Modification of epoxy resin using reactive liquid (ATBN) rubber

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Abstract

Epoxy resins are widely utilised as high performance thermosetting resins for many industrial applications but unfortunately some are characterised by a relatively low toughness. In this respect, many efforts have been made to improve the toughness of cured epoxy resins by the introduction of rigid particles, reactive rubbers, interpenetrating polymer networks and engineering thermoplastics within the matrix.

In the present work liquid amine-terminated butadiene acrylonitrile (ATBN) copolymers containing 16% acrylonitrile is added at different contents to improve the toughness of diglycidyl ether of bisphenol A epoxy resin using polyaminoimidazoline as a curing agent. The chemical reactions suspected to take place during the modification of the epoxy resin were monitored and evidenced using a Fourier transform infrared. The glass transition temperature (T_g) was measured using a differential scanning calorimeter. The mechanical behaviour of the modified epoxy resin was evaluated in terms of Izod impact strength (IS), critical stress intensity factor, and tensile properties at different modifier contents. A scanning electron microscope (SEM) was used to elucidate the mechanisms of deformation and toughening in addition to other morphological features. Finally, the adhesive properties of the modified epoxy resin were measured in terms of tensile shear strength (TSS).

When modifying epoxy resin with liquid rubber (ATBN), all reactivity characteristics (gel time and temperature, cure time and exotherm peak) decreased. The infrared analysis evidenced the occurrence of a chemical reaction between the two components. Addition of ATBN led to a decrease in either the glass transition temperature and stress at break accompanied with an increase in elongation at break and the appearance of some yielding. As expected, the tensile modulus decreased slightly from 1.85 to about 1.34 GPa with increasing ATBN content; whereas a 3-fold increase in Izod IS was obtained by just adding 12.5 phr ATBN compared to the unfilled resin. It is obvious that upon addition of ATBN, the Izod IS increased drastically from 0.85 to 2.86 kJ/m^2 and from 4.19 to 14.26 kJ/m^2 for notched and unnotched specimens respectively while K_{IC} varies from 0.91 to 1.49 MPa m$^{1/2}$ (1.5-fold increase). Concerning the adhesive properties, the TSS increased from 9.14 to 15.96 MPa just by adding 5 phr ATBN. Finally SEM analysis results suggest rubber particles cavitation and localised plastic shear yielding induced by the presence of the dispersed rubber particles within the epoxy matrix as the prevailing toughening mechanism. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Epoxy resins are considered as one of the most important classes of thermosetting polymers and find extensive use in various fields of coating, high performance adhesives and other engineering applications. Once cured, they are characterised by high chemical and corrosion resistance as well as good mechanical and thermal properties. However, in many applications they have one major disadvantage, they are very brittle with poor resistance to crack propagation and low impact strength (IS), i.e. they exhibit low toughness [1].

The aim, when attempting to toughen brittle polymers, is to increase their toughness without significantly

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decreasing other important properties such as modulus and heat distortion temperature. Most of the reported studies were carried out using glass beads, alumina trihydrate, silica and one of the most successful involves the addition of a suitable rubber such as liquid amine-terminated (ATBN), carboxyl-terminated (CTBN), hydroxyl-terminated (HTBN) copolymers of butadiene and acrylonitrile and more recently through the use of thermoplastics (polyphenyl oxide: PPO) and interpenetrating polymer networks (IPN) structures.

Considerable work relating to particulate fillers effect on the mechanical properties of thermoplastic and thermosetting polymers has been reported in the literature. Parameters such as volume fraction of filler [2–6], the particle size [4,6–8], the modulus and strength of the filler [3,9], the resin–filler adhesion [3] and the toughness of the matrix have been extensively studied. The variation of some of these parameters leads to improved toughness of the filled material while increasing its strength and modulus. Several studies have demonstrated that the fracture energy of filled epoxies reaches a maximum at a specific filler content [2–5,10].

Recently, highly crosslinked thermosetting resins have been toughened by tough, ductile, chemically and thermally stable engineering thermoplastics such as polyethersulfones [11,12], polyetherimides [13], phenolic hydroxyl-terminated bisphenol A polysulfone [14], and PPO [15].

IPNs are a novel type of polymer alloys, intended in the case of epoxy resins to modify this latter in terms of impact resistance. Interpenetrating or the permanent entanglement usually leads to improved compatibility which means a decreased degree of phase separation. Morphology, which plays a major role in affecting IPN properties is controlled by the chemical compatibility of the polymers, interfacial tension, crosslinking densities of the networks, polymerisation method, and the IPN composition [16,17].

The most successful method to toughen epoxy resins involves the addition of suitable rubbers which are copolymers with variable acrylonitrile content to the uncured epoxy resin. The effect of the acrylonitrile content of copolymer type, M_W, concentration and solubility parameters of the rubber and its functional end groups on the fracture toughness or on the impact strength of the epoxy resin have been studied. In these studies, epoxy resins were modified with liquid CTBN [18–28], ATBN [27,29–31], HTBN [32] and epoxy-terminated (ETBN) [29,33–35] copolymers of butadiene and acrylonitrile.

Kalfoglou and Williams [18] have studied the dynamic mechanical properties of a CTBN modified diglycidyl ether of bisphenol A (DGEBA) epoxy resin. They found that the addition of CTBN, at least at levels below 20 phr, resulted in the enhancement of β the relaxation peak occurring at around −40 °C. Small temperature shifts in the location of the β peak were also observed.

Similar work has been done by Sanjana and Kupchella [19]; they found that fracture toughness and dynamic mechanical properties are affected by rubber content, rubber/epoxy compatibility and changes in the curing agent stoichiometry. It is interesting to note that the tensile modulus of the chemically reacted system increases slightly with increasing rubber inclusions in low HTBN content formations (<6%).

A study which has included measurements at temperatures in the (−110 to 20 °C) range [20] showed that the CTBN (27% AN) modified material which has both the smallest particles and the highest toughness at room temperature generally shows no further reduction in G_{IC} at temperature below −80 °C and for materials containing CTBN (with 18% and 10% AN) however the G_{IC} values continue to drop significantly below −80 °C, and at −110 °C approaches the level of pure epoxy.

Kinloch and co-workers [21,22] have found that the toughness of CTBN modified thermosets increases with volume fractions of the dispersed rubbery phase, but the modulus and yield strength usually decrease slightly.

Bucknall and Partridge [24] observed that the miscibility of a particular grade of CTBN rubber depends on the type of epoxy resin used. Rubber-particle size appeared to be another material parameter that influences the fracture toughness of rubber-modified epoxies.

Bartlet et al. [25] observed an optimum of the mechanical properties for 15% of initial CTBN; this toughening effect is attributed to the presence of small rubber particles with a narrow size distribution.

For this reason Pearson and Yee [26] have used several liquid rubbers (CTBNs) which produced precipitated rubber particles with a variety of diameters. They found that the fracture toughness is very dependent on particle size where large particles provide only a modest increase in fracture toughness via a particle bridging/crack deflection mechanism. In contrast, smaller particles provide a significant increase in toughness through cavitation-induced shear banding.

Kunz et al. [27] compared the morphology and toughness of two types of rubber-toughened epoxies (ATBN and CTBN). ATBN modified epoxies have a diffuse-appearing interface between the dispersed rubber phase and the epoxy matrix attributed to an irregular particle shape which unexpectedly, produces the same toughness as the more spherically shaped particles in CTBN modified epoxies. They also suggested that toughening is not enhanced by large particles instead, toughness may be dependent on small particle concentration.

Verchere et al. [28] have found that the miscibility of epoxy (DGEBA) decreases when decreasing the acrylonitrile content from 26% to 10% of CTBN whereas increasing M_n from 349 to 383 g/mol led to a significant

shift in the miscibility. This effect is due to the increase in secondary OH group concentration.

Montarnal et al. [33] discussed results for an ETBN modified DGEBA epoxy cured with MNDA. The obtained results showed that both gelation and vitrification were delayed in the rubber modified system and phase separation occurred prior to gelation and vitrification. Raising the cure temperature from 27 to 100 °C increased the average diameter of particles from 0.5 to 1.1 μm with a nearly constant volume fraction. Similar results were obtained by Verchere et al. [34] for another epoxide type. It was found that the value of glass transition temperature decreases in a roughly linear way with the initial amount of rubber added to the formulation; and that the above value does not depend on cure temperature for a given rubber concentration. In another paper [35] they have analysed and discussed the mechanical properties. It has been shown that IS, fracture toughness (K_{IC}) and fracture energy (G_{IC}) increased slightly with increasing volume fraction of the dispersed phase. They also found that the variation of the mean diameter between 0.27 and 0.46 μm for the same volume fraction of the rubber phase has no significant effect on the mechanical properties.

Hwang et al. [29] used ETBN and ATBN to establish the relationship between the microstructural parameters and mechanical properties. They found that IS, plane strain fracture toughness and fracture energy were increased while Young's modulus and yield strength decreased slightly with rubber incorporation. The ATBN toughened system with the greatest amount of epoxy sub-inclusion formation in the rubbery phase demonstrated the best fracture toughness. In fact, the adequate choice of cure conditions is of more importance than rubber presence; hence the fracture toughness changes by a factor of about 2.7 by varying the cure conditions while it has been shown that rubber (ATBN) addition does not necessarily lead to an increase in fracture resistance. Furthermore, it has been found [30] that the K_{IC} value of the pure resin cured at 120 °C is much higher than the values of the 10% ATBN epoxy blends cured below 80 °C. Curing at low temperature promoted the formation of homogeneous materials with poor fracture resistance whereas at high temperature tough heterogeneous blends were obtained [30,31].

This work is an exhaustive study of the effect of a reactive liquid rubber on most physico-chemical properties of an epoxy resin. It attempts to improve the toughness of DGEBA epoxy resin using polyaminoimidazoline as a curing agent. The modifying agent is liquid ATBN copolymers containing 16% acrylonitrile. The chemical reactions that possibly take place during the modification of the epoxy resin were monitored using a Fourier transform infrared (FTIR), while glass transition temperature (T_g) was measured using a differential scanning calorimeter (DSC). The mechanical behaviour of modified epoxy resins was evaluated in terms of the Izod IS (high speed of crack propagation), the critical stress intensity factor (low speed of crack growth), and tensile properties (stress and strain at break, tensile modulus, and energy at break) at different modifier contents. The fractured surfaces were studied using a scanning electron microscope (SEM) to elucidate the mechanisms of deformation and toughening as well as other morphological features. Finally, the adhesive properties of the modified epoxy resin were evaluated in terms of tensile shear strength (TSS).

2. Experimental

2.1. Materials

The materials used are: DGEBA Araldite GY 260, epoxy resin with a M_W of 381 (without diluent), an Epoxy index (Eq/kg) of 5.1–5.4 and Epoxy equivalent (g/Eq) of 185–196 from Schering Company France. The curing agent is polyaminoimidazoline (EUREDUR 460) with an amine index of 230–260 from Schering Company France. The modifying agent is an ATBN copolymer 1300 × 16 with 16% of acrylonitrile liquid reactive rubber with 16% of acrylonitrile from BFGoodrich Hycar Chemical group. For the adhesive tests, aluminium plates ($l = 100$ mm, $w = 23$ mm, $t = 2$ mm) were used as substrates.

2.2. Sample preparation

2.2.1. Epoxy/amine-terminated butadiene acrylonitrile/curing agent

Resin and rubber (5–20 phr) were first mixed together and heated for 15 min at approximately 60 °C in a water bath and degassed while stirring. Once the mixture had cooled to below 60 °C, the curing agent which was heated to approximately 40 °C was then added prior to hand mixing for a short time (1–2 min). Next, the resin mixture was poured into a polyurethane (PTFE) coated mould, cured for 24 h at room temperature, and then post-cured at 120 °C for 3 h. At this stage the cured specimens were allowed to cool slowly in the mould at room temperature.

2.2.2. Adhesion preparation

The aluminium specimens were immersed for 10 min at 65–70 °C in a 25% sulphuric acid and 2.5% sodium dichromate solution prior to their washing with water and acetone successively before bonding [36]. About 0.1 g of epoxy/ATBN/curing agent adhesive (prepared as indicated previously) was manually spread as uniformly as possible on both surfaces of the substrates (4.6 cm²).

After deposition of the adhesive on the substrate surfaces, and forming an adhesive layer, a 1500 g weight was placed over the overlap area of sample to ensure continuous contact for 24 h at room temperature. The sample was then post-cured at 120 °C for 3 h. Before curing, the excess of adhesive was cleaned off the joint using a knife.

3. Testing

3.1. Characterisation methods

3.1.1. Reactivity

Additives are known to have a direct influence on the curing parameters like gel time, cure time, gel temperature and cure temperature of the resin. For exothermic curves, 15 g of epoxy resin was cured with stoichiometric content of curing agent and various ATBN content in a glass beaker. This beaker was immersed in an oil bath (80 °C) and the temperature was recorded using a thermocouple. Finally, the cure conditions were determined from the exothermic curves i.e. temperature as function of time.

3.1.2. Infrared spectroscopy (FTIR)

FTIR spectroscopy has been used to monitor the extent of cure of the DGEBA/ATBN/hardener epoxy resin system and the reactions which occur when such modifiers are used. For the infrared (IR) measurements, a small portion of the cured epoxy system was ground to a fine powder, mixed with potassium bromide (KBr) powder and pressed into a pellet. FTIR spectra were recorded on a Perkin Elmer 1000 PC spectrometer.

3.1.3. Differential scanning calorimetry

The glass transition temperature (T_g) of cured and modified DGEBA resin with various ATBN rubber content were measured at a heating rate of 10 °C/min using a Perkin Elmer DSC 7 differential scanning calorimeter.

3.2. Mechanical properties evaluation

3.2.1. Tensile properties

The load–elongation curve was obtained using an axial extensometer coupled to an Instron mechanical tester with a 5000 N load cell and a crosshead speed of 10 mm/min. All tests were performed at room temperature according to BS 2782 method 302 A. Using the load–elongation curves tensile strength and modulus of elasticity with different contents of ATBN were obtained (the tensile modulus is taken at 0.2% extension).

3.2.2. Izod impact strength

Izod IS was measured according to ASTM D 256 using a standard notched (1 mm) specimen. Samples were prepared by casting into rectangular shaped cavities ($65 \times 15 \times 4$ mm^3). Tests were run on a TMT N 431 impact tester type machine equipped with a hammer. Six samples from each formulation were broken. Average IS values along with the standard deviations were reported. The Izod IS is calculated as follows:

$$IS = \frac{U_1 - U_2}{(w - a)t} \quad (kJ/m^2)$$

where U_1 is the impact energy (kJ), U_2, the residual energy (kJ), w, the specimen width (m), t, the specimen thickness (m), a, the notch length (m).

3.2.3. Critical stress intensity factor

The fracture toughness was measured in terms of critical stress intensity, K_{IC}. Fracture toughness values have been determined using pre-cracked (0.9–1 mm), single edge notched specimens in three point bending with a span of 50 mm dimension. These tests were performed using an Instron tensile machine type 1185 at a crosshead speed of 5 mm/min at room temperature. K_{IC} was determined according to ASTM E 399–78, using the following relationship [37]:

$$K_{IC} = \frac{3PSa^{1/2}Y}{2tw^2}$$

where P is the critical load for crack propagation (N), S, the length of the span (mm), a, the pre-crack length (mm), t, the specimen thickness (mm), w, the specimen width (mm), Y, the geometrical factor given by

$$Y = 1.93 - 3.07(a/w) + 14.53(a/w)^2 - 25.11(a/w)^3 + 25.80(a/w)^4$$

3.2.4. Adhesive properties (tensile shear strength)

The TSS test was carried out on an Instron tensile testing machine at a crosshead speed of 10 mm/min and at room temperature. TSS values reported represent the average of 6–8 samples. The TSS is given as follows:

$$TSS = F/A \quad (N/m^2)$$

where F is the force at fracture (N) and A, the surface of bond area (m^2).

3.3. Scanning electron microscopy analysis

Impact fractured surfaces of samples of epoxy resin modified with different ATBN content were coated with a thin palladium layer and examined using a scanning electron microscope (SEM, Philips XL 20).

4. Results and discussion

4.1. Characterisation

4.1.1. Reactivity

The effect of ATBN on the reactivity of epoxy resin is summarised in Table 1. The exothermic curves for both neat and 12.5 phr ATBN modified epoxy resin is illustrated in Fig. 1. The temperature evolution during crosslinking reaction is recorded as function of time. Using the cure curve, the gel time, gel temperature, exotherm peak and cure time have been obtained. The exotherm peak during crosslinking reaction of both neat and 12.5 phr ATBN modified epoxy resin reached a maximum at 112.5 °C after 19 min and 103.5 °C after 16 min respectively. The increase in temperature of these compounds might be attributed to the energy released as the epoxy groups react.

On adding ATBN, all reactivity characteristics (gel time and temperature, cure time and exotherm peak) decrease as shown in Table 1. Such behaviour can be explained by the fact that during the reaction of ATBN

with the epoxy resin some of the exothermic energy released during epoxy crosslinking might have been consumed by ATBN resulting in a decrease in gel and cure time (more rapid reaction) as well as a decrease in the exotherm peak. Frigione et al. [38] have reported that the use of ATBN rubber modifiers is attractive because of the high reactivity of the end groups with the epoxide ring which will result in shorter gel times.

4.1.2. Infrared spectroscopy

Series of IR spectra (Fig. 2(a) and (b)) have been obtained to evidence the occurrence of any chemical interaction between epoxy resin and ATBN. Fig. 2(a) and (b) are the magnification of IR spectra of hydroxyl and epoxy group in epoxy/ATBN/hardener reaction mixture respectively. A comparative study of such spectra will be used to draw conclusions relating to the chemical linkages formed during the modification reaction. The main conclusion drawn is that an incomplete chemical reaction between the epoxy and the hardener led to the appearance of epoxy absorption peaks at 876 cm^{-1}.

Fig. 2(a) and (b) illustrate a magnification of the IR transmission spectrum of neat epoxy further to its modification with different ATBN contents (5, 10, 12.5, 15 and 20 phr) at specific intensity peaks (hydroxyl and epoxy). For simplicity and clarity only spectra of neat, 5 and 15 phr ATBN modified epoxy resin are shown. It is interesting to note, on the one hand, (Fig. 2(a)) that the absorption of the hydroxyl group at ∼3400 cm^{-1} increases upon addition of 5 phr ATBN and remains relatively constant upon further addition of ATBN. This increase in hydroxyl intensity peak has been attributed to the following factors: first the reaction between the amine group of ATBN and the unreacted parts of epoxy

Table 1
Effect of ATBN content on the reactivity of epoxy resin

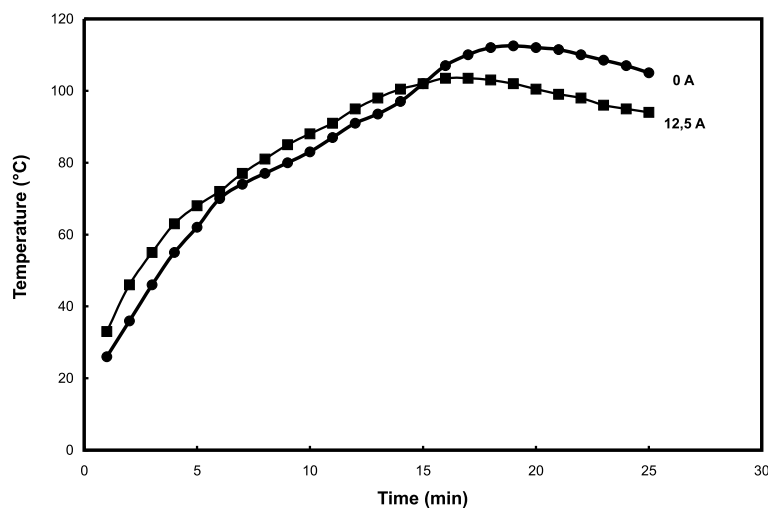| ATBN (phr)	Gel time (min)	Cure time (min)	Gel temperature (°C)	Exotherm peak (°C)
0	13.0	19.0	93.5	112.5
5.0	12.0	17.0	92.0	108.0
10.0	10.5	16.5	91.5	103.0
12.5	11.0	16.0	91.0	103.5
15.0	10.0	16.0	89.0	100.5
20.0	10.5	17.0	83.0	96.0

Fig. 1. Exothermic curves of both neat epoxy (0 A) and 12.5 phr ATBN (12.5 A) modified epoxy resin.
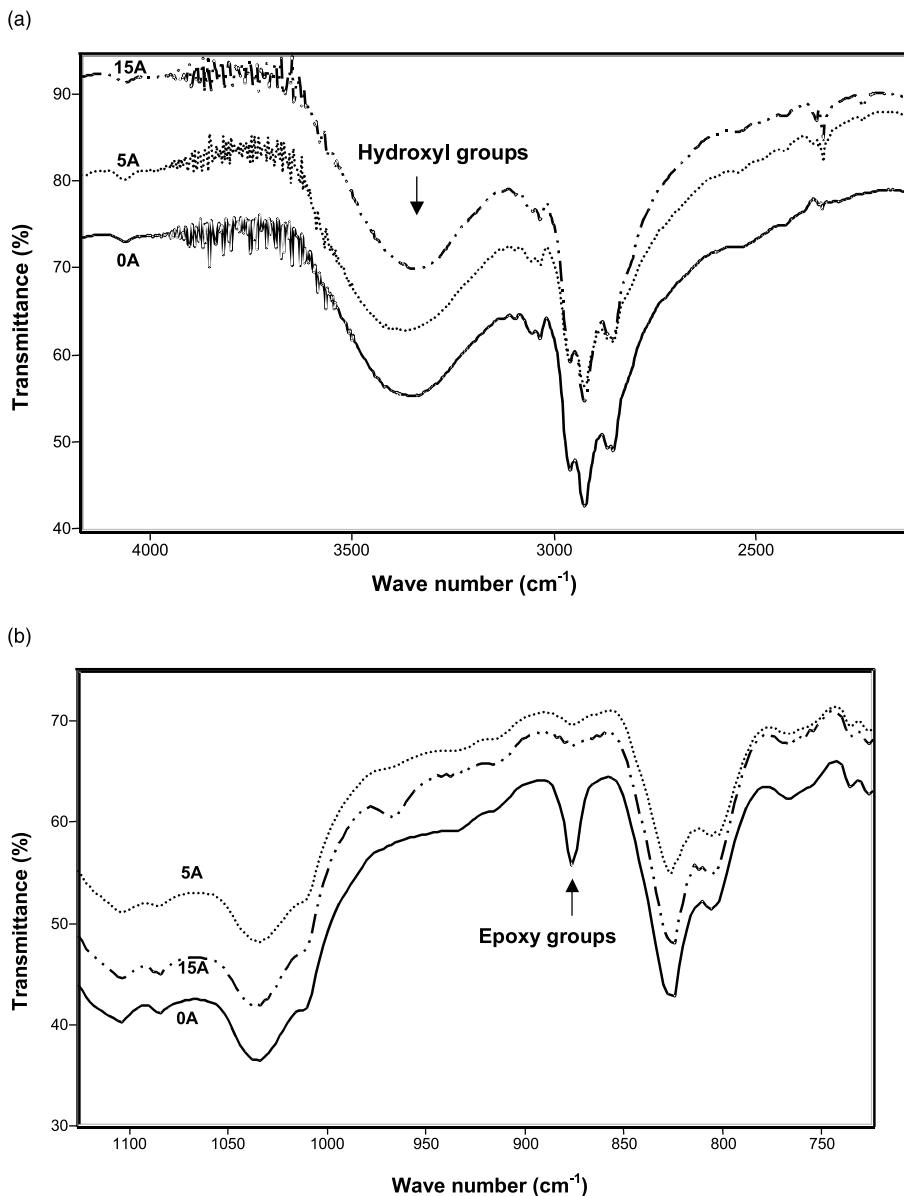
(a)

(b)

Fig. 2. Magnification of the IR spectra in epoxy/ATBN/hardener reaction mixture of: (a) hydroxyl groups, (b) epoxy groups.

resin cured at room temperature [40], second the unreacted amine group (either of ATBN or hardener) absorbing at the same wavelength as the hydroxyl group and finally the creation of hydrogen bonding between amine, ether and OH groups within the mixture. On the other hand Fig. 2(b) shows that the absorption of the unreacted epoxy group at $\sim$876 cm^{-1} decreases drastically upon addition of merely 5 phr ATBN. This is to be considered as a clear indication of the reaction of ATBN with epoxy resin.

The above results concerning the decrease in epoxy groups intensity peaks are further confirmed by a quantitative measurement of the degree of cure. This has been achieved by monitoring the ratio of the absorbance of epoxy ($\sim$876 cm^{-1}) to that of an aromatic carbon–hydrogen deformation band at 828 cm^{-1} (unreacted group). These ratios are plotted against ATBN content and presented in Fig. 3. This figure indicates clearly that the absorbance ratio decreases drastically at 5 phr ATBN then levels off.
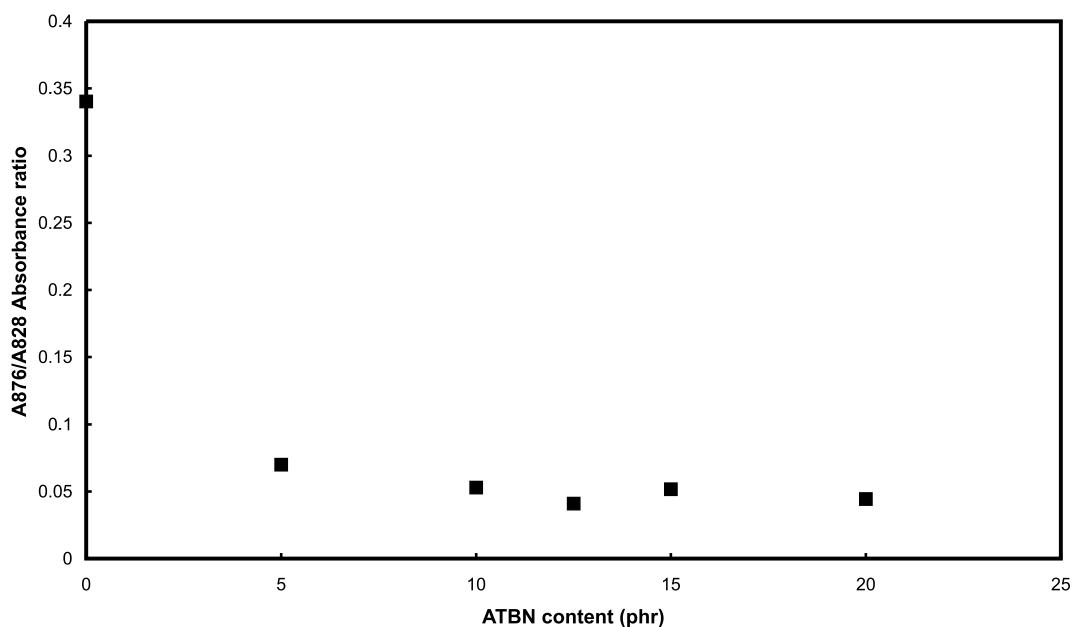
Fig. 3. Effect of ATBN content on the absorbance 876 cm^{-1}/828 cm^{-1} of epoxy resin.

4.1.3. Differential scanning calorimetry

Fig. 4 shows the glass transition temperature (T_g) as obtained from DSC thermograms of epoxy resin against ATBN content. Addition of ATBN causes a slight decrease in the glass transition temperature which is at-tributed to an increase in the dissolved rubber within the epoxy matrix. The T_g falls from 75 °C for neat epoxy resin to 68 °C for 20 phr ATBN modified epoxy resin. This decrease in T_g can be related to the fact that a chemical reaction occurred between the flexible ATBN
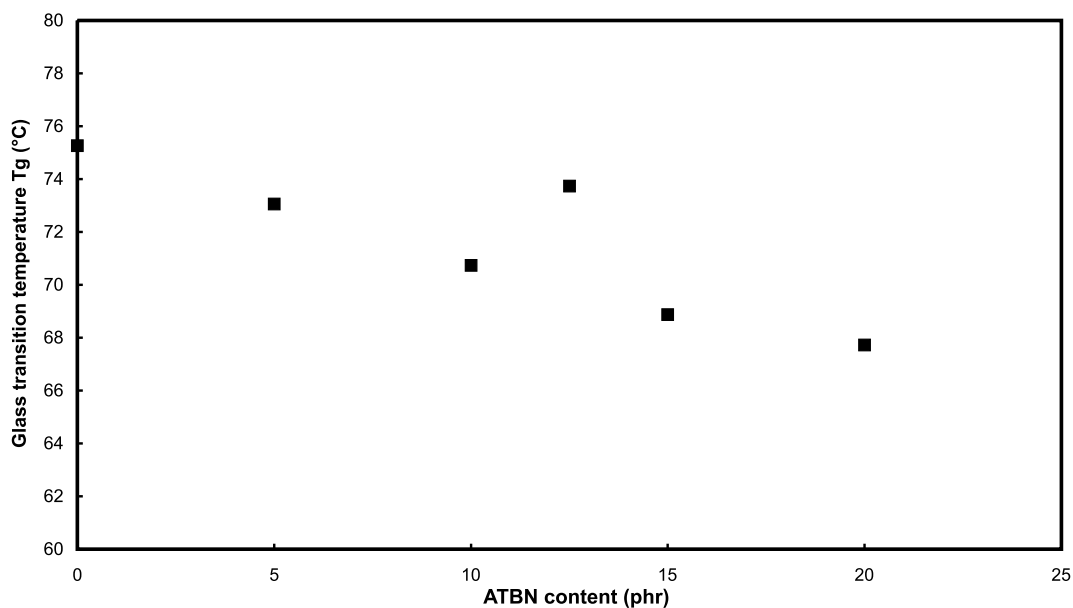

Fig. 4. Effect of ATBN content on the glass transition temperature of epoxy resin.

rubbery phase and the rigid epoxy resin as proved previously with the IR results. Similar results have been reported elsewhere [40].

4.2. Mechanical properties

4.2.1. Tensile properties

Table 2 shows that the tensile properties of epoxy resin vary with the ATBN content.

Rubbers are generally well known to affect tensile properties depending on their compatibility with the epoxy matrix, the surface area of contact, particle size, shape and content as well as the intrinsic strength of the rubber phase.

Fig. 5 represents the stress versus strain curves of both neat epoxy resin, 12.5 and 15 phr ATBN modified epoxy resin. Brittle fracture is evidenced for the neat epoxy resin (0 phr) i.e. absence of yielding. Whereas; the 12.5 and 15 phr ATBN modified epoxy exhibit a ductile

deformation with the appearance of an upper yield stress. A similar behaviour is noticed for the remaining concentrations as presented in Table 2. It is reported in the literature [33] that the lower yield stress values observed indicate that shear yielding might be the prevailing mechanism of deformation in such systems.

As shown in Table 2, a decrease in stress at break accompanied by an increase in elongation at break as well as the appearance of yielding are observed. As expected, the tensile modulus gradually decreases with increasing ATBN content; a decrease that might be due to the effect of the softy segment structure of ATBN. Similar explanation holds true for the decrease in the stress at break as a consequence of ATBN addition.

It is also well known [41] that in order to toughen an epoxy resin with a liquid polymer, first, the liquid polymer should form a rubbery second phase which is dispersed throughout the matrix and second, the rubbery second phase should be bonded to the matrix through the functional groups of the liquid polymer.

In Table 2, the strain at break peaks around 15 phr ATBN content; a drastic increase of about 2.5 is observed. The magnitude of this optimum value is expected to depend on the rubber-matrix compatibility. In agreement with many studies [14,40] the tensile modulus decreases with increasing soft rubber content. It is interesting to note that the modulus decreases slightly from 1.85 to about 1.34 GPa with increasing ATBN content (Table 2). This might be related to the fact that the modulus of the ATBN is much lower than that of the epoxy phase. Furthermore, it is common knowledge that an increase in elongation at break can be an indication of a good adhesion via a chemical reaction between ATBN and epoxy resin; a reaction that could be evi-

Table 2
Effect of ATBN content on the tensile properties of epoxy resin

ATBN (phr)	E (GPa)	σ_y (MPa)	ε_y (%)	σ_B (MPa)	ε_B (%)
0	1.8	–	–	34.4	3.5
5.0	1.7	31.7	3.0	31.3	3.6
10.0	1.7	29.8	3.8	28.0	6.0
12.5	1.6	29.5	4.0	26.9	6.7
15.0	1.3	24.1	4.0	21.6	8.8
20.0	1.4	25.9	3.8	24.6	7.3

Standard deviation: modulus, E—10%; stress at yield, σ_y—6%; strain at yield, ε_y—10%; stress at break, σ_B—5% and strain at break, ε_B—12%.
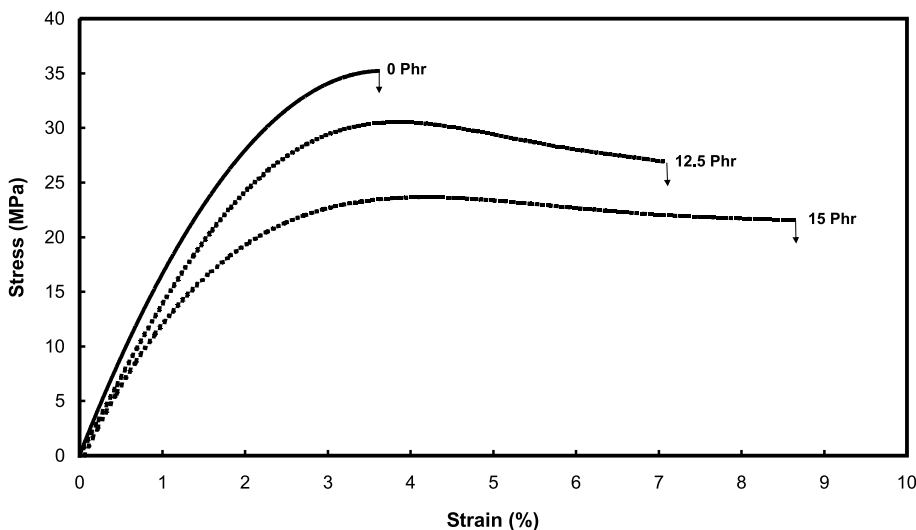

Fig. 5. Stress–strain curves of neat epoxy, 12.5 and 15 phr ATBN modified epoxy.
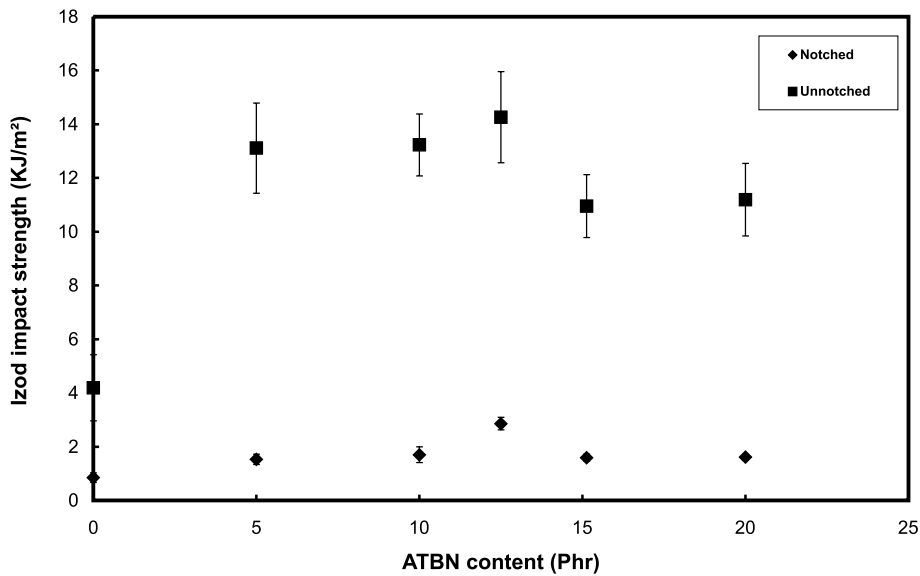
Fig. 6. Effect of ATBN content on the Izod IS of epoxy resin.

denced using IR spectroscopy and explained by the fact that both ATBN and the curing agent contain amine groups, one of them hides the effect of the second.

4.2.2. Izod impact strength

Fig. 6 represents the Izod IS of the notched and unnotched epoxy modified samples as function of ATBN content. The Izod IS of both notched and unnotched specimens exhibit a bell shaped curve with a maximum at 12.5 phr ATBN content. Although and within experimental errors, it can be said that 5 phr ATBN seems to be sufficient to bring this drastic increase in IS of unnotched samples compared to neat epoxy resin. A slight increase in Izod IS is observed at 12.5 phr followed by a decrease at higher ATBN levels. It is obvious that notched samples show lower values than the unnotched ones. The main reason behind this behaviour is that notches act as stress concentrators inducing a decrease in the IS. The energy to initiate a crack is emphasised in unnotched specimens, and this energy is added onto the energy required to propagate the crack. It has to be reminded that, in both cases for notched and unnotched samples, the IS reaches maximum values of 2.86 and 14.26 kJ/m² at 12.5 phr compared to 0.85 and 4.19 kJ/m² of the unmodified resin respectively prior to decreasing with increased ATBN content. In other words; a 3-fold increase in IS has been obtained by merely adding 12.5 phr ATBN compared to the unmodified resin for both notched and unnotched specimens. A behaviour that might possibly be attributed to the improved adhesion between ATBN and epoxy resin due to the chemical reaction as well as

the particle size of ATBN which are factors known to improve impact properties. Furthermore, the interfacial adhesion is known to lead to improved stress transfer while the presence of much tougher phase finely dispersed in a continuous matrix can increase strength of the overall composition by means of damping the stresses at the point of impact and at the crack tip, hence reducing stress concentration. The results of the present study seem to be in accordance with previous studies [2,5,17,19,21].

4.2.3. Critical stress intensity factor (K_{IC})

Fig. 7 illustrates the effect of ATBN on the critical stress intensity factor (K_{IC}). A bell shaped trend is observed. The addition of 12.5 phr of ATBN led to a 1.5-fold maximum increase in the K_{IC} (from 0.91 to 1.49 MPa m$^{1/2}$) followed by a decrease. A similar behaviour to the IS is noticed as well as tensile properties where yielding has taken place upon addition of ATBN.

The most probable mechanism for the improved toughness when the epoxy resin possesses a multiphase microstructure of dispersed rubber particles arises from a greater extent of energy-dissipating deformations occurring in the material in the vicinity of the crack tip. Kinloch and co-workers [21,22] and Yee and Pearson [42] proposed that the deformation processes are (1) cavitation in the rubber particles, or at the particle/matrix interface, and (2) multiple but localised plastic-shear yielding in the matrix, initiated by the rubber particles. The localised cavitation of the rubber gives rise to the stress whitening often associated with crack growth.
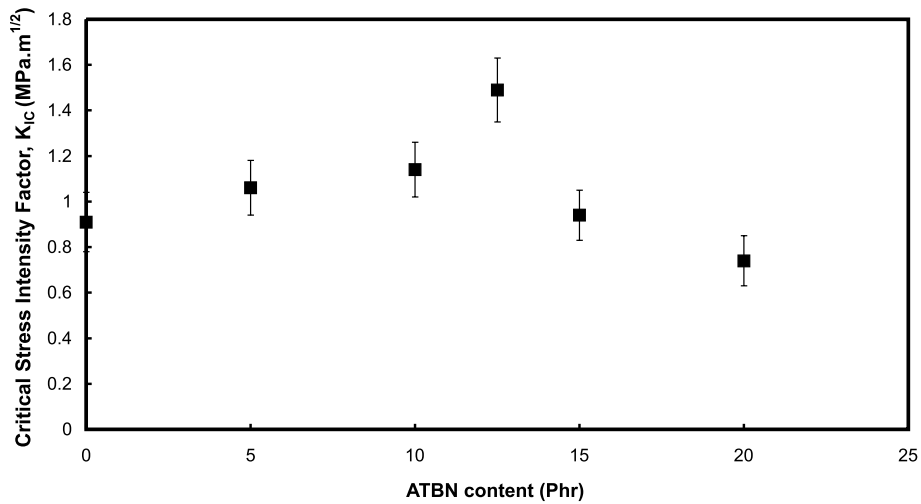
Fig. 7. Effect of ATBN content on the critical stress intensity factor (K_{IC}) of epoxy resin.

These mechanisms of deformation seem to be supported by the results of the present study.

Beyond 12.5 phr ATBN, a decrease in K_{IC} is observed. The effect of the ATBN content on the toughness can be explained as follows: with increased ATBN content, the reaction between the ATBN and epoxy increases so that the ATBN phase becomes more strongly bonded to the matrix leading to better stress transfer increasing thereby the toughness of this system. However, when the ATBN content goes beyond 12.5 phr, the reactivity of ATBN with the epoxy levels off, phase separation initiates with more unreacted rubber particles having poor interfacial adhesion and which might possibly act as stress concentrators. It can be concluded that the toughness of epoxy modified with ATBN is determined by the competition between the extent of reaction
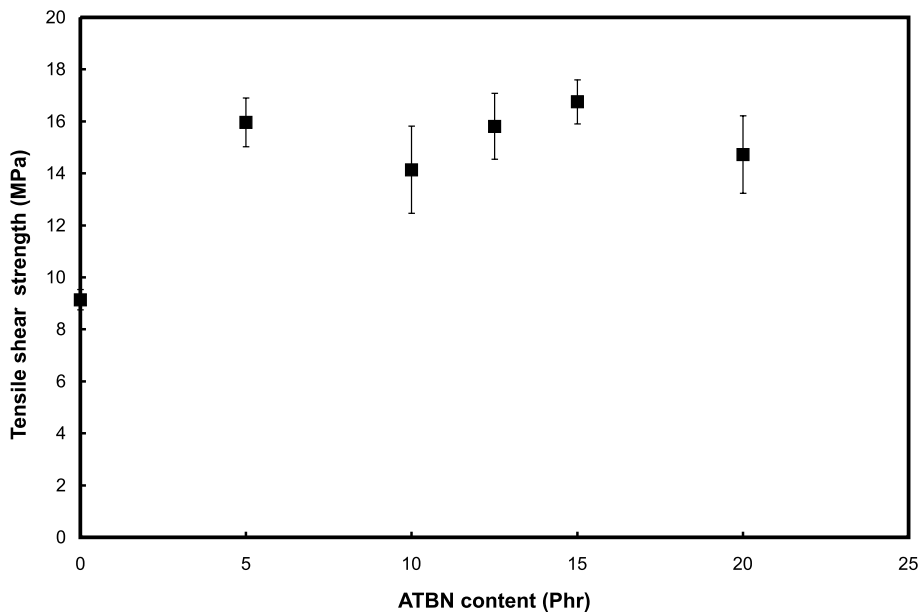

Fig. 8. Effect of ATBN content on the TSS of epoxy resin.

at the particle–matrix interface, and the compatibility of the ATBN with epoxy matrix [40].

4.2.4. Adhesive properties (tensile shear strength)

The adhesive properties have been monitored using the adhesive TSS versus ATBN content (Fig. 8). It can be seen that using only 5 phr ATBN led to a two 1.7-fold increase in TSS (from 9 to 16 MPa) and remains relatively constant with further addition of ATBN. This is in agreement with previous results of either IR and IS where it is reported that maximum chemical interaction between ATBN and the epoxy resin occurs at 5 phr ATBN content.

Furthermore, it was suggested to use ATBN to improve the flexibility of epoxy adhesives. It can be considered that, in the case of aluminium as a substrate, high temperature is necessary to ensure complete curing. Takemura et al. [39] reported that ATBN is thought to reduce the amount of the unreacted part of the epoxy resin and, if enough time and temperature are available, perfect curing can be reached leading to maximum properties with adhesive strengths almost 1.5-fold higher than those of unmodified resin.

4.2.5. Fractography

Fig. 9 represent micrographs of notched impact fractured samples of 5 phr ATBN (a, b), 10 phr ATBN (c, d), 12.5 phr ATBN (e, f) and 20 phr ATBN (g, h). Micrographs (a) and (b) are a general view and its magnification of 5 phr ATBN modified epoxy resin respectively. On adding 5 phr ATBN, some cavitation of the rubber particles accompanied by stress whitening zones developed on the fracture surface of the modified epoxy; this stress whitening effect is related to the local plastic deformation at the crack tip. Furthermore, the cavitation is followed by the onset of the shear localisation process. Similar results have been reported elsewhere [42]. It has to be mentioned once more that the significant increase in Izod IS has been obtained at 5 phr ATBN for unnotched samples. It has been proved using IR spectra that a chemical reaction has occurred between ATBN and epoxy resin leading to strong interaction between the two phases.

Micrographs (c) and (d) are respectively a general view and magnification of 10 phr modified epoxy resin. Both a rough fracture surface and homogeneous structure are observed. A denser structure is observed with a large number of small holes (1.5 μm diameter) acting as stress concentrators. The rubber particles cavitate and are suspected to cause some localised plastic shear yielding resulting in the observed increase in toughness. Similar results have been reported by Kinloch et al. [43] and Yee and Pearson [42].

Addition of 12.5 phr ATBN (Fig. 9(e) and (f)) produces materials containing ATBN nodules perfectly spherical (5–10 μm diameter), and uniformly distributed throughout the matrix. Micrograph (f) shows holes relatively deep with different diameters as well as a multitude of ATBN particles coated with epoxy resin. This is the onset of phase separation as reported elsewhere [38]; as it is also to be considered as an indication of strong interactions between the two phases corresponding to maximum toughness. In fact, it has been reported that some improvement in the fracture toughness is obtained provided that a phase separation with good interfacial adhesion is achieved [14]. In addition to that, the results suggest that the microvoids are produced during ductile stable crack growth either by cavitation of the rubbery particles or debonding at the particle/matrix interface. There is now, however, considerable evidence in literature [21,22] that the high toughness derives from crack blunting produced by cavitation of the rubber particles under the triaxial stress state at the crack tip. This cavitation lowers the local yield stress and provokes extensive shear yielding. In addition to that, the presence of these rubber nodules well anchored to the epoxy matrix might have caused some localised plastic shear yielding leading to the observed increase in toughness. Once more, these results are in accordance with those of tensile properties where some yield occurred upon addition of ATBN rubber accompanied by an increase in elongation at break.

When adding 20 phr ATBN (Fig. 9(g) and (h)), a similar morphology as above is obtained with the size of the nodules almost constant. A layered structure of rubber particles can be noticed. The excess of ATBN led to some agglomeration further to the fact that this excess has not reacted with the epoxy resin hence the resulting poor interface. This might explain the observed decrease in most properties.

5. Conclusions

Based on the results obtained and discussed previously the following conclusions may be drawn: With ATBN incorporation, the entire cure parameters decreased. The IR analysis evidenced the occurrence of a chemical reaction between ATBN and epoxy resin leading to improved compatibility and decreased T_g. On adding ATBN the stress at break decreased accompanied by an increase in elongation at break with the appearance of yielding. The tensile modulus decreases slightly from about 1.85 to 1.34 GPa with increasing ATBN content. A 3-fold increase in both notched and unnotched IS is obtained by adding just 12.5 phr ATBN (2.86 and 14.26 kJ/m^2) compared to the unfilled resin (0.85 and 4.19 kJ/m^2) while K_{IC} varies from 0.91 to 1.49 MPa m$^{1/2}$ (1.5-fold increase). Using only 5 phr of ATBN leads to a 1.7-fold increase in TSS (from 9.14 to16 MPa). Finally SEM analysis indicates rubber particles
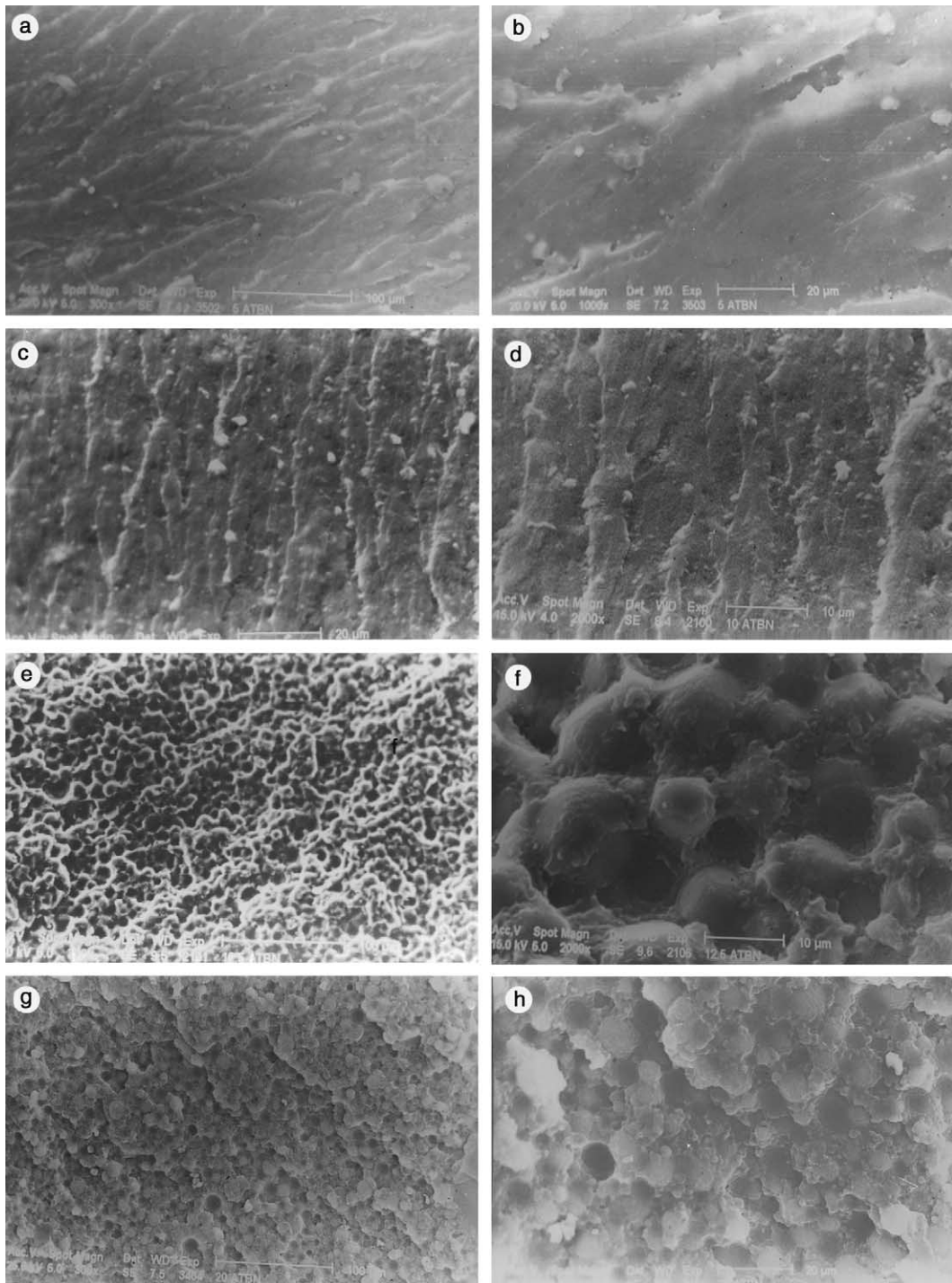
Fig. 9. Micrographs of impact fractured surfaces of neat epoxy/ATBN: at 5 phr: (a) ×300, (b) ×1000; at 10 phr: (c) ×1000, (d) ×2000; at 12.5 phr: (e) ×300, (f) ×1000 and at 20 phr: (g) ×300, (h) ×1000.

cavitation and localised plastic shear yielding induced by the presence of the dispersed rubber particles within the epoxy matrix as the prevailing toughening mechanisms.

Acknowledgements

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