Tensile behaviour of rubber-modified polyester resin materials

M.O. Munyati,¹ P.A. Lovell²

¹Department of Chemistry, University of Zambia, P. O. Box 32379, Lusaka, Zambia +260-95-791532; e-mail: omunyati@natsci.unza.zm
²Manchester Materials Science Centre, UMIST, Manchester, M1 7HS, UK; +44 161 200 3568; pal@umist.ac.uk

(Received: 26 November, 2007; published: 21 May, 2010)

Abstract: Polymer blends comprising an unsaturated polyester resin and dispersed particles were prepared. Rubbery particles were synthesized by sequential emulsion polymerization and had core-shell morphology. Curing of materials was carried out at ambient temperature and subsequently post cured at elevated temperatures to obtain materials of consistent properties. Materials made of different particle content were prepared and their tensile properties evaluated. Effect of matrix ductility was investigated by inclusion of ethyl acrylate in the polyester resin composition. Deformation mechanisms involved in these materials were examined using transmission electron microscopy (TEM) and real-time small angle X-ray spectroscopy (RT-SAXS). Incorporation of rubbery particles in the polyester resin was found to generally improve the tensile properties of the materials. Furthermore, the deformation mechanisms were found to involve cavitation/debonding processes as evidenced from stress whitening in the failed specimen and from real-time small angle X-ray scattering experiments.

Introduction

Unsaturated polyester resins (UPE) are desired in many applications due to their excellent properties such as high stiffness and glass transition temperature of the material. At ambient temperature the materials tend to have low ductility and toughness, and therefore susceptibility to brittle fracture. It is therefore often necessary to modify the materials to be able to meet the end use requirements. Various ways have been attempted to overcome this deficiency in property and thus allow these materials to be used in a greater range of applications.

Three techniques are generally recognised for the modification of polyester resins. The basis of modification essentially involves the introduction of discrete elastomeric particles into the matrix. Elastomeric phases may be introduced during polymerization or dispersed by blending prior to curing of the resin. Previous methods for modification have involved the use of reactive liquid rubbers [1-5]. This is, in part, due to the experiences in toughening epoxy resin materials. These techniques however lacked good control of particle size after phase separation and also, the morphology of particles was less well defined.

Incorporation of core-shell particles offers greater control of particle size and particle morphology, and is therefore more suitable for studies involving these parameters. However, inclusion of elastomeric particles alone may not be sufficient to achieve the desired levels of toughening. Several factors affect the degree of toughening that is
ultimately achieved. Factors that need to be considered include the matrix and rubbery glass transition temperature, rubber domain size in the matrix, quality of the dispersion and the rubber-matrix adhesion.

Preformed particles were prepared and blended with the polyester resin which was then cured at room temperature. The resulting materials were evaluated for their tensile properties and deformation mechanisms using transmission electron microscopy (TEM) and real time-time small angle X-ray spectroscopy (RT-SAXS).

**Results and discussion**

Typical stress-strain curves of the materials prepared are shown in Fig. 1 and 2. The plots are typical of brittle glassy materials. At low strain levels the plots are linear (<1.0) but curve on further deformation. Deviation from linear behaviour is particularly noticeable in BA-S (20/28/30) materials which contained 12 phr (Fig. 1). The significant elongation observed in these materials is indicative of plastic deformation often associated with rubber-toughened materials.

![Stress-strain curve for BA-S(20/28/30)](image1)

**Fig. 1.** Typical stress-strain curves of materials containing different amounts of toughening particles in BA-S(20/28/30).

![Stress-strain curve for 8 phr particles](image2)

**Fig. 2.** Typical stress-strain curves of materials containing 8 phr particles: (a) Unmodified, (b) BA-S(15/47/50), (c) BA-S(20/28/30), (d) BA(15/47/50) and (e) BA(20/28/30).
Fig. 3. Variation of (a) modulus (b) fracture stress and (c) fracture strain with particle weight fraction for rubber-toughened polyester resin moulding materials. Key: □ unmodified resin, ⊗ BA–S(20/28/30), ⋄ BA–S(15/47/50), □ BA(20/28/30), ▼ BA(15/47/50).

Tensile test data for the various materials are shown in Fig. 3. The fracture stress ($\sigma_f$) shows deterioration as the particle content increases. This may be due to inhomogeneities in the materials, which could lead to premature failure. The inhomogeneities could be the result of poor particle-matrix bonding and/or clustering of particles in which particles are in direct contact. Both situations could give rise to void formation. This may explain the scatter in the fracture stress data.

The fracture strains ($\varepsilon_f$) of the materials are seen to diminish initially but rise at higher particle content. At lower particle loading, the particles function more as flaws than tougheners, hence the low fracture strain. Increases from 2.1% in unmodified to 4.0% in materials modified using BA-S(20/28/30) were observed. For each type of material, Young’s modulus ($E$) decreases consistently as the particle content increases. Addition of rubbery particles resulted in a reduction of modulus by as much 33% (BA(20/28/30), $W_p = 12$ phr).

**Tensile properties of ethyl acrylate/styrene resin materials**

Matrix ductility plays a significant role in the level of toughening capable of being achieved in a material. The presence of particles in the matrix must be able to initiate and accelerate processes responsible for toughening such cavitation and/or yielding. Thus, materials modified by addition of ethyl acrylate were expected to have enhanced toughening and ductile deformation due to the inherent ductility of the
matrix. Incorporation of ethyl acrylate in addition to styrene increases the polymerizable monomers in the polyester resin; consequently, also increased the molar mass between the crosslinks and decreased the crosslink-density. Additionally, this created interchain links comprising styrene and ethyl acrylate which have a lower glass transition temperature than polystyrene.

Systems incorporating ethyl acrylate systems were prepared as shown Table 1 and tested for their tensile properties using conditions similar for UPE mentioned earlier.

**Tab. 1.** Nomenclature used to define ethyl acrylate materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Mole fraction EA</th>
<th>Modifier particle (8 phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EA0</td>
<td>0</td>
<td>None</td>
</tr>
<tr>
<td>EA10</td>
<td>0.10</td>
<td>None</td>
</tr>
<tr>
<td>EA15</td>
<td>0.15</td>
<td>None</td>
</tr>
<tr>
<td>EA20</td>
<td>0.20</td>
<td>None</td>
</tr>
<tr>
<td>BA-S(20/28/30)EA20</td>
<td>0.20</td>
<td>BA-S(20/28/30)</td>
</tr>
<tr>
<td>BA-S(15/47/50)EA20</td>
<td>0.20</td>
<td>BA-S(15/47/50)</td>
</tr>
<tr>
<td>BA(20/28/30)EA20</td>
<td>0.20</td>
<td>BA(20/28/30)</td>
</tr>
<tr>
<td>BA(15/47/50)EA20</td>
<td>0.20</td>
<td>BA(15/47/50)</td>
</tr>
</tbody>
</table>

**Fig. 4.** Plots showing the effect of mole fraction of ethyl acrylate on the tensile properties of polyester resin/styrene matrix.

Tensile properties of (polyester resin)-styrene-ethyl acrylate materials are shown in Fig. 4 and 5. No change in the fracture stress is observed as the ethyl acrylate
content is increased. The modulus and fracture strain, however, change significantly. The lowering of modulus and increase in fracture strain is to be expected since incorporation of ethyl acrylate bring about greater segmental motion and reduction in $T_g$ of the inter chain polymer molecules. The EA20 modified matrix, more ductile matrix, showed a slight improvement in tensile properties compared to the less ductile one EA0. The modulus of EA20 materials exhibit an unusual behaviour in that the modulus increased instead of decreasing due to the presence of the particles. This behaviour may be attributed to ethyl acrylate partitioning into the particles and polymerizing within and/or on the surfaces, though this hypothesis cannot be proven.

The failed specimen showed stress-whitening in almost all the specimen unlike only a few in the unmodified matrix. This phenomenon is not commonly observed in polyester resin materials [8]. It is normally associated with formation of voids and in this case suggests increased cavitation/debonding processes.

![Fig. 5. Comparison of tensile properties in ethyl acrylate modified materials: (a) Young's modulus, (b) fracture stress and (c) fracture strain. Toughened materials contained 8 phr of the particles indicated on the x-axis.](image_url)

**Investigations into deformation processes**

Transmission electron microscopy and real-time small angle X-ray scattering were used to investigate the deformation mechanisms in the UPE materials. TEM involves taking thin sections of the sample after loading tests have been conducted hence analysis is after the deformation event. Furthermore, deformation of the sample may occur during sample preparation and relaxation of the sample as well thereby masking evidence of the deformation processes. Small angle X-ray scattering offers the advantage of less elaborate procedures and data acquisition of the deformation processes in real time.

Fig. 5 shows typical TEM micrographs from unstained sections cut just below the fracture surface of failed tensile pieces in materials containing particle content of 8 phr. The micrographs clearly show the particles dispersed in the matrix together with knife marks which appear as lines running across the pictures. Despite the stress-whitening observed on the samples, the micrographs show no evidence of void formed or other types of deformation. Higher magnifications were attempted for closer examination of the particles but poor contrast images was obtained. Whilst
staining (using ruthenium tetroxide) could improve contrast it also obscures the voids [7]. Another possibility is that TEM being a post-mortem method, the voids may have closed due to relaxation of the materials before being examined. The electron radiation impacting on the sections could also lead to closure of the voids.

![Fig. 5](image-url)

**Fig. 5.** TEM micrographs of ultramicrotomed sections from stress-whitened regions of tensile test specimen from (a) BA-S(20/28/30), (b) BA-S(15/47/50), (c) BA(20/28/30) and (d) BA(15/47/50) modified materials.

**Real-time small angle X-ray scattering**

Real-time small angle X-ray scattering was used to probe further the stress-whitening phenomenon observed in tensile test samples. Typical data obtained showing the variation of load and scattering intensity (given in arbitrary units but self-consistent units) are depicted in Fig. 6 – 9.

![Fig. 6](image-url)

**Fig. 6.** Diagram showing results of simultaneous SAXS and tensile testing of the unmodified polyester resin/styrene matrix.

The scattering patterns are 2-dimensional contour plots of the scattered intensity integrated over the whole of the detector area. They show the shape, in reciprocal
space of voids formed during deformation. Patterns of the unmodified and modified material (Fig. 7, 8 phr) are similar except that the intensity is seen to increase rapidly just before fracture in the modified material. Whereas the scattering patterns remain unchanged during the experiment, suggesting no evidence of microscopic void formation during deformation for unmodified materials, evolution of the patterns is observed for the modified materials. This suggests the formation of and growth of the voids in the sample. Also, patterns are slightly elongated in the tensile direction. It may be further inferred that the matrix lacks ductility since the voids are only marginally stretched as the strain increases.

![Diagram showing results of simultaneous SAXS and tensile testing of BA-S(20/28/30) modified materials containing 8 phr particles.](image)

**Fig. 7.** Diagram showing results of simultaneous SAXS and tensile testing of BA-S(20/28/30) modified materials containing 8 phr particles.

![Diagram showing results of simultaneous SAXS and tensile testing of BA-S(150/47/50) modified materials containing 2 phr particles.](image)

**Fig. 8.** Diagram showing results of simultaneous SAXS and tensile testing of BA-S(150/47/50) modified materials containing 2 phr particles.

The absence of a cross-shape is consistent with literature which shows that fully-cured thermosets are unlikely to craze. Fig. 8 shows a typical plot showing SAXS...
patterns for materials modified at 2 phr particles loading. The patterns depicted are of a diamond-shape. Similar patterns have been reported in high impact polystyrene (HIPS) by Bubeck et al [8]. The diamond-shape is a departure from the cross due to broadening of the scattering streaks. Broadening occurs because of inhomogeneous stress fields around rubber particles that cause deviation of the craze plane from normal. Examination of the patterns in Fig. 8 suggests that crazing may be taking place in the initial stages with the deformation through void formation commencing just before fracture.

Real-time measurements for materials containing ethyl acrylate

Materials modified by incorporating ethyl acrylate show patterns consistent with crazing phenomenon occurring indicative in Fig. 9 (a) whilst Fig. 9 (b) shows a pattern consistent with voids formation.

![Diagram showing results of simultaneous SAXS and tensile testing](image)

**Fig. 9.** Diagram showing results of simultaneous SAXS and tensile testing of (a) EA20 material and (b) BA(20/28/30)EA20 modified materials containing 8 phr particles.

These differ from patterns observed in Fig. 6 for the unmodified polyester resin/styrene matrix which are oval. The rare occurrence of crazing in thermosets
materials is due to the lack of flexibility in the network. These results therefore confirm that inclusion of ethyl acrylate increased the flexibility of the matrix. The cause of crazing in thermoset is still not well understood. This fact is evident in the absence of scattering patterns consistent with crazing in materials having a particle content of 8 phr but present in materials with low particle content. Also, materials containing ethyl acrylate exhibited evidence of crazing demonstrating that crazing occurs under a variety of conditions.

However, despite no evidence of crazing in most of the materials, there is indication of formation of voids which are elongated in the tensile direction. The SAXS data clearly show a change in the fracture mechanism from the matrix as a result of incorporated particles.

Conclusions

Polyester resins comprising core-shell particles were prepared by dispersing rubbery particles of varied chemistry and particle size. Tensile properties of the materials showed an increase in the ductility and fracture strain as the particle content increased. The modulus decreased, signifying greater ductility whilst the fracture stress diminished. Incorporation of rubbery particles into the polyester resin succeeded in increasing the ductility of the matrix and therefore toughness of the polyester resin material. Increasing matrix flexibility by incorporating ethyl acrylate resulted generally in better tensile properties.

Subsurface analysis using TEM did not reveal any features that could be associated with a deformation mechanism, presumably due to relaxation of the material prior and during examination of specimen. However, Real-time SAXS during tensile testing showed scattering patterns consistent with formation of voids. Craze-like deformation mechanisms were also indicated by real-time SAXS/tensile test measurements.

Experimental

Materials

The polyester resin used in this study was a commercial resin (BIP Beetle, 8592) containing 28 % by weight styrene. Materials with particle content ranging from 0–12 phr were blended using methods described elsewhere [6]. The materials were cured at ambient temperature using a system comprising benzoyl peroxide (0.5 % w/w) and N,N–dimethyl aniline (0.1 % w/w). This base resin was modified in some samples to enhance the toughening of the matrix by incorporating ethyl acrylate monomer into the system.

Particles used in this study were prepared with a core-shell particle morphology using previously established methods [6].

Processing

Cured polymer blends were prepared by dispersing the particles in the unsaturated polyester resins (250 g) using a Silverson L4R high shear mixer followed by removal of air trapped during blending. The mixing beaker was placed in an ice bath to remove heat generated during the blending process. Materials prepared contained particles in the range 0–12 phr. Curing was carried out over a 24 h period.
As significant amounts of heat are generated during curing, moulds were placed in a water bath so that heat generated could be conducted away. Plaques of 3 mm thickness were produced for use in tensile testing of the materials. Post-curing of plaques was carried out first at 120 °C for 6 h and then at 180 °C for 4 h under a nitrogen atmosphere.

Tensile Testing
The test pieces were prepared from 3 mm thick plaques. The plaques were cut into rectangular strips, which were routed into test dimensions and geometry. Test pieces were polished successively using finer grades of silicon carbide paper to remove surface flaws. The tensile tests were then carried out on an Instron 1122 tensile testing machine at room temperature with a clamping distance of 70 mm. All tests were done using a constant crosshead speed of 5 mm min⁻¹. At least five (5) specimens were done for each material.

Transmission electron microscopy studies
Failed stress-whitened fracture surfaces were obtained and examined under a transmission electron microscope (Philips 301) operated under at 100 kV [6].

Simultaneous real-time small angle X-ray scattering/tensile testing
Simultaneous SAXS/tensile test experiments were carried out on beamline 8.2 at the EPSRC Daresbury Laboratories as described by Lovell et al [7]. Test specimens were deformed in a Polymer Laboratories Minimat tensile testing machine. Testing was done at room temperature using a beam line intensity of approximately 4 x 10⁷ photons s⁻¹ and focused at a distance of 4.5 m behind the sample stage. Two-dimensional scattering patterns were recorded at 20 s intervals using a multiwire detector with spatial resolutions of about 500 µm.

Acknowledgements
The authors are grateful to the Beit Trust and the University of Zambia for their financial support that made possible realization of this project.

References