g chloroform) and a monomer mixture as dispersed phases, respectively. The monomer mixture containing an initiator (AIBN, 0.005 g per g of monomers) was partially polymerized at 50°C for 1 h, before preparing the concentrated emulsion, in order to moderately increase the viscosity, and thus to ensure the stability of the concentrated emulsion during subsequent heating. The concentrated emulsion based on monomers was kept at 50°C for 30 min in order to generate incipient latexes which can keep after mixing, to a high extent, their identity. Subsequently, the three concentrated emulsions were mixed, and the mixture was further heated at 50°C for 16 h to complete the polymerization of the monomers, and to allow the reactions of the amine groups with the epoxy resin and GMA units to take place. The product was washed with methanol and dried in a vacuum oven. The dried product was treated for a number of hours $\leqslant 12$, at 75°C to carry out the post-curing reaction.

Preparation of the epoxy/anhydride composites

The preparation was similar to the one above, but only two concentrated emulsions in water were mixed: one based on PBPAE and another one based on a partially polymerized monomer mixture containing MAn. After the two concentrated emulsions were mixed, the mixture was kept in a water bath at 50°C for 24 h. No post-curing was employed, for reasons which are explained later.

Preparation of the concentrated emulsion

An aqueous solution of SDS (10 wt%) was first placed in a flask provided with a magnetic stirrer. The flask was sealed with a rubber septum, after which the air inside was replaced with nitrogen. The dispersed phase was added dropwise with vigorous stirring into the flask with a syringe, until the volume fraction of the SDS aqueous solution became 0.2. The whole addition process lasted about 15 min, and took place at room temperature.

Tensile testing

The powders (fine and/or coarse) were thermopressed with a Laboratory Press (Fred S. Carver INC.) at 150°C for 3–5 min, and then cooled to room temperature. The sheets thus obtained were cut with a die to the size required by ASTM D.638. The tensile testing was conducted at room temperature, using an Instron Universal Testing Instrument (Model 1000). The elongation speed of the instrument was 20 mm min^{-1}.

Measurement of the insoluble species content and of swelling

A pre-weighed sample sheet prepared as for tensile testing was immersed in chloroform in a test tube at room temperature, using 20 ml of solvent for each g of sheet. The solvent in the tube was changed with a fresh one every 8 h, until all the soluble species had been removed (less than 48 h). The swollen sheet was first weighed and subsequently dried in a vacuum oven for 24 h to remove the solvent. The ratio of the remaining weight to that of the original sheet is denoted as the insoluble species content, and the ratio of the weight of the swollen sample to that of the dried one is the swelling ratio.

Differential scanning calorimetry

The thermal behaviour of both the intermediate and final products was determined by differential scanning calorimetry (d.s.c.), with a DuPont d.s.c. instrument. Each sample was scanned twice. The first scanning was from −80 to 200°C. After the first scanning, the specimen was cooled to below −80°C and then heated for a second time from −80 to 140°C. The heating rate was 10°C min^{-1}.

Table 1 Insoluble species content and glass transition of epoxy/amine systems

Amounts of the components (g)							Time of post-curing (h)	Insoluble species content $\times 10^2$	Swelling ratio $\times 10^2$	T_g (°C)
E4000	E1800	PBAn	St	BMA	MMA	GMA				
5		5	5	5	–	0.4	0	84.0	1569	–
							4	87.9	1466	–
							8	90.3	1204	70–105
							12	90.7	1179	70–105
	5	5	5	5	–	0.4	0	84.6	1449	–
							4	86.5	1211	–
							8	89.6	1070	75–110
							12	90.1	1028	75–110
5	–	5	10	–	–	0.4	8	92.0	1203	77–105
5	–	5	5	–	5	0.4	8	90.8	1188	80–105
–	5	5	5	–	5	0.4	8	91.2	1050	83–100
5	–	5	5	–	–	0.4	8	95.3	1044	70–110
–	5	5	5	–	–	0.4	8	95.2	978	75–115
5	–	5	2.5	2.5	–	0.4	8	94.2	1052	65–100
–	5	5	2.5	2.5	–	0.4	8	95.2	992	70–105
5	–	3	2.5	2.5	–	0.4	8	89.8	1152	70–95
–	5	3	2.5	2.5	–	0.4	8	90.2	1040	75–105

Table 2 Insoluble species content and glass transition of epoxy/anhydride systems

Amounts of the components (g)						Insoluble species content $\times 10^2$	Swelling ratio $\times 10^2$	T_g (°C)
E4000	E1800	BMA	St	An	MAn			
5	–	5	–	–	0.25	82.2	1180	83
5	–	5	2.5	–	0.25	80.5	1266	84
5	–	5	2.0	0.5	0.25	78.2	1232	87
–	5	5	–	–	0.25	86.1	1022	87
–	5	5	2.5	–	0.25	82.9	1176	88
–	5	5	2.0	0.5	0.25	80.5	1147	90
–	5	5	–	–	0.375	88.2	852	90
–	5	5	–	–	0.125	70.4	1354	–

Infra-red spectra

The Fourier transform infra-red (*FT*i.r.) absorption spectra were obtained with a Perkin-Elmer (1720) *FT*i.r. instrument.

RESULTS AND DISCUSSION

Insoluble species content

The insoluble species content of the samples is listed in *Tables 1* and *2*. One can see that the wt% of the crosslinked structure of the final product is near or above 90%. In the ideal case, all the chains should be linked to a complete network and the insoluble species content should be 100%. However, in actual reactions, several non-ideal situations may occur: (i) the curing may be incomplete; and (ii) some linear polymer chains may not be linked to the network. It is reasonable to consider that most of these linear chains are copolymers of the monomers. Because these copolymers are random, most of the functional groups, GMA or MAn units, are not located at the end and, therefore, their reactivity is lower. Some copolymer chains may contain fewer reactive units. Indeed, *Tables 1* and *2* show that the larger the amount of monomers introduced in the initial system, the lower the insoluble species content in the final product. The insoluble species content for epoxy/amine systems is, for comparable molar ratios between the curing agent and the epoxy groups, generally higher than those for the epoxy/anhydride systems, because in the latter case the amount of monomer employed is larger. However, the presence of the uncrosslinked soluble chains has a positive effect because it improves the flowability of the materials.

For the epoxy/amine systems, the post-curing time has an important effect on the insoluble species content. A longer curing time results in a higher fraction of chains linked to the network. Indeed, *Table 1* shows that the insoluble species content increases initially with the curing time. However, the insoluble species content no longer increases for curing times longer than 8 h. This happens because the highest possible crosslinking is achieved in 8 h.

Obviously, the molar ratio of epoxy/curing agent also plays a role, the systems with a higher curing agent content having a higher insoluble species content.

One can note that the molecular weight of PBPAE has an effect on the insoluble species content of the epoxy/

anhydride systems, but a more moderate one on the epoxy/amine systems. For the same weight amount, the PBPAE of low molecular weight possesses a larger number of epoxy groups, hence the curing should be in the latter case more advanced. However, in epoxy/amine systems, there is a competition between the epoxy groups of PBPAE and of the copolymers for the reaction with the amine groups. The increase in the crosslinking of PBPAE is in such cases offset by the decrease in the crosslinking of the copolymers. As a result the effect is moderate. In contrast, in the epoxy/anhydride systems, the PBPAE is cured by the MAn groups of the copolymer and the crosslinking increases as the number of epoxy groups increases.

Swelling ratio

The swelling ratio, which is a measure of the extent of crosslinking, is listed in *Tables 1* and *2*. As expected, *Table 1* shows that the swelling ratio decreases with increasing time of post-curing. However, the swelling ratios for 8 and 12 h post-curing are comparable. This again indicates, as noted above, that the highest possible curing is achieved in 8 h. For both systems, a lower swelling ratio is associated with a higher amount of curing agent employed. For the same post-curing time and the same amount of curing agent, the system with a greater amount of monomer possesses a higher swelling ratio, because of the lower extent of crosslinking.

Fourier transform infra-red determinations

The extent of curing of the epoxy/anhydride systems was also assessed on the basis of the *FT*i.r. spectra (*Figures 1* and *2*). The spectrum in *Figure 1* is for MAn, and the three spectra in *Figure 2* are for the pure E4000 and the composites after 12 and 24 h of reaction at 50°C, respectively. MAn can be characterized by three consecutive sharp peaks between 1300 and 1200 cm^{-1}, and one can see that these peaks became smeared after 12 h, and completely disappear after 24 h of reaction. The epoxy group can be characterized by the sharp peak near 3050 cm^{-1}, pointed by an arrow. It becomes weaker after 12 h and can hardly be detected after 24 h of reaction. The disappearance of the MAn peaks is partly due to the curing, but also to hydrolysis. However, the weakening and disappearing of the characteristic peak of the epoxy group provides indications about the extent of curing.

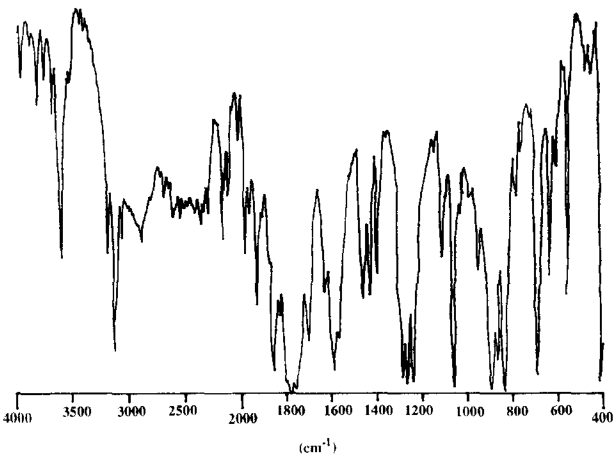

Figure 1 *FT*i.r. spectrum of maleic anhydride

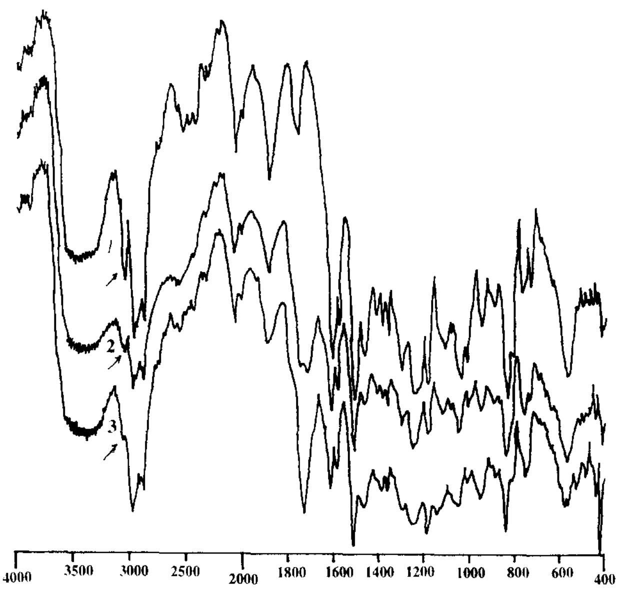

Figure 2 *FT*i.r. spectra. (1) Poly(bisphenol A-*co*-epichlorohydrin), molecular weight = 4000. (2) Epoxy/anhydride composite after 12 h reaction. (3) Epoxy/anhydride composite after 24 h reaction. Amounts of the components (g) for the composite: E4000: 5; MAn: 0.25; MBA: 5

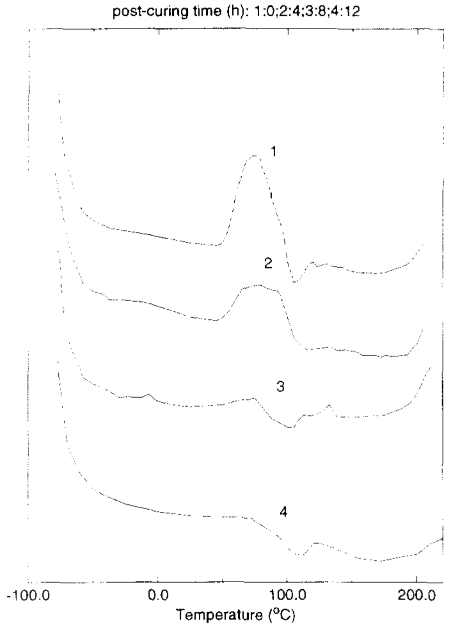

Figure 3 D.s.c. diagrams for the composites. Post-curing time (h): (1), 0; (2), 4; (3), 8; (4), 12. Amounts of the components (g) for the composite: E4000: 5; PBAn: 5; St: 5; BMA: 5; GMA: 0.4

Differential scanning calorimetry

In this paper, the d.s.c. measurements have two purposes: assessment of the extent of curing of the epoxy/amine systems; and the determination of the glass transition temperatures T_gs for both the epoxy/amine and epoxy/anhydride composites. As described in Experimental, the polymerization and curing of the epoxy/amine system were carried out in two steps. Because the mixture of concentrated emulsions became unstable at temperatures higher than 50°C, the mixture was kept at 50°C for 16 h and subsequently at 75°C for post-curing. The post-curing was monitored by d.s.c.

measurements. The d.s.c. curves for the samples subjected to 0, 4, 8, and 12 h of post-curing are presented in *Figure 3*. One can see that the curves for the samples subjected to 0 and 4 h post-curing exhibit an exothermic peak between 50 and 100°C with a maximum at 75°C. The peak for the 4 h post-curing sample is smaller and narrower. The curves for the 8 and 12 h post-curing samples do not exhibit any exothermic peak, but an endothermic stage. Since the samples were previously washed with methanol, radical polymerization is unlikely to have occurred during the d.s.c. measurements. For this reason, the exothermic peak is likely a result of the reaction between the epoxy and amine groups. The d.s.c. information indicates that after 16 h of reaction at 50°C, about 8 h more are needed at 75°C to complete the curing of the system. From the location of the maximum of the exothermic peaks, one can conclude that the optimum curing temperature for the epoxy/amine system is around 75°C.

For the fully cured samples of the epoxy/amine systems, the d.s.c. curves exhibit a wide endothermic stage, which can be as wide as 40°C; no other stages or peaks are present on the d.s.c. curves. This indicates that the samples possess only one T_g range. A fully compatible homogeneous polymer blend usually has a single T_g[12,13], which is not wide (3–5°C). Wide T_gs can be associated[14,15] with heterogeneous materials. The wide T_g of the epoxy/amine systems occurs because of the heterogeneity at the colloidal scale of the materials which were generated via the crosslinking of three types of latexes. A wide T_g range material can be used as a damping medium, since it can absorb vibrations in a wide range of frequencies.

No reaction peak was observed in the d.s.c. measurements for the epoxy/anhydride system after 24 h of reaction. For this reason, the post-curing was not applied to these systems. In addition, no wide glass transition was exhibited. All the samples of epoxy/anhydride system provided a narrow T_g (*Table 2*). In contrast to the epoxy/amine systems which involved three concentrated emulsions, the epoxy/anhydride systems involve only two concentrated emulsions. Obviously, the latter systems should be less heterogeneous than the former.

Mechanical properties

The solubility measurements and the *FT*i.r. and d.s.c. characterizations have provided information about the extent of reaction in the systems. In what follows we characterize the compatibilization via the mechanical properties of the materials obtained, since good mechanical properties imply compatabilization.

Effect of the extent of post-curing

The tensile properties for various extents of post-curing of the samples are listed in *Table 3*. One can see that as the extent of post-curing increases, the tensile strength and Young's modulus increase, and the elongation at break decreases. This is as expected. At low crosslinking, the flexible chains of PBAn and BMA segments have a high freedom of motion. The rigid chains of epoxy and the polystyrene (PS) segments to which the flexible chains are attached act like physical crosslinking points. The material behaves as an elastomer with an elongation higher than 100%. As the crosslinking increases, the segment movements are gradually impeded and, at the same time, the interactions among the segments are strengthened. As a result the tensile strength and Young's modulus increase and the elongation at break decreases. In the latter case, the material has a tough plastic behaviour. The tensile properties of the 8 and 12 h post-curing samples are comparable. This is because the curing reaction was completed in 8 h, and the further treatment at 75°C provided no structural changes.

Molecular weight of the PBPAE

Differences occur in the tensile properties of the

Table 3 Tensile properties of epoxy/amine systems

Amounts of the components (g)								Tensile properties (std error)			
E4000	E1800	PBAn	St	BMA	MMA	GMA	Time of post-curing (h)	Tensile strength strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Toughness (MJ m^{-3})
5	–	5	5	5	–	0.4	0	24.5 (1.5)	126 (11.1)	613 (27)	15.4 (1.2)
							4	30.1 (1.4)	87 (4.2)	831 (21)	19.6 (1.1)
							8	37.6 (1.7)	65 (3.1)	922 (12)	21.6 (2.0)
							12	36.9 (2.2)	63 (4.7)	966 (35)	21.2 (1.7)
–	5	5	5	5	–	0.4	0	27.5 (0.9)	108 (8.1)	634 (32)	14.8 (0.9)
							4	34.6 (1.8)	74 (5.5)	884 (15)	19.2 (1.3)
							8	42.6 (1.3)	58 (3.7)	984 (16)	22.2 (1.6)
							12	43.0 (2.0)	57 (2.6)	991 (34)	22.0 (1.3)
5	–	5	10	–	–	0.4	8	47.4 (2.5)	31 (1.8)	1022 (23)	12.9 (1.1)
5	–	5	5	–	5	0.4	8	48.6 (2.0)	21 (1.9)	1191 (25)	8.5 (0.4)
–	5	5	5	–	5	0.4	8	51.5 (3.7)	14 (1.1)	1224 (44)	6.1 (0.6)
5	–	5	5	–	–	0.4	8	41.7 (2.7)	55 (3.4)	966 (35)	20.6 (1.8)
–	5	5	5	–	–	0.4	8	45.3 (3.1)	51 (4.2)	1075 (21)	20.0 (0.7)
5	–	5	2.5	2.5	–	0.4	8	35.4 (1.1)	69 (3.5)	822 (10)	21.4 (2.2)
–	5	5	2.5	2.5	–	0.4	8	40.1 (2.0)	62 (4.2)	916 (29)	21.6 (1.3)
5	–	3	2.5	2.5	–	0.4	8	39.7 (2.8)	56 (3.3)	917 (17)	17.9 (0.8)
–	5	3	2.5	2.5	–	0.4	8	44.6 (3.1)	51 (2.5)	1016 (26)	18.2 (1.4)

Table 4 Tensile properties of epoxy/anhydride systems

Amounts of the components (g)						Tensile properties (std error)			
E4000	E1800	BMA	St	An	MAn	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Toughness (MJ m^{-3})
5		5			0.25	48.5 (1.4)	66 (3.3)	1048 (96)	23.8 (1.7)
5		5	2.5		0.25	53.2 (2.1)	21 (1.6)	1224 (54)	8.9 (0.9)
5		5	2.0	0.5	0.25	55.6 (2.4)	25 (1.3)	1322 (47)	11.1 (0.8)
	5	5			0.25	51.2 (1.7)	57 (2.7)	1152 (32)	22.1 (1.9)
	5	5	2.5		0.25	55.4 (2.5)	15 (1.0)	1304 (27)	6.7 (0.5)
	5	5	2.0	0.5	0.25	58.1 (2.7)	19 (0.7)	1414 (36)	8.7 (1.1)
	5	5	–		0.375	55.8 (3.2)	34 (1.5)	1378 (25)	14.4 (0.7)
	5	5			0.125			–	

composites based on E1800 or E4000 (*Tables 3* and *4*). The samples based on E1800 provide higher tensile strengths and Young's moduli and lower elongations at break. This can be easily explained as a result of the extent of crosslinking of the epoxy resin. For the same weight amounts, E1800 contains a larger number of epoxy groups. Consequently, E1800 can have a higher extent of crosslinking than E4000 and the composites based on E1800 can be stiffer and less flexible.

Amount of curing agent

For the epoxy/anhydride systems (see *Table 4*), the higher amount of curing agent (MAn) results in higher crosslinking and thus in a less flexible material. If the amount of curing agent is too low, the system cannot be properly cured, and the composite possesses hardly any mechanical strength. However for the epoxy/amine system (see *Table 3*), the situation is more complicated. PBAn is both a curing agent, because its amine groups can react with the epoxy groups, and a toughener, since its flexible segments toughen the glass matrix of epoxy and PS segments. In *Table 3*, the systems with the weight ratios PBAn/PBPAE = 5/5 and 3/5 are compared. The decrease of the PBAn/PBPAE weight ratio from 5/5 to 3/5 changes the amine/epoxy molar ratio from 1.5 to 0.94; this decreases the crosslinking and increases the flexibility of the system. On the other hand, a decrease in the PBAn content decreases the flexibility. The net effect depends which of the two effects prevails. The data in *Table 3* show that the samples with less PBAn provide a higher tensile strength and Young's modulus but a lower elongation at break. This means that the rubber provides in this particular case the dominant effect.

Effect of the monomers

Several monomers were used in different weight ratios. *Tables 3* and *4* show that the tensile properties are sensitive to the nature(s) and amount(s) of monomer(s). St, MMA and An units increase the tensile strength and Young's modulus but decrease the elongation at break; the BMA units change the above properties in the opposite direction.

Toughness

The toughness of the samples, as measured by the area under the stress–strain curve, is listed in *Tables 3* and *4*, which show that most of them possess a high toughness near 20 MJ m^{-3}. As shown by *Table 3*, a sufficient extent of crosslinking results in a high toughness. Longer post-curing times and higher contents of the curing agent provide usually higher toughness. However, a too high crosslinking may cause a decrease in toughness, because the flexibility becomes too small. Rigid monomer units, such as those of St and MMA, are harmful to toughness.

CONCLUSION

Polymer composites based on epoxy resins are prepared via the mixing of concentrated emulsions of various components. This is followed by polymerization and by the heterogeneous crosslinking which occurs simultaneously with the transformation of the cells of the concentrated emulsion to latexes. All the samples exhibit a single T_g, which is wide for some systems and narrow for other systems. They possess excellent mechanical properties, which indicates that the components of the composites were satisfactorily compatibilized. The curing time affects for some systems the extent of crosslinking and hence both the mechanical and thermal properties. Suitable compositions and curing lead to composites with a wide glass transition range, as wide as 40°C, which can be employed as energy-damping materials.

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