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Preparation of thermoset rubbery epoxy particles as novel toughening modifiers for glassy epoxy resins

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Abstract

By curing of in water dispersed droplets of an aromatic or aliphatic epoxy resin, respectively, glassy or rubbery thermosetting epoxy spheres can be prepared in a relatively easy way. The rubbery epoxy particles can successfully be applied as a toughening agent for glassy epoxy matrices. The advantage of these preformed modifiers is the control over the final morphology as the size and concentration of the dispersed rubber phase can be chosen independently. The improvement in fracture toughness and the morphological features of the fracture surfaces are identical to standard, but also more complex, toughening routes, such as the application of liquid rubbers [Sultan JN, Laible RC, McGarry FJ. Appl. Polym. Symp. 1971;16:127; Sultan JN, McGarry FJ. Polym. Eng. Sci. 1973;13:29]. The use of this new class of rubber modifiers is not restricted to glassy epoxy resins, but may also be applied to produce impact-modified thermoplastics with a predetermined particle size and rubber content. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Epoxy resin; Preformed epoxy particles; Toughening

1. Introduction

Glassy, highly crosslinked epoxy resins are known as brittle thermosetting polymers which need to be toughened for various applications. Sultan et al. [1,2] were the first to show that the fracture toughness of epoxies can be improved by the introduction of a dispersed rubber phase. Accordingly, a number of studies were reported concerning the application of liquid rubbers, like carboxyl, amine or epoxy terminated butadiene–acrylonitrile (CTBN, ATBN and ETBN) as toughening agents. These liquid rubber modifiers are initially miscible with epoxy resin but will phase separate upon curing. Hence, the rubber morphology and, consequently, the final mechanical properties of the blend are determined by this chemically-induced phase separation process [3–11]. The relation between the improvement of the fracture toughness and the curing conditions, the rubber particle size and concentration used, was extensively studied. Moreover, a wide range of deformation mechanisms were proposed in order to explain the observed improvements in toughness [12]. Based upon these analyses, various routes were explored to circumvent the drawback of rubber modification, viz. the reduction in the stiffness and strength, e.g. by using a high T_g thermoplastic modifier. A number of thermoplasts were explored, such as polyetherimide [13,14], polysulphone [15], polyethersulphone [16–18] and poly(dimethylphenylene ether) [19]. The toughening efficiency was, however, in most cases lower compared with the liquid rubber modified epoxies.

In all routes explored, the resulting morphology proved to be the most important parameter that influences the toughness enhancement [3,5,6]. Other important parameters are the ductility of the epoxy applied, related to its network density [7,8], the modulus of the dispersed phase and the properties of the interface between modifier and resin [9,10]. The morphology generated in these blending routes is relatively difficult to control as the blend preparation involves chemically induced phase separation (CIPS) during curing of the epoxy resin. The final size of the rubber particles is mainly determined by the rubber concentration, rubber type, curing temperature and curing agent [20–23]. The influence of these parameters is partially interrelated, which reduces the reproducibility of the morphologies obtained and complicates a systemic study of the final blend properties independent of blend constitution and preparation conditions. These problems can, at least partially, be circumvented by the application of preformed core-shell particles [6,24–27], which allows for the preparation of a predetermined morphology, independent of the curing conditions. Moreover, the properties and the internal

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morphology of core-shell particles can be tailored during, for example, emulsion polymerisation. The main drawback of the application of core-shell particles is their limited particle size (in the range of 100–500 nm) and the laborious synthesis necessary to prepare larger particles, which are advantageous for toughening highly crosslinked glassy epoxies.

The purpose of this study is to explore the ability of a new kind of preformed rubber particles to toughen glassy epoxy resins. These particles are prepared by curing droplets of an aliphatic epoxy in an aqueous medium. Next, these particles are transferred in an aromatic epoxy which is, subsequently, cured. The fracture toughness and the microscopic fracture behaviour of the resulting blend is determined and compared with carboxyl terminated butadiene–acrylonitrile (CTBN) modified epoxy resin.

2. Experimental

2.1. Materials

The two types of liquid epoxy resin with an aromatic backbone were supplied by SHELL Research (Louvain-la-Neuve, Belgium); a diglycidyl ether of bisphenol A (DGEBA, SHELL Epikote 828 EL) and a diglycidyl ether of bisphenol F (DGEBF, SHELL Epikote 862). The aliphatic epoxy resin was a diglycidyl ether of polypropyleneoxide (DGEPPO, SHELL Epikote 877) supplied by Chemische Fabriek Zaltbommel (CFZ, Zaltbommel, The Netherlands).

Four different curing agents were used: piperidine (Aldrich), polypropyleneoxide diamine (Jeffamine D230, Huntsman), diethyltoluenediamine (DETDA, The Ethyl Cooperation) and Epikure DX-6510 (a cycloaliphatic amine curing agent supplied by SHELL Louvain-la-Neuve, Belgium). As liquid modifier a carboxyl-terminated butadiene acrylonitrile rubber (CTBN, Hycar CTBN 1300X8) supplied by Goodrich Chemicals Co. was used.

2.2. Synthesis of the epoxy particles

The preformed cured epoxy particles were prepared in an aqueous medium. The low viscous epoxy resin, aromatic or aliphatic, was added to a simple stirred reactor (one litre glass reactor with an internal diameter of ~ 10 cm using a blade stirrer at ~ 300 rpm) containing water at 90°C in which a stabiliser was dissolved (5 g/l SDS, sodium dodecyl sulphate, or HEC, hydroxyethylcellulose). After stirring for approximately 15 min, a dispersion of liquid droplets was obtained. Next, a stoichiometric amount of amine curing agent was added to cure the epoxy droplets and stirring was continued during polymerisation up to a maximum conversion (5–12 h depending on the curing agent). The resulting thermosetting particles could easily be extracted by filtration and/or drying.

In order to demonstrate that the proposed route to prepare these particles is independent of the epoxy resin used, both aromatic and aliphatic epoxy resin was used resulting in, respectively, glassy and rubbery particles. The latter were applied in the subsequent part of the study as toughening agents.

The rubbery spheres were obtained by using an aliphatic epoxy resin (Epikote 877) and curing agent (Jeffamine D230), which are both based on a polypropyleneoxide backbone (DGEPPO particles). The glassy particles were prepared by using an aromatic epoxy (Epikote 828) which was cured using DETDA. This curing agent was insoluble in water, in contrast to the Jeffamine curing agent. The solubility proved, however, to be of minor importance, as DETDA could still successfully be applied to cure a dispersion of epoxy droplets.

2.3. Blend preparation

The rubbery epoxy particles were used as toughening agents for the Epikote 828 epoxy resin. Two methods were used to isolate the particles from the aqueous dispersion and to disperse these in the liquid epoxy. In the first method, dry particles (a powder), obtained by film evaporation and freeze–drying of the aqueous dispersion, were dispersed in the aromatic epoxy resin at 80°C, using an Ultra Turrax mixer. In the second method, a different route was followed. An equal amount of toluene was added to the aqueous dispersion which was stirred for several hours. Most of the rubbery particles were transferred to the toluene phase, which could easily be separated from the aqueous phase using a separation funnel. Next, the aromatic epoxy resin was dissolved in the obtained toluene dispersion. After evaporation of the toluene, eventually using film-evaporation in order to remove all traces of toluene, a dispersion of particles in epoxy resin was obtained.

The curing procedure applied was similar for both the neat epoxy resin and the rubber modified systems. After degassing the epoxy at 80°C, using vacuum, the curing agent (5 phr piperidine or 25 phr DETDA) was added while slowly stirring the mixture. Next, the reactive mixture was degassed again for 3 min and, subsequently, poured in a preheated mould (180 × 100 × 6 mm). For the DGEBA (Epikote 828) epoxy resin a curing time of 16 h at 120°C was applied after which the mould was slowly cooled to room temperature. In the case DETDA was used as curing agent, this curing schedule was followed by a post-curing step of 5 h at 180°C. For the DGEBF epoxy (Epikote 862), which was cured with the cycloaliphatic amine (31 phr), a curing schedule adopted from SHELL was used: 75°C, 100°C, 125°C each for 1 h and 150°C for 2 h.

2.4. Mechanical testing

The fracture toughness of the epoxy systems was determined by a single edge notched three point bending test. The test specimens, dimensions 6 × 15 × 70 mm, were prepared and tested following the ASTM standard D5045-91a. Sharp

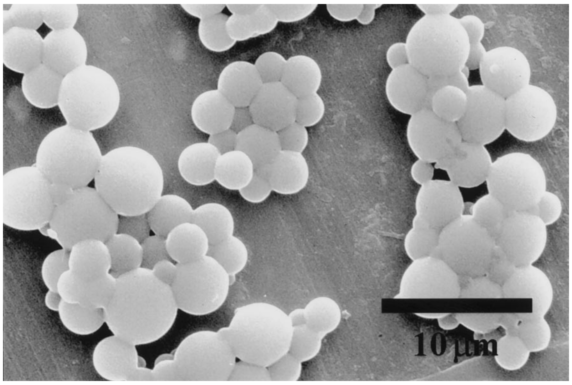

Fig. 1. Scanning electron micrograph of dried preformed rubbery epoxy particles, Epikote 877 cured with Jeffamine D230.

cracks were obtained by tapping a liquid nitrogen chilled fresh razor blade into the machined notch. The tests were performed at a displacement rate of 10 mm/min using a Zwick 1445 testing machine. The calculated critical stress intensity factor in plane strain, K_{Ic}, is reported.

2.5. Scanning electron microscopy

The morphology and fracture surfaces of the blends were studied using scanning electron microscopy (Cambridge Stereo Scan 200). Samples of the synthesised particles were prepared by drying a diluted dispersion of droplets on a sample holder. The degree of dispersion in the epoxy matrix was visualised by fracture and oxygen etching of the blends. Finally, also the fracture surfaces of the tested fracture toughness specimen were studied. All samples were coated with a gold–palladium layer.

2.6. Thermal analysis

Dynamic Mechanical Thermal Analysis (DMTA, Polymer Laboratories MKII dynamic mechanical thermal analyser) was performed for all materials prepared using a frequency of 1 Hz, a strain of 40 μm and a heating rate of 2°C/min. The reported glass transition temperatures (T_g) correspond to the maximum of the loss angle (tan δ).

Differential scanning calorimetric measurements (DSC, Perkin-Elmer 7 series, heating rate 10°C/min) were performed to determine the T_g of the dried epoxy particles prepared in the synthesis step.

Table 1
T_g of different epoxy resins cured in dispersion and bulk

Epoxy resin	Curing agent	Stabilizer	T_g°C
DGEPPO	Jeffamine D230	None (bulk)	− 43
DGEPPO	Jeffamine D230	HEC	− 41
DGEPPO	Jeffamine D230	SDS	− 40
DGEBA	DETDA	None (bulk)	170
DGEBA	DETDA	HEC	124

3. Results and discussion

3.1. Synthesis of the epoxy particles

Aim of the first part of this study is to demonstrate that the dispersed epoxy droplets can be cured resulting in preformed thermoset epoxy particles. As an example, the scanning electron micrograph in Fig. 1 shows some rubbery epoxy particles which are extracted from the aqueous dispersion. In Table 1, the T_g's of dried epoxy particles, both rubbery and glassy, are compared with bulk cured epoxy resin. For the rubbery epoxy, the T_g of the particles matches that of the bulk epoxy resin which indicates that the epoxy droplets have successfully been cured in the aqueous dispersion. For the aromatic epoxy a higher T_g is found which is, however, considerably lower compared to the bulk cured resin. As the polymerisation temperature does not exceed 90°C, the occurrence of vitrification will prevent full conversion which, consequently, results in a reduced T_g. However, post-curing after extraction of the particles from the aqueous dispersion may be applied to enhance the final T_g.

Table 2 gives an indication of the particle size dependence of the epoxy concentrations using the same stirring conditions and a fixed SDS concentration. The particle size decreases with the initial resin concentration, indicating that the particle size is the result of the equilibrium between droplet break-up and coalescence [28]. In this study, we chose to examine the toughening efficiency of the rubbery DGEPPO particles prepared in this new way, rather than focusing on the optimisation of the particle synthesis steps by e.g. systematically varying the epoxy concentration, dispersing equipment and surfactant type and concentration. The performance of the particles is determined by measuring the fracture toughness and studying the morphological features which are compared with CTBN modified epoxy resin.

3.2. Preparation of the rubber modified epoxy

The sticky character of the preformed rubbery epoxy particles causes coagulation which may yield some problems during the dispersion process. For the CTBN modified epoxy blends, see Fig. 2(a), the well dispersed particles are the result of phase separation during curing. As can be observed in Fig. 2(b), dispersing the dried rubbery particles directly in the aromatic resin at elevated temperatures prior to curing (preparation route one) yields unfavourable coagulation. Relatively long mixing times, in the order of 24 h, are necessary to obtain a reasonable degree of dispersion. The preparation of a suitable dispersion becomes even more difficult as the particle size is decreased. For this reason, the second preparation route was employed, where toluene is used as phase transfer medium to prepare the blends. In this method coagulation is prevented and a well dispersed rubber morphology is obtained which is

Table 2
Particle size versus epoxy concentration in water (wt%) (5 g/l SDS)

DGEPPO (wt%)	Particle size (m)
1	0.6
5	3
10	15

comparable to that of the CTBN modified blend, see Fig. 2(a) and (c).

As the aliphatic and aromatic epoxy resins used are compatible, curing a mixture of both resins will result in one single network which possesses an intermediate glass transition temperature T_g [29]. In the present case, however, two separate epoxy phases are obtained. Nevertheless, the preformed rubbery particles might swell upon the addition of aromatic resin which may affect the T_g of the dispersed rubber phase after curing. In the DMTA measurements, Fig. 3, three transitions in the loss angle (tan δ) are distinguished; the β-transition of the aromatic epoxy matrix at -70°C, the T_g of the dispersed epoxy particles at -30°C, and the T_g of the epoxy matrix at 90°C. The introduction of the rubber phase does not result in any changes in the β-transition or the T_g of the glassy epoxy phase. For the rubber phase itself, however, a slight increase in T_g is observed as a T_g of -35°C is found for the dispersed epoxy rubber phase in PMMA/epoxy blends [30]. This discrepancy is most likely the result of the expected swelling of the rubber particles with aromatic epoxy prior to curing the latter.

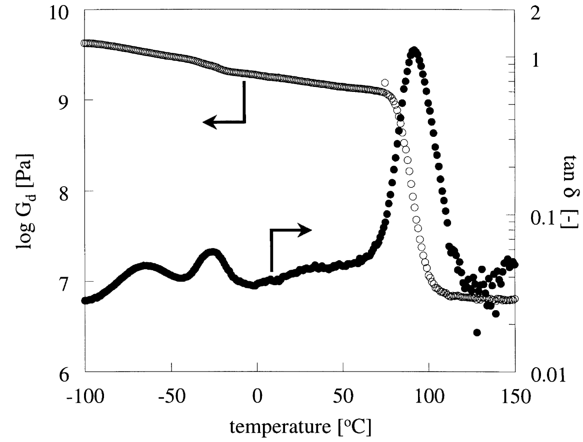

Fig. 3. DMTA measurement of rubber modified Epikote 828 epoxy resin with 15 wt% of preformed rubbery epoxy particles.

3.3. Mechanical properties

The performance of the preformed rubbery epoxy particles as a new toughening agent for glassy epoxies is verified by comparing the blend properties with a standard CTBN modified epoxy, see Fig. 4. The first experiments with this reference system gave rather unexpected results, see Fig. 4(a). A decrease in K_{Ic} is found with increasing rubber content. A closer investigation of these results show that all fracture toughness values are remarkably high compared to those reported in the literature [3,4,6]. The origin of the problem appeared to be the preparation of the precrack in the fracture toughness specimens [31]. By chilling the razor

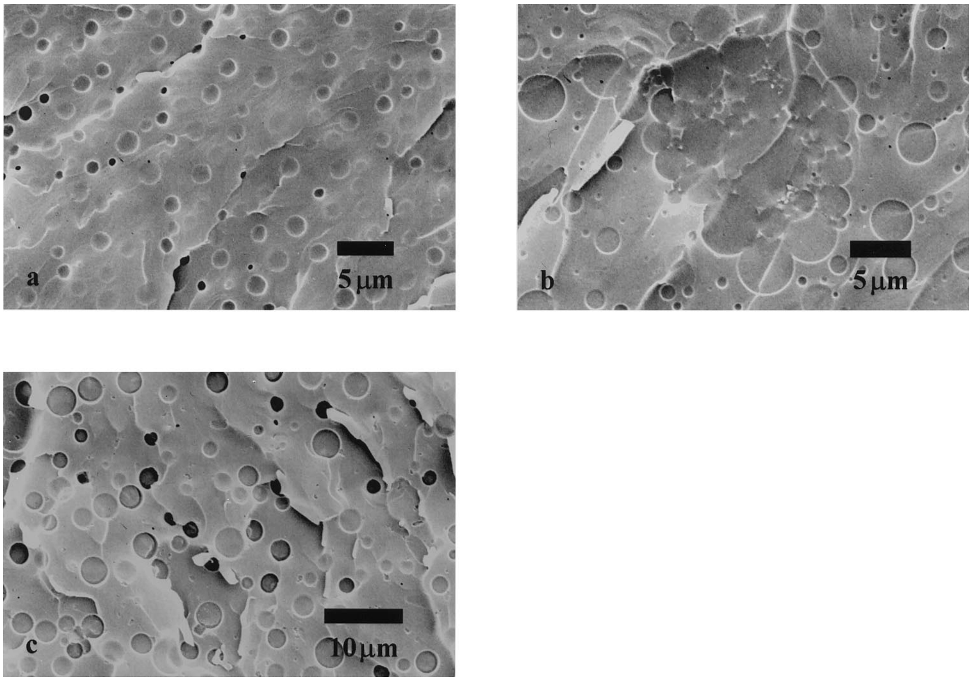

Fig. 2. Degree of rubber dispersion for three different systems, (a) CTBN modified system, (b) dried rubbery particles directly dispersed in the epoxy resin, (c) rubbery epoxy particles dispersed in epoxy via the phase transfer route using toluene.

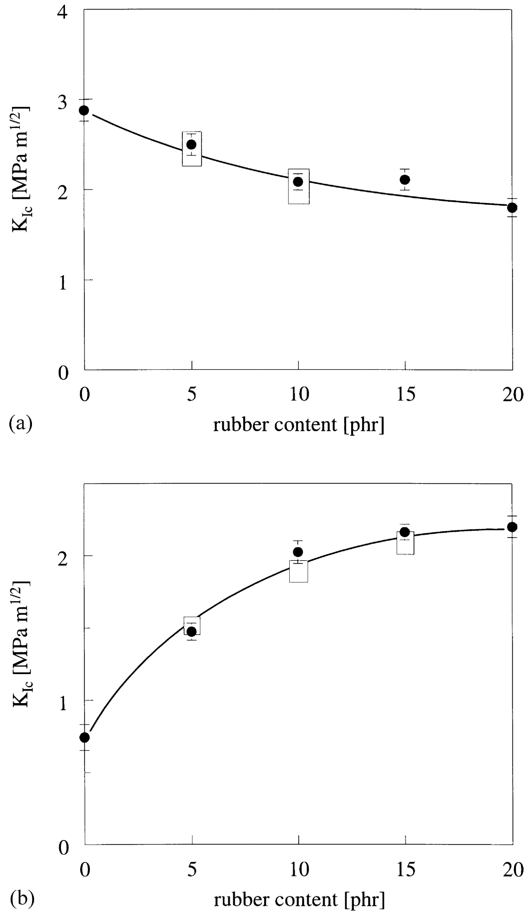

Fig. 4. Fracture toughness versus rubber content for CTBN (particle size ~ 1 μm) modified Epikote 828, precrack prepared by tapping a razor blade, (a) at room temperature, (b) chilled in liquid nitrogen.

blade in liquid nitrogen prior to tapping the notch, K_{Ic} values are obtained which match those reported in literature and, in contrast to the previous experiments, result in a toughness improvement with increasing rubber fraction, see Fig. 4(b).

The K_{Ic} values for the epoxy modified with DGEPPO particles are shown in Fig. 5. The most important conclusion is that the particles indeed possess the ability to toughen the aromatic epoxy resin. The performance is, however, somewhat less effective compared to the CTBN modified blends which is, most probably, the result of the difference in particle size. By decreasing the particle size from approximately 3 to 1 μm, the K_{Ic} of the 10 wt% blend is increased up to a value which is comparable to that of a 10 wt% CTBN blend (see Fig. 5).

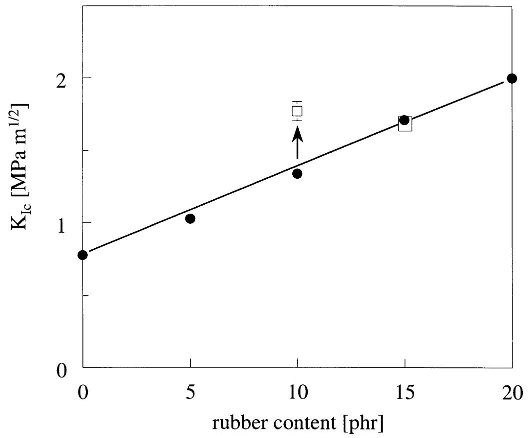

Fig. 5. Fracture toughness versus rubber content for rubbery particle modified Epikote 828, particle size 3 μm (●) and ~ 1 μm (□).

Rubber toughening is known to be less effective for epoxies with a higher network density and, consequently, a higher T_g [7,8]. In Table 3 the K_{Ic} and T_g of three different epoxy networks are presented for neat and two rubber modified epoxy resins. The toughening efficiency is clearly most effective for the blends possessing the lowest matrix T_g. The difference in K_{Ic} between the CTBN and rubbery particle modified epoxy systems is relatively small. Especially for the epoxy with the highest T_g, the T_g-depression in comparison to neat epoxy is less if the preformed particles are used as modifiers. In the case of the CTBN blends, incomplete phase separation may suppress the T_g as a result of the rubber residuals in the epoxy matrix which is avoided in case of the use of preformed particles.

Besides the fracture toughness of the blends, the fracture behaviour of the mixtures based on the new toughening agent is studied and compared with the CTBN blends [4]. Within the fracture surface of a test specimen, see Fig. 6(a) and (b), five different zones are distinguished which are identical for both rubber blends. The first three are part of the sample preparation and include the machined notch, the razor cut and the precrack. The fracture surface consists of a stress whitened zone and a fast fracture zone which exhibits a rougher surface for the particle modified system. As is evident from Fig. 6(c) and (d), rubber cavitation is responsible for the white appearance of the plastic deformation zone behind the precrack. In this region the difference in particle size between both modifiers is clearly visible. This is in contrast to the remaining crack surface in which the rubber phase is not cavitated and, thus, hardly visible, see Fig. 6(e) and (f). In this zone, fast fracture occurred without any noticeable plastic deformation. In conclusion, the rubbery DGEPPO epoxy particles are promising modifier for glassy epoxy matrices as both the K_{Ic} and the fracture behaviour are comparable to CTBN rubber. Moreover, as the application of chemically induced phase separation is avoided, the epoxy matrices will possess a higher T_g.

4. Conclusion

This study is a first attempt to prepare preformed rubbery aliphatic epoxy particles in a dispersion and to apply these particles as a toughening agent for glassy aromatic epoxy matrices. We successfully cured epoxy droplets in an aqueous medium resulting in thermoset particles with a controllable and adjustable diameter which cannot be

Table 3
Fracture toughness and T_g for different epoxy systems

Epoxy resin	Curing agent	Rubber (15 wt%)	K_{Ic}	T_g°C
Epikote 828	DETDA	—	0.51 ± 0.03	190
		CTBN	0.67 ± 0.03	176
		DEGPPO-particles	0.69 ± 0.02	185
Epikote 862	EpikureDX-6510	—	0.83 ± 0.02	133
		CTBN	1.52 ± 0.07	130
		DGEPPO-particles	1.47 ± 0.04	132
Epikote 828	Piperidine	—	0.74 ± 0.08	96
		CTBN	2.16 ± 0.05	92
		DGEPPO-particles	1.71 ± 0.03	93

melt-processed but can be used in systems where a stable predetermined morphology is required.

In order to verify the performance of the rubbery epoxy particles as toughening agents, they are blended with epoxy and compared with the performance of CTBN rubber. The advantage of the preformed epoxy particles over CTBN is the absence of a need for chemically-induced phase separation processes, which prevents a T_g-depression of the epoxy matrix as result of some liquid-rubber residuals. As expected, no improvement in fracture toughness is observed for high T_g epoxy networks. For the piperidene cured epoxy resin, however, the fracture toughness is clearly improved and is similar for both the CTBN and the rubbery epoxy particles. Moreover, the morphological fracture behaviour is identical for both systems.

From this study, it can be concluded that preformed rubbery epoxy particles are promising new toughening agents. Their application is, however, not necessarily restricted to the toughening of epoxy resins, because they can also be applied as impact modifiers in thermoplastics. In this case the predetermined morphology can be obtained by melt blending of the rubber particles in the desired concentration and size. Therefore, first a more detailed study of the

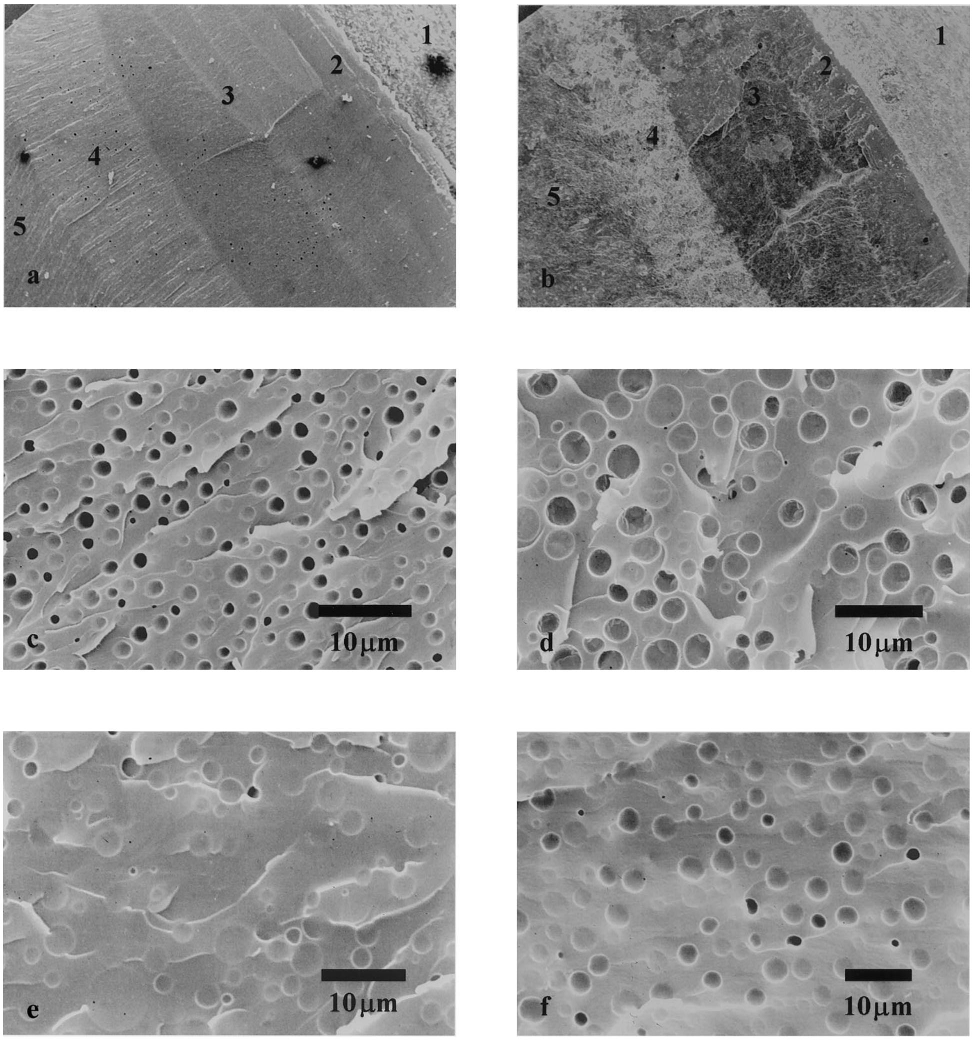

Fig. 6. Scanning electron micrographs of rubber modified Epikote 828, (a) overview of the fracture surface for CTBN modified epoxy, (1) machined notch, (2) razor cut, (3) precrack, (4) stress whitened zone, (5) fast fracture zone, (b) same overview for the rubbery particle modified epoxy, (c) stress whitened zone of the fracture surface of CTBN modified epoxy showing cavitated rubber particles, (d) same zone for the rubbery particle modified epoxy, (e) the fast fracture zone of the fracture surface of CTBN modified epoxy, (f) same zone for the rubbery particle modified epoxy.

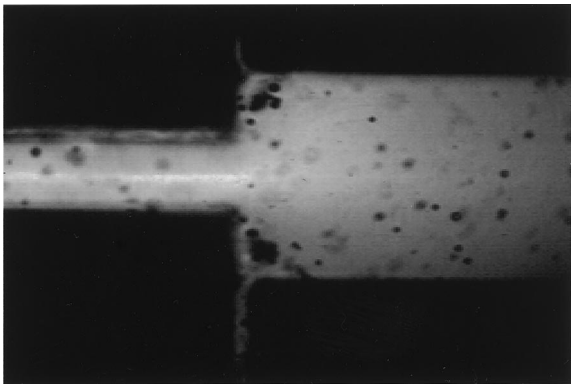

Fig. 7. Flow visualisation of a polyethylene melt flowing into a contraction by means of the addition of glassy epoxy beads (black dots, size ~ 0.1 mm) prepared by curing a dispersion of Epikote 828 using DETDA as curing agent [32].

particles synthesis is essential in order to accurately control their size. Next, the applicability of the particles in a wide range of polymers and processes can be investigated.

As demonstrated, the preparation route can be applied for several types of epoxy resins. By curing an aromatic instead of an aliphatic epoxy resin, glassy particles were prepared. An interesting, be it somewhat esoteric, direct use of these particles with relatively large dimensions (~ 0.1 mm, using HEC as stabiliser), is as tracers in flow visualisation techniques, where velocities are measured using particle tracking velocimetry (PTV). An example of this is given in Fig. 7 in which glassy epoxy spheres are used in flow-visualisation of polymeric melts [32]. The digital image analyses requires detectable coloured particles of a minimum size which remain spherical in the viscous flow. This is accomplished by curing DGEBA epoxy resin using DETDA as curing agent which yields highly crosslinked, unmeltable and undeformable yellow particles, with approximately the same density as the melt to be investigated.

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