JOURNAL OF MATERIALS SCIENCE **36** (2001) 845–852

Ultimate properties of rubber and core-shell modified epoxy matrices with different chain flexibilities

M. ORMAETXEA
Dpto. Ingeniería Química y M. Ambiente, Escuela Ingeniería Técnica Industrial, Universidad País Vasco/Euskal Herriko Unibertsitatea, Avda. Felipe IV, 1 B. 20011 San Sebastián - Donostia, Spain

J. FORCADA
Dpto. Química Aplicada, Facultad de Ciencias Químicas, Universidad País, Vasco/Euskal Herriko Unibertsitatea. B° Ibaeta. San Sebastián - Donostia, Spain

F. MUGIKA, A. VALEA, M. D. MARTIN, C. MARIETA
Dpto. Ingeniería Química y M. Ambiente, Escuela Ingeniería Técnica Industrial, Universidad País Vasco/Euskal Herriko Unibertsitatea, Avda. Felipe IV, 1 B. 20011 San Sebastián - Donostia, Spain

S. GOYANES
Dpto. Física, Fac. C. Exactas y Naturales, Universidad Buenos Aires, Pabellón I, Ciudad Universitaria, 1428 Buenos Aires, Argentina

I. MONDRAGON*
Dpto. Ingeniería Química y M. Ambiente, Escuela Ingeniería Técnica Industrial, Universidad País Vasco/Euskal Herriko Unibertsitatea, Avda. Felipe IV, 1 B. 20011 San Sebastián - Donostia, Spain
E-mail: iapmoegi@scehu.es

Preformed polystyrene-co-butylacrylate (PScoBu) core-shell particles and polystyrene microspheres as well as amine-terminated butadiene nitrile (ATBN) rubber have been used for modification of both rigid and more flexible crosslinked DGEBA-based epoxy networks having significantly different crosslink densities. Some variations in cure kinetics have been shown by both thermal and rheological measurements. Independently of the crosslink density of the neat epoxy matrix, function of the cycloaliphatic or aliphatic hardener used, the toughening effect via core-shell modification has been found as good as that for rubber modification but with a better retention of thermal properties. Results are investigated as a function of the morphologies obtained by scanning electron microscopy (SEM) but also by atomic force microscopy (AFM). Larger fracture toughness was obtained for every -unmodified and modified- epoxy matrices cured with the aliphatic hardener as a consequence of the lower crosslink density of the corresponding mixtures.

1. Introduction

Epoxy resins have long been used for adhesives, electronics encapsulation, and as matrices for composite laminates. The many useful properties of the cured matrices, such as high elastic modulus, low creep, and good performance at elevated temperatures, have as counterpart their brittleness and poor resistance to crack propagation.

Several methods have been proposed to increase the toughness of epoxy resins. Traditionally, one of the most successful involves the addition of a suitable rubber to the uncured resin furtherly controlling the polymerization reactions in order to induce phase separation [1–5]. Core-shell modification of epoxy resins has also been extensively investigated in the latter years [6–15] in order to enhance the fracture toughness of these matrices with minimal lowering of their glass transition temperature. On the other hand, nowadays it is well known that one of the main factors controlling the fracture behavior of cured thermosetting matrices is their crosslink density [9, 13, 16, 17]. Moreover, other factors such as interphase between dispersed phase and

---

* Author to whom all correspondence should be addressed.

epoxy matrix as well as morphology, both of them depending upon the kinetics/thermodynamics through curing and upon the existence of reactive groups in the modifier, play also an important role on the ultimate properties of polymer-modified thermosetting matrices.

The primary objective of the current investigation was to establish comparatively the efficacy of rubber and core-shell modification for toughening different epoxy matrices. In this way, parameters related to the chemical rigidity of the matrix as well as to the chemical structure of added microparticles have been analysed. Two different microparticles with styrene cores have been emulsion synthetised, ones without any shell and the others with an acrylate shell since acrylate polymers are compatible with uncured epoxy matrices [18]. Results for core-shell modification are compared to those obtained for rubber modification in different crosslink density matrices obtained by curing the epoxy resin with cycloaliphatic or aliphatic curing agents. Morphology has been investigated by both atomic force microscopy (AFM) and scanning electron microscopy (SEM).

2. Experimental

The epoxy resin, DER 332, gently gifted by Dow Chemical, was a diglycidyl ether of bisphenol-A (DGEBA). This resin was cured with two hardeners: polyoxipropylenetriamine (PPO), D230 kindly supplied by Hunstman Co., and 4,4′-diamino-3,3′-dimethylcyclohexylmethane (3DCM), Laromin C260, from Basf. The core-shells have been manufactured in our laboratories by emulsion polymerization. The first ones were polystyrene-co-butylacrylate (PScoBu) particles of 300–400 nm diametre, and the second particles consisted of polystyrene particles with 50–150 nm diametre. Water from emulsion polymerization was removed by maintaining the core-shell particles dispersion in a wide recipient for 10 days at room temperature, and the particles were stored in a dissicator before using. In order to analyse the mechanical behaviour of the core-shell modified DGEBA/3DCM mixtures, systems containing Hycar 1300 × 16, an amine terminated butadiene nitrile (ATBN) rubber, kindly provided by Goodrich, were also used.

The core-shell particles were added, in percentages ranging from 5 to 15 wt%, to the resin and stirred with a high speed mixer previously to the addition of the hardener. The ATBN modifier was added in amounts ranging from 5 to 15 wt%. The hardener/epoxy stoichiometric ratios, r, used were 1.0 and 0.8.

Mixing was carried out by using the following procedure. After heating the DGEBA to 60°C, core-shell particles or ATBN rubber were added into the epoxy resin and then these components were mixed by using a mechanical stirrer at 250 rpm for 15 min. Finally, the curing agent, 3DCM or PPO, was added while slowly stirring. The 3DCM containing mixture was poured into a preheated mould at 70°C and cured for 2 h 30 min degassing it with vacuum during the first hour, and ulteriorly it was post-cured at 200°C for 2 h and allowed to cool gradually to room temperature. Cure schedules with different pre-cure temperatures (50, 70 or 100°C) were also employed for the 10 wt% core-shell particles containing mixtures. The cure cycle for the epoxy matrix cured with PPO was 3 h at 60°C, the first 1 h 30 min in vacuum, followed by post-curing at 180°C for 2 h.

Rheology of curing of the mixtures was followed in a Metravib viscoanalyser at 70°C using an annular shearing device by recording the evolution of the loss modulus, G'', and that of the loss factor, tan δ, through isothermal polymerization.

Isothermal scans carried out by differential scanning calorimetry (Perkin-Elmer, DSC-7) or annular shearing, shown in Fig. 1, indicated that, although no evident for the 10 wt% ATBN rubber containing mixture, the stoichiometric DGEBA/ATBN system needed around 50 min for reacting at 70°C, though that mixture did not vitrify at these cure temperatures as seen by the lack of G'' maximum in the corresponding rheological curve. Therefore, some DGEBA/hardener mixtures were performed by pre-reacting the rubber and the epoxy resin for 1 h before the hardener addition.

The glass transition temperatures of the mixtures, T_g, obtained performing DSC scans at 10°C/min, were taken as the midpoint of the heat flow variation corresponding to the glass transition region.

The dynamic mechanical behavior of the neat and modified epoxy mixtures was studied in the same viscoanalyser from 20 to 250°C at 3°C/min and 10 Hz using $60 \times 12 \times 5$ mm^3 samples with a bending device. The temperature corresponding to the maximum for the α relaxation in the loss factor plotting was recorded as the glass relaxation temperature, T_α. The rubber modulus, E'_r, taken as the modulus at $T_\alpha + 40°\mathrm{C}$, was used to compare the crosslink densities of the networks by taking in account its inverse dependence upon the average molecular weight between crosslinks, $\bar{M}_c$ ($E'_r = \rho RT/\bar{M}_c$), ρ being the density of the network and T the absolute temperature.

Mechanical measurements were performed in a Instron 4206 test machine equipped with a 5 kN load

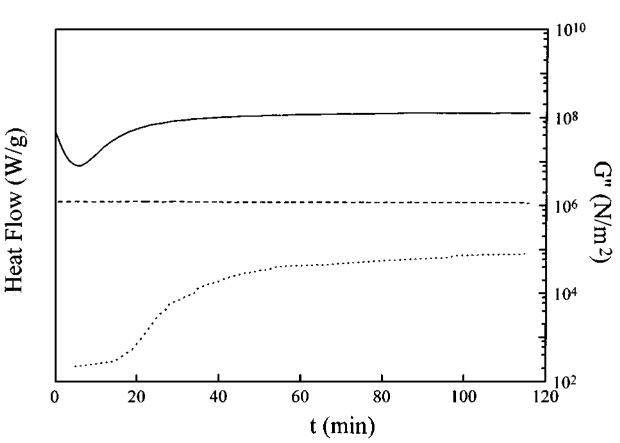


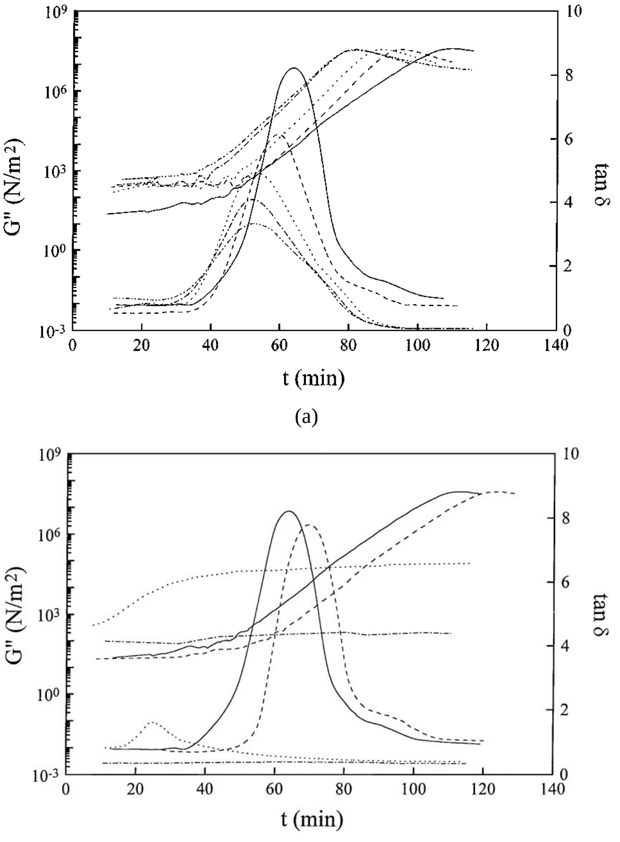
Figure 1 Isothermal evolution during polymerization of DGEBA with ATBN rubber: (—) - DSC scan at 70°C for the stoichiometric mixture, (– –) - DSC scan for the 10 wt% ATBN containing epoxy matrix without 3DCM; (· · ·) loss modulus for the DGEBA/ATBN stoichiometric mixture at 70°C.

cell. Flexural properties were carried out according to the ASTM D230 standard at a crosshead rate of 1.7 mm/min using $80 \times 12 \times 5$ mm^3 specimens. Fracture toughness tests were made following the European Structural Integrity Society (ESIS) protocol [19, 20] using single-edge-notched type samples ($60 \times 12 \times 5$ mm^3) in a three point bending geometry. For both tests a minimum of 5 specimens were used. Poisson's ratio was taken as 0.35 for every matrices used.

The AFM examinations were performed using a Nanoscope IIIa (Digital Instruments) operating in contact mode (the tip was always touching the surface when the feedback loop was on) in air, using commercial silicon nitride probes with V-shaped cantilevers of length 200 nm and spring constant 0.12 N/m. Images are presented without any image processing except horizontal leveling. SEM measurements were performed in a Jeol JSM 35 CF instrument.

3. Results and discussion

The evolution of the dynamic mechanical properties G'' and $\tan\delta$ of the core-shell-modified epoxy mixtures is plotted as a function of curing time at 70°C in Fig. 2a. Nowadays it is well recognized that gelation occurs after the maximum in the loss factor appears. The increasing viscosity corresponding to chain-interconnection through network formation in the gelation region leads to a sharp increase in the loss modulus for every mixtures. Thereafter a maximum in G'', usually related to the vitrification in the system, happens. A clear catalytic effect, higher as higher the core-shell content was in the mixture, appeared in both core-shell modified mixtures, possibly because of the existence of some residual water not completely removed in the drying process of these particles.



(a)

(b)

Figure 2 (a) Viscoelastic behavior during curing at 70°C for core-shell-modified DGEBA/3DCM matrices: (—) - neat matrix; PScoBu modification: (– –) - 5 wt%, (–·–) - 12 wt%, (–··–) - 15 wt%.; and (· · ·) - 10 wt% PS modification. (b) Viscoelastic behavior during curing at 70°C for: (· · ·) - stoichiometric DGEBA/ATBN mixture; (–·–) - 10 wt% ATBN containing epoxy resin without 3DCM; (—) - stoichiometric DGEBA/3DCM mixture; (– –) - stoichiometric DGEBA/3DCM matrix with a 10 wt% ATBN.

As inferred from G'' and $\tan\delta$ variations reported in Fig. 2b, the reactive process occurred well before for the stoichiometric ATBN cured epoxy mixture non containing 3DCM than for the DGEBA/3DCM stoichiometric epoxy matrix, so indicating that for the epoxy mixtures modified with 10 or 15 wt% ATBN the rubber reacted with the epoxy resin faster than the cycloaliphatic hardener. On the other side, it is worth-noting that after the plateau was attained, G'' values were clearly lower for the DGEBA/ATBN stoichiometric mixture than for the DGEBA/3DCM one as the T_g of the first mixture did not reach the cure temperature used after completion of reactions between the terminal amine groups of the rubber and the epoxy resin. For the DGEBA/ATBN (10 wt%) mixture non containing 3DCM only very small changes were observed in G'' through curing because of the low extent of reaction occuring for this mixture. On the other hand, the addition of a 10 wt% ATBN to the stoichiometric DGEBA/3DCM epoxy matrix slightly delayed the rheokinetics of curing.

Though not shown, for ATBN modified DGEBA/PPO mixtures the Hycar also reacted with the epoxy matrix before its gelation which occurred at around 80 min of curing at 60°C.

The different testing results, including dynamic mechanical and thermal ones, obtained for the stoichiometric DGEBA/3DCM mixtures modified with several amounts of PScoBu core-shell and PS particles are summarized in Table I. Increasing in PScoBu core-shell particle content led to slightly lower glass relaxation temperatures (and also T_g's) of the epoxy matrix possibly because of some interactions in the interphase between matrix and that type of core-shell particles. The decrease of the T_g was lower for PS microparticles modification surely because of the existence of lower interactions with the epoxy matrix than for PScoBu core-shell particles.

As shown in Fig. 3, the incorporation of PScoBu core-shell particles into the DGEBA/3DCM matrix resulted in a small but progressive lowering of mechanical properties as flexural modulus and strength when the amount of core-shell particles increased in the mixture. The lowering in stiffness as microparticles amount increased was possibly a consequence of the lower rigidity of these particles with respect to that for the neat epoxy matrix. On the other hand, the strain to break smoothly increased as core-shell particles content was higher but the strength decreased at core-shell contents higher than 5wt%.

On the contrary, as reported in Fig. 4, the mode I critical strain energy release rate, G_{Ic}, increased

TABLE I Mechanical and physical properties of DGEBA/3DCM epoxy matrices modified with core-shell particles

Modifier (%)	E (MPa)	σ (MPa)	ε (mm/mm)	K_{Ic} (MPa $\cdot$ m$^{1/2}$)	G_{Ic} (J/m^2)	T_α (°C)	$E'_{\mathrm{r}}(\times 10^8)$ (N/m^2)	T_{g} (°C)
0	2600 ± 26	119 ± 5	0.060 ± 0.005	0.63 ± 0.04	135 ± 20	198	0.683	169.5
5	2515 ± 50	124 ± 5	0.077 ± 0.010	0.71 ± 0.06	175 ± 30	193	0.595	—
7,5	2365 ± 47	107 ± 7	0.089 ± 0.008	1.03 ± 010	395 ± 60	192	0.564	—
10	2315 ± 48	103 ± 6	0.089 ± 0.002	1.05 ± 0.20	420 ± 100	189	0.548	163
12	2320 ± 93	97 ± 9	0.077 ± 0.004	1.17 ± 0.09	520 ± 50	187.5	0.366	161.5
15	2270 ± 23	97 ± 8	0.096 ± 0.007	1.01 ± 0.05	395 ± 30	187.5	0.484	—
10% (PS)	2230 ± 22	103 ± 4	0.093 ± 0.015	1.10 ± 0.04	475 ± 20	193	0.465	166

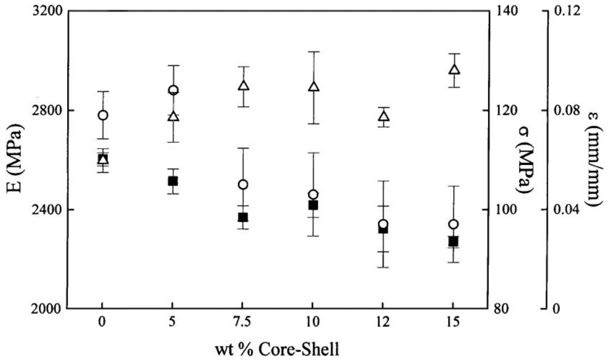


Figure 3 Mechanical properties of DGEBA/3DCM epoxy matrices containing different amounts of PScoBu core-shell particles: (■) - flexural modulus, (○) - flexural strength, and (△) - deformation to break.

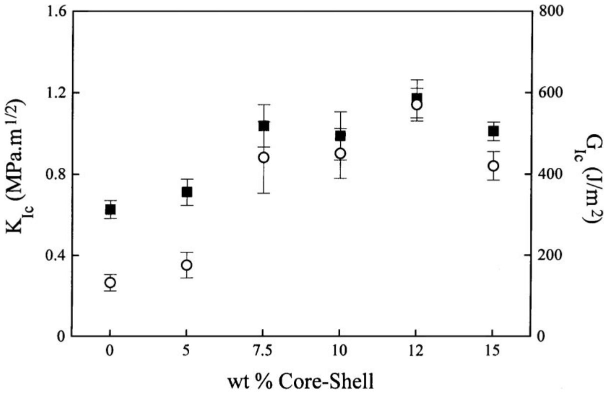


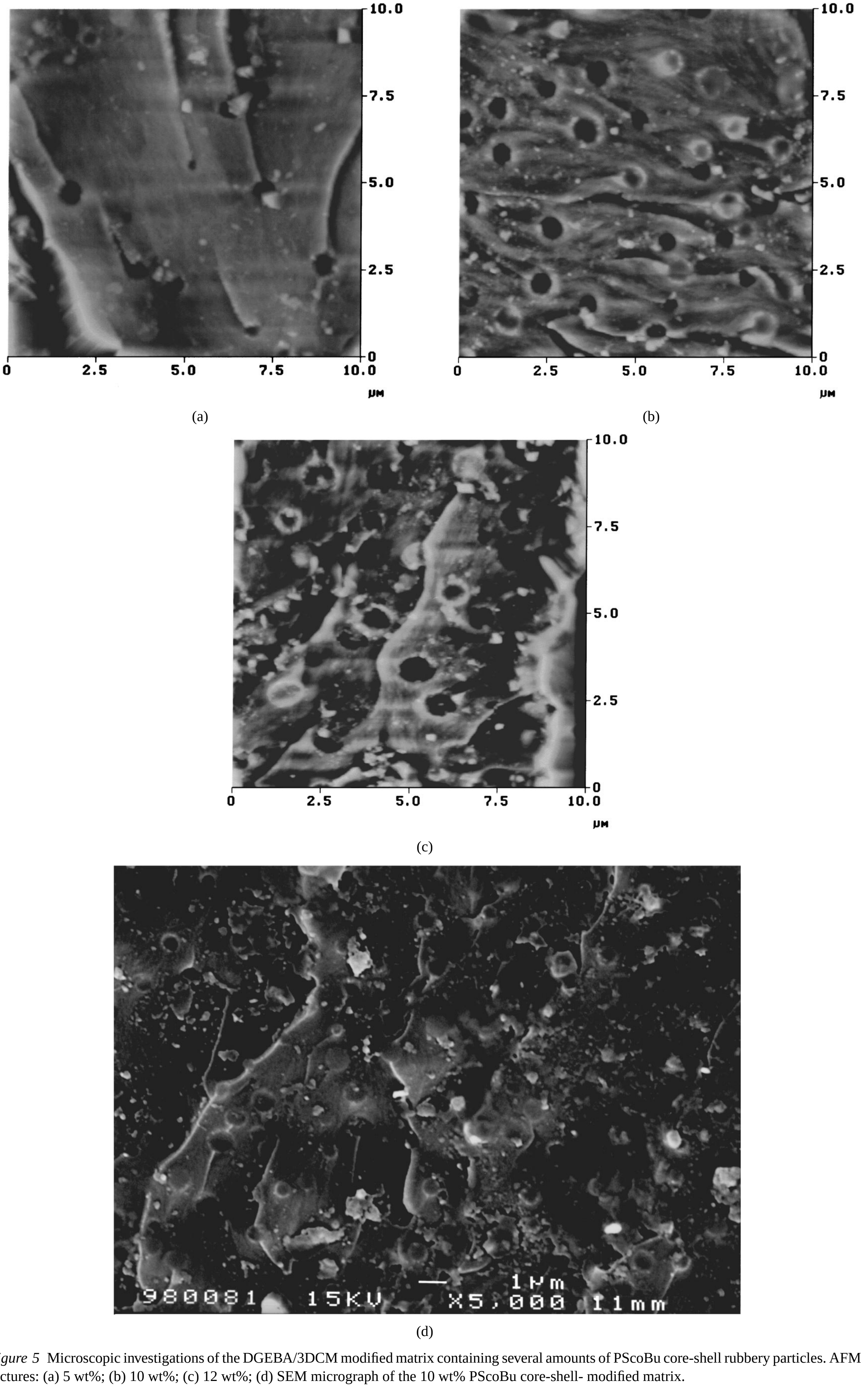
Figure 4 Fracture toughness of DGEBA/3DCM epoxy matrices containing different amounts of PScoBu core-shell particles: (■) - K_{Ic} and (○) - G_{Ic}.

continuously with the core-shell particles amount in the mixture when compared to that for the neat matrix but only up to core-shell contents of 10–12 wt% (threefold increase in G_{Ic}) thereafter decreasing again, so indicating that there exists a maximum content of particles when fracture toughness needs to be improved [21, 22]. AFM and SEM measurements, presented in Fig. 5a–d, indicate that the low toughness improvement attained for the 5 wt% core-shell containing mixture was due to the low amount of particles in the matrix which were not enough to stabilize the propagating crack. However, as inferred from Figs 3 and 4, adding of a 7.5 wt% core-shell rubbery particles to the epoxy matrix was enough to result in a clear increase in fracture toughness. The lower fracture toughness for the 15 wt% PScoBu core-shell particles containing matrix can be due to some agglomeration of these particles inside the matrix. As reported in Table I, the decrease in the small deformation mechanical properties that corresponded to a higher toughness was also observed for the modification with the PS microparticles mixed in a 10 wt%. However, in the same way than that shown by other authors for rubber and core-shell modified epoxy matrices [9, 13, 17], the toughness increase reported for the modified mixtures was not very high (toughening effect of around twofold increase in K_{Ic} for the 12 wt% modified mixture) because of the difficulty in achieving high toughness in epoxy matrices with high chemical rigidity. The similar improving obtained in strain to break and fracture toughness for the modification with both types of microparticles seems to indicate that for the epoxy matrix investigated the interphase amongst the dispersed phase and the epoxy matrix was not the main responsible for controlling the ultimate properties.

Rubber modification is undoubtly the most used way for toughness improving on thermoset resins [23–28]. Therefore, in order to test the interest of core-shell modification, the DGEBA/3DCM epoxy matrix has also been modified with a 10 wt% ATBN rubber. Modified mixtures with or without pre-reaction between the epoxy resin and the rubber and also a modified non-stoichiometric mixture (Amine equiv./Epoxy equiv. = 0.8) have been tested. Results are reported in Table II. The decrease in the T_{g} of the ATBN-modified mixtures with respect to that for the unmodified epoxy matrix is possibly due to incomplete phase separation of the elastomeric phase. The existence of ATBN rubber reactions with the epoxy resin prior to those corresponding to the cycloaliphatic hardener led to a slight

TABLE II Mechanical and physical properties of DGEBA/3DCM epoxy matrices containing 10 wt% ATBN

Composition (r)	E (MPa)	σ (MPa)	ε (mm/mm)	K_{Ic} (MPa $\cdot$ m$^{1/2}$)	G_{Ic} (J/m^2)	T_α (°C)	$E'_{\mathrm{r}}(\times 10^8)$ (N/m^2)	T_{g} (°C)
1.0 (without prereaction)	2235 ± 20	106 ± 1	0095 ± 0.004	0.93 ± 0.05	340 ± 30	182	0.628	153
1.0 (with prereaction)	2365 ± 25	101 ± 2	0.092 ± 0.008	1.06 ± 0.20	415 ± 90	179	0.590	149
0.8 (with prereaction)	2495 ± 55	112 ± 3	0.090 ± 0.008	1.04 ± 0.15	500 ± 70	164	0.368	133



(a)

(b)

(c)

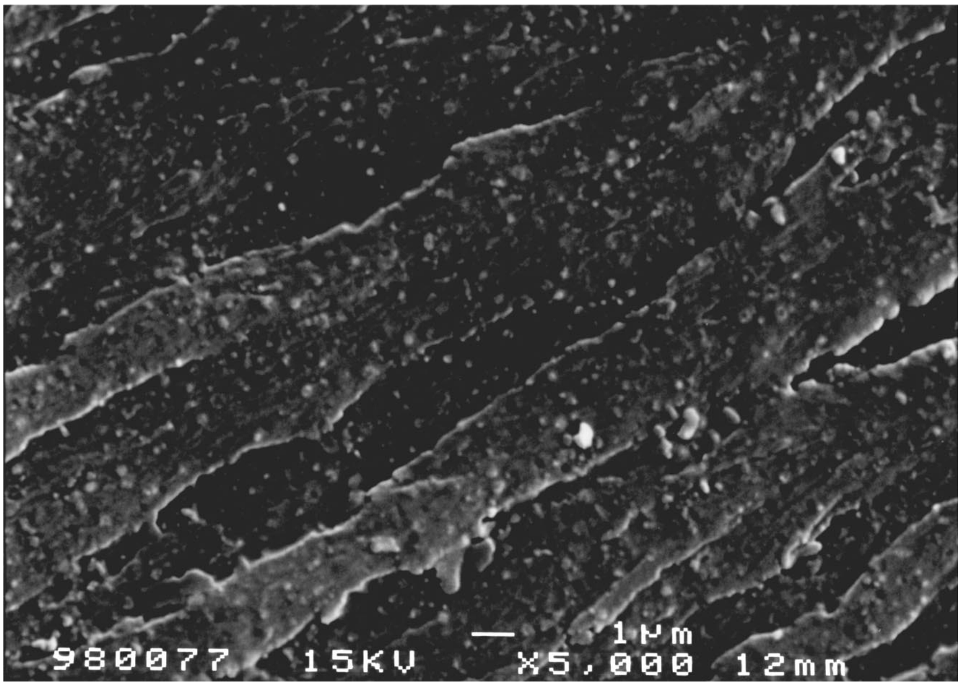
(d)

Figure 5 Microscopic investigations of the DGEBA/3DCM modified matrix containing several amounts of PScoBu core-shell rubbery particles. AFM pictures: (a) 5 wt%; (b) 10 wt%; (c) 12 wt%; (d) SEM micrograph of the 10 wt% PScoBu core-shell- modified matrix.

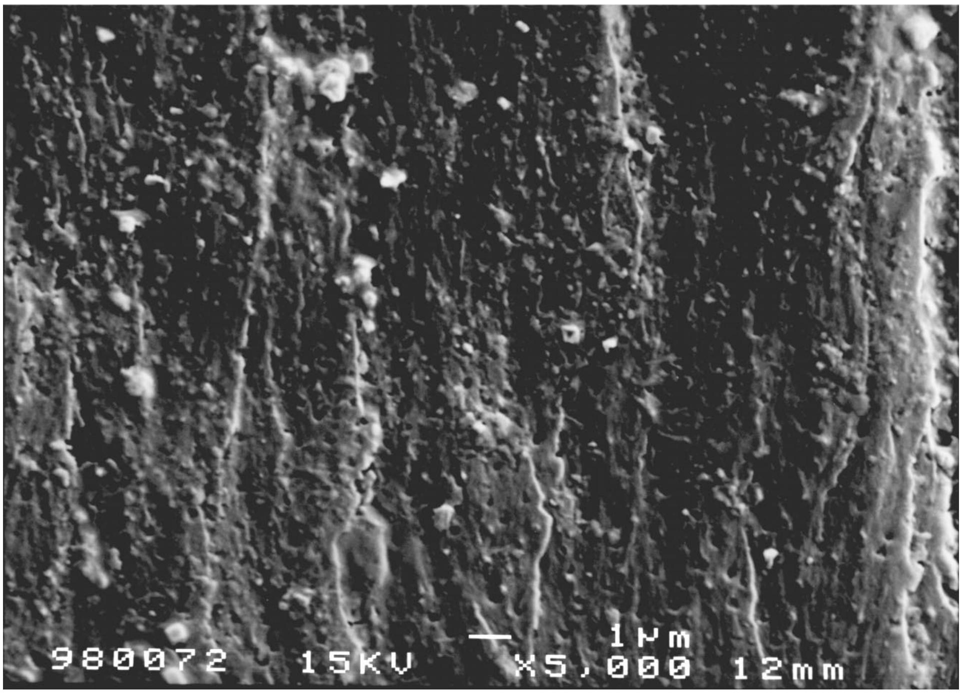
increase on small deformation mechanical properties and also on fracture toughness for both dissimilarly prereacted mixtures. In spite of the lower size of rubber particles, shown in Fig. 6a–c, their mechanical properties were comparable to those obtained for the matrices with the same percentage of core-shell modification. The higher thermal properties for core-shell modification proves the interest for using this type of particles for improving fracture toughness.

As inferred from Table II, in the same way than previously shown for modification with liquid elastomers [29], for the non-stoichiometric matrix, although similar, fracture toughness and also small-deformation mechanical properties were a few higher than for the very rigid stoichiometric mixtures but the T_g clearly decreased. As rubber modulus values prove, this behavior is connected to the lower crosslink density existing for the non-stoichiometric modified mixture.

In order to analyse the influence of the chemical structure of the epoxy matrix in the ultimate properties of core-shell modified mixtures, the DGEBA resin was also cured with a hardener with flexible chains as PPO. Results are summarized in Table III. As inferred from E'_r values, the crosslink density of these

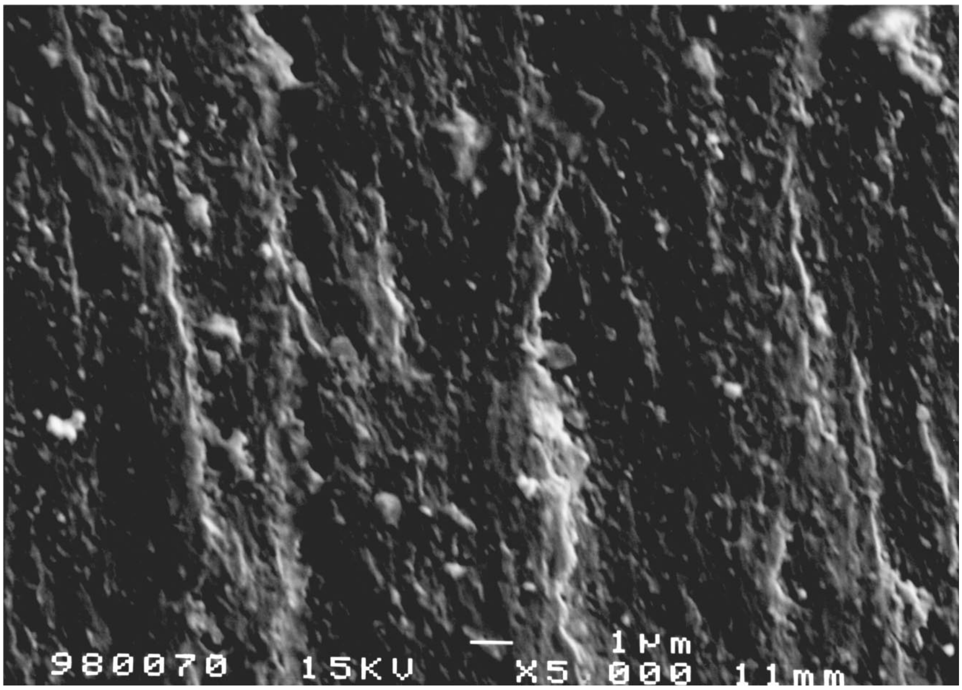


(a)



(b)

Figure 6 SEM micrographs of 10 wt% ATBN-modified DGEBA/3DCM matrices. (a) prereacted stoichiometric matrix; (b) stoichiometric matrix; (c) Epoxy-rich matrix, $r = 0.8$. (*Continued*)



(c)

Figure 6 (*Continued*).

TABLE III Mechanical and physical properties of DGEBA/PPO epoxy matrices modified with ATBN and core-shell particles

Modifier (%)	E (MPa)	σ (MPa)	ε (mm/mm)	K_{Ic} (MPa $\cdot$ m$^{1/2}$)	G_{Ic} (J/m^2)	T_α (°C)	$E_r'(\times 10^8)$ (N/m^2)
0	3145 ± 65	114 ± 1	0.110 ± 0.004	2.15 ± 0.20	1320 ± 20	102	0.225
5	2785 ± 30	94 ± 2	0.120 ± 0.006	2.39 ± 0.21	1950 ± 25	—	—
10	2430 ± 25	81 ± 2	0.130 ± 0.002	2.39 ± 0.06	1850 ± 10	95	0.212
15	2410 ± 25	84 ± 1	0.140 ± 0.002	2.55 ± 0.40	3200 ± 40	94	0.167
10 prereacted	2605 ± 26	91 ± 1	0.160 ± 0.010	2.90 ± 0.20	2850 ± 40	99.5	0.150
10 (r = 0.8)	2780 ± 100	92 ± 5	0.140 ± 0.030	2.40 ± 0.15	1850 ± 25	91.5	0.126
10 PScoBu	2720 ± 50	91 ± 1	0.120 ± 0.005	2.39 ± 0.24	2250 ± 20	100	—

epoxy networks was lower than that for the 3DCM-cured epoxy matrices. As previously reported [30], the stiffness of this unmodified matrix was higher than that corresponding for the similar mixture cured with the cycloaliphatic hardener possibly as a consequence of the higher free volume existing in the crosslinked network of the DGEBA/3DCM epoxy matrix because of the higher rigidity of its chemical chains.

As shown in Fig. 7, both elastic modulus and strength lowered as higher the content of ATBN was in the mixture, being this decrease more pronounced than that observed for similar mixtures cured with 3DCM. On the other hand, as pictured in Fig. 8, the larger deformability of the DGEBA/PPO epoxy matrix was responsible for the higher fracture toughness of both neat and rubber-modified mixtures with respect to the modified DGEBA/3DCM matrices. Once again, modification with core-shell particles produced an even higher increase in fracture toughness than that obtained for rubber modification.

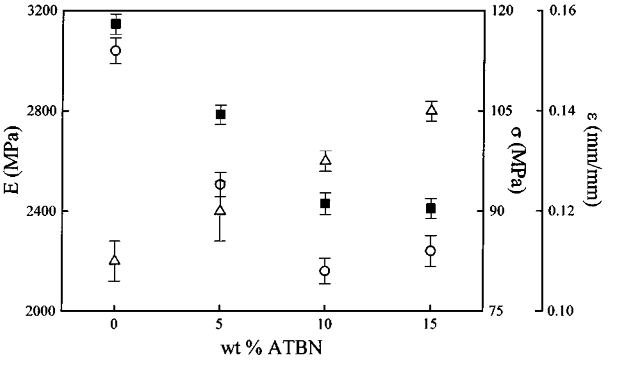


Figure 7 Mechanical properties of DGEBA/PPO epoxy matrices containing different amounts of ATBN rubber. (■) - elastic modulus, (○) - strength, and (△) - deformation to break.

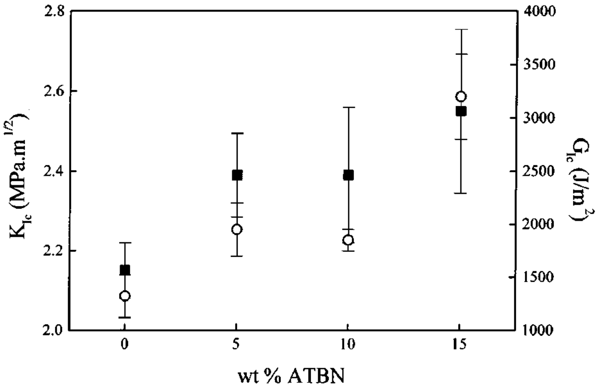


Figure 8 Fracture toughness of DGEBA/PPO epoxy matrices containing different amounts of ATBN rubber: (■) - K_{Ic} and (○) - G_{Ic}.

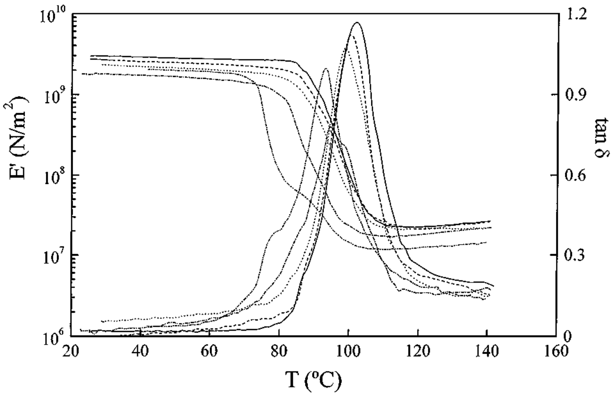


Figure 9 Dynamic mechanical behavior for DGEBA/PPO epoxy matrices with different contents of ATBN.

It is worth to note that the stiffness and strength for the mixture prereacted with a 10 wt% ATBN were higher than those for the mixture in which PPO and ATBN were simultaneously added. Besides, the better low deformation mechanical properties and fracture toughness observed for the 10 wt% ATBN-prereacted mixture cured with PPO with respect to those for the corresponding unreacted mixture are possibly connected to the existence of a better interphase between the epoxy matrix and the dispersed particles. As reported in Fig. 9 and Table III, this behavior would agree with the higher glass relaxation temperature and the lower rubber modulus observed by dynamic mechanical measurements in the prereacted mixtures. Again, core-shell modification conducted to higher stiffness and thermal behavior for the same amount of modifier added.

4. Conclusions

Rubbery modification but also core-shell microparticles adding were used to toughen both rigid and flexible epoxy resins. The use of emulsion polymerised microparticles allowed to reach a similar toughening of the modified matrix to that attained for rubber-modified matrices with a minimal lowering of their glass transition temperatures. A lower decrease in important properties such as modulus and strength was also obtained for microparticle modification of the epoxy matrix.

Using of emulsion polymerised microparticles can lead to higher rates of curing of the epoxy resin because of the catalyst action of some residual water in the particles.

In the case of rubber modification, prereacting into the epoxy resin can allow to reach a similar enhancement in the fracture toughness without decrease so much the rigidity and strength of the matrix. The fracture toughness of the modified matrices depends upon the crosslinking density in the epoxy matrix, being lower for the epoxy matrix cured with the chemically more rigid cycloaliphatic hardener. Rubber prereaction with the epoxy resin allowed to obtain mixtures with higher mechanical properties without decreasing their fracture toughness.

The fracture toughness of epoxy matrices modified with reactive rubbers such as amine-terminated acrylonitrile butadiene (ATBN) copolymers can also be reached by modification with core-shell particles with lower loosing in the thermal properties of the neat epoxy matrix.

Acknowledgement

Financial support of the Eusko Jaurlaritza/Gobierno Vasco (Grant no. GV96/0003) is greatly appreciated.

References

1. S. KUNZ-DOUGLASS, P. W. R. BEAUMONT and M. F. ASHBY, *J. Mater. Sci.* **49** (1980) 442.
2. J. M. SCOTT, G. M. WELLS and D. C. J. PHILLIPS, *ibid.* **15** (1980) 1436.
3. A. J. KINLOCH, S. J. SHAW, D. A. TOD and D. L. HUNSTON, *Polymer* **24** (1983) 1355.
4. A. F. YEE and R. A. PEARSON, *J. Mater. Sci.* **21** (1986) 2462.
5. Y. HUANG and A. J. KINLOCH, *ibid.* **27** (1992) 2753.
6. H.-J. SUE, *Polym. Eng. Sci.* **31** (1991) 275.
7. G. LEVITA, A. MARCHETTI and A. LAZZERI, *Makromol. Chem., Macromol. Symp.* **41** (1991) 179.
8. B. J. CARDWELL and A. F. YEE, *Polymer* **34** (1993) 1695.
9. M. C. M. VAN DER SANDEN and H. E. H. MEIJER, *ibid.* **34** (1993) 5063.
10. H.-J. SUE, E. I. GARCIA MEITIN and N. A. ORCHARD, *J. Polym. Sci.: Part B: Polym. Phys.* **31** (1993) 595.
11. B. GEISLER and F. N. KELLEY, *J. Appl. Polym. Sci.* **54** (1994) 177.
12. H.-J. SUE, J. L. BERTRAM, E. I. GARCIA MEITIN and P. M. PUCKETT, *J. Polym. Sci.: Part B: Polym. Phys.* **33** (1995) 2003.
13. F. LU, H. H. KAUSCH, W. J. CANTWELL and M. FISCHER, *J. Mater. Sci. Lett.* **15** (1996) 1018.
14. H.-J. SUE, E. I. GARCIA MEITIN, D. M. PICKELMAN and C. J. BOTT, *Colloid Polym. Sci.* **274** (1996) 342.
15. J. Y. QIAN, R. A. PEARSON, V. L. DIMONIE, O. L. SHAFFER and M. S. EL-AASSER, *Polymer* **38** (1997) 21.
16. J. D. LEMAY and F. N. KELLEY, *Adv. Polym. Sci.* **78** (1986) 115.
17. R. A. PEARSON and A. F. YEE, *J. Mater. Sci.* **24** (1989) 2571.
18. I. MONDRAGON, P. M. REMIRO, M. D. MARTIN, A. VALEA, M. FRANCO and V. BELLENGUER, *Polym. Intern.* **47** (1998) 152.
19. European Structural Integrity Society, "Testing Protocol for Polymers" (ESIS, 1992).
20. J. G. WILLIAMS and M. J. CAWOOD, *Polym. Testing* **9** (1990) 15.
21. J. W. KIM, J. Y. KIM and K. D. SUH, *J. Macromol. Sci. - Pure Appl. Chem.* **A35** (1998) 249.
22. J. HE, D. RAGHAVAN, D. HOFFMAN and D. HUNSTON, *Polymer* **40** (1999) 1923.
23. E. BUTTA, G. LEVITA, A. MARCHETTI and A. LAZZERI, *Polym. Eng. Sci.* **26** (1986) 63.
24. R. A. PEARSON and A. F. YEE, *J. Mater. Sci.* **21** (1986) 2475.
25. C. G. DELIDES, D. HAYWARD, R. A. PETHRICK and A. S. VATALIS, *J. Appl. Polym. Sci.* **47** (1993) 2037.
26. A. J. KINLOCH and D. L. HUNSTON, *J. Mater. Sci. Lett.* **6** (1987) 131.
27. S. HOTIUCHI, A. C. STREET, T. OUGIZAWA and T. KITANO, *Polymer* **35** (1994) 5283.
28. D. VERCHERE, J. P. PASCAULT, H. SAUTEREAU, S. M. MOSCHIAR, C. C. RICCARDI and R. J. J. WILLIAMS, *J. Appl. Polym. Sci.* **43** (1991) 293.
29. I. MONDRAGON, I. QUINTARD and C. B. BUCKNALL, *Plast. Rubb. Comp. Proc. Applic.* **23** (1995) 331.
30. F. FDEZ NOGRARO, A. VALEA, R. LLANO-PONTE and I. MONDRAGON, *Eur. Polym. J.* **32** (1996) 257.

Received 17 February
and accepted 31 July 2000