Ageing of the DGEBA/TETA Epoxy System with off-Stoichiometric Compositions

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An investigation was carried out on the room temperature ageing of off-stoichiometric DGEBA/TETA epoxy formulations. The results obtained show that the epoxy rich mixtures have their inherent brittleness increased by the ageing treatment due to recrystalization of the unreacted epoxy monomers, although homopolymerization could also play a minor role. The initial reaction steps dominated by the amine addition reactions control the macromolecular structure and the mechanical performance of the stoichiometric and near stoichiometric formulation with excess of epoxy monomer. Plasticization due to absorbed -OH results on a significant increase of the deformability of these formulations. The amine rich mixtures have the more stable structures, although plasticization due to moisture absorption from the surrounding environment also produces an increase on the deformability of all, but one, of the formulations investigated.

keywords: *epoxy resins, ageing, mechanical properties*

1. Introduction

Epoxy resins are one of the most versatile polymers under use today. Their use ranges from matrix in high performance composite materials for aerospace structures, to organic coatings and common adhesives for domestic applications[1-3]. This versatility is a consequence of the many epoxy systems that can be fabricated by using different chemical compounds to open the epoxy ring and set the epoxy monomers. Therefore, by the use of anhydrides and aromatic or aliphatic amines as hardeners, different epoxy systems with a large range of chemical and physical properties can be obtained[3-6].

Among the most widely used epoxy systems, those that can be cured at room temperature are largely applied[3]. The epoxy system based on the reaction of the difunctional epoxy monomer diglycidyl ether of bisphenol-A, DGEBA, with aliphatic amines is such an example. The properties of this and other epoxy systems can be varied as a function of the molecular weight of the hardener molecule[7-10], by variations in processing conditions[11-13] or by the use of different hardener to monomer ratios[8,11,13-21]. This last variable introduces

off-stoichiometric mixtures. For the particular system made of the triethylene tetramine, TETA, hardener and the DGEBA monomer the variation of the hardener to monomer ratio promotes strong changes on the mechanical behavior[18-21]. Of particular interest with respect to these changes is the very sharp increase in the impact strength, when amine rich mixtures were used[21].

The problem of working with off-stoichiometric mixtures is that latent reaction sites could remain on the macromolecular structure developed and under the proper conditions the structure can evolve, resulting in changes on the mechanical performance of the material. Temperature is clearly one external parameter that could cause changes to the system, but, even at room temperature, ageing due to exposure of the epoxy resin to humid environments could also be important[22-24].

The changes observed on the mechanical properties when the epoxy monomer to hardener ratio is varied, and the possible changes due to aging, are a direct consequence of the different macromolecular structures that are developed and/or the possible reactions that could occur given a

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boundary condition (i.e., when a variable like temperature or the amount of monomers is changed). For this epoxy system, the cure reactions scenarios are led by the primary amino addition reaction, occurring between the primary amines (~NH$_2$) and the epoxide group according to the following reaction[1,25]
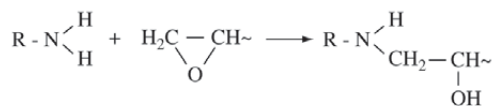

which leads to the formation of strongly hydrophilic hydroxyl groups (-OH). For non-stoichiometric formulations with excess of epoxy monomer the epoxy ring can react with hydroxyls groups, leading to the formation of ether groups according to the reaction[1,12].
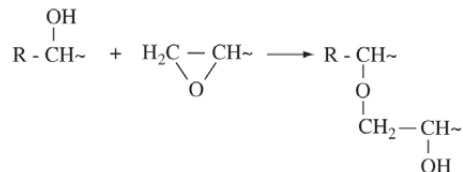
The effect of this reaction is, however, restricted for reactions taking place below 150 °C [26]. Finally, homopolimerization reactions can be catalysed by steric hindered tertiary amines[27], leading to the formation of the p-dioxane ring structure
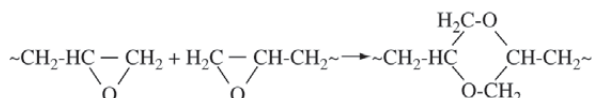
or to the step like structure.
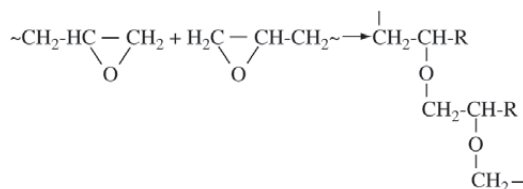
The formation of p-dioxane rings is, however, of minor relevance for non-stoichiometric reactions[28], although it can be responsible for the consumption of about 1/16 of all epoxy rings.

In this work a study was undertaken in order to analyse the variation on the tensile properties of the DGEBA/TETA epoxy system formulated with different hardener to epoxy monomer ratios after its exposure for 6 months to a common room temperature – moderately high humidity environment.

2. Experimental Methods And Materials

The stoichiometric formulation for the DGEBA/TETA epoxy system is obtained using 13 parts of hardener, in weight, per 100 parts of resin, 13 phr. This is the hardener to epoxy monomer recommended by the resin manufacturer (Dow Chemical, MI), based on the epoxy equivalent weight of the monomer and on the amine hydrogen equivalent weight of the hardener. The description of the calculation is given, for example, in Ref. 29. It is worth to note that although 13 phr is the recommended stoichiometric ratio for this epoxy system, and therefore is ordinarily used on usual applications, an earlier analysis by FTIR showed that the consumption of epoxy rings is not complete when the cure is carried out at room temperature[18].

Eight formulations were prepared covering epoxy rich and amine rich mixtures, besides the stoichiometric one, as shown in Table 1. Each formulation was prepared weighting the proper amounts of epoxy monomer and hardener within ± 0.001 g. The departure from the nominal ratios showed in Table 1 was, therefore, always maintained below 3%. The chemicals were thoroughly mixed for at least 10 min and were cast in dog bone shaped open silicone rubber moulds. The tensile specimens could then be obtained directly from castings. After 24 h the specimens were pulled out from the moulds and their surface and edges were ground with silicon carbide paper to remove any surface defect and to guarantee specimens with flat and parallel sides. The average dimensions of the test specimens used are shown in Fig. 1.

Two series of specimens were fabricated for each hardener to epoxy ratio analysed. One was maintained at room temperature, 23 ± 3 °C, and relative humidity of 65 to 70%, and tested 6 months after their fabrication. The other group was tested within 15 days of their fabrication and is thereafter called as the "as fabricated" material.

The tensile tests were carried out on a mechanically driven test machine with 100 kN of capacity and at least 6 specimens were tested per hardener to epoxy ratio. The stress, σ_r, and strain, ε_r, at rupture were determined and the overall macroscopic shape of the tensile curve was also reported.
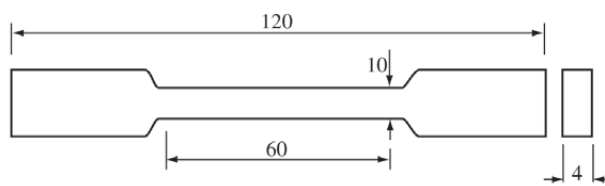

Figure 1. Tensile specimens. All dimensions are in millimetres.

Table 1. Tensile properties of the DGEBA/TETA epoxy formulations.

hardener content (phr)	σ_r (MPa[(1)])	σ_r (MPa[(2)])	$\Delta\sigma^*$ (%)	ε_r (%[(1)])	ε_r (%[(2)])	$\Delta\varepsilon^*$ (%)
7	61.9 ± 28.3	33.7 ± 6.4	-45.6	4.4 ± 2.5	2.7 ± 0.7	-38.6
9	38.2 ± 9.8	25.7 ± 3.4	-32.7	4.4 ± 1.9	2.0 ± 0.3	-54.5
11	46.7 ± 7.1	52.8 ± 5.0	+13.1	3.4 ± 1.4	4.0 ± 0.7	+17.6
13	50.0 ± 9.3	63.6 ± 9.1	+27.2	5.1 ± 2.3	7.9 ± 1.9	+54.9
15	54.7 ± 7.1	46.9 ± 5.3	-14.3	4.4 ± 1.2	4.1 ± 0.7	-6.8
17	52.4 ± 4.7	46.9 ± 3.6	-10.5	4.8 ± 1.3	6.3 ± 1.6	+31.3
19	51.3 ± 5.9	49.5 ± 6.4	-3.5	5.7 ± 2.3	6.8 ± 1.2	+19.3
21	46.9 ± 9.0	42.9 ± 4.7	-8.5	5.0 ± 2.0	8.6 ± 2.4	+72.0

* variation between the mean values of the as fabricated[(1)] and the aged[(2)] specimens.

The fracture surfaces of the tested specimens were analysed by scanning electron microscopy, using secondary electrons with the electron beam voltage ranging between 10 to 15 kV.

3. Experimental Results and Discussion

The experimental results obtained are shown in Table 1. It can be seen that the room temperature ageing produced strong changes on the mechanical performance of the majority of the formulations analysed. Nevertheless, as shown by the variation, $\Delta\%$, between the values measured for the as fabricated and for the aged specimens, different trends were obtained as a function of the hardener to epoxy monomer ratio used. The $\Delta\%$ values for the stress and strain at rupture are plotted as a function of the hardener to epoxy ratio in Fig. 2.

From Fig. 2a one can see that the most off-stoichiometric epoxy rich formulations, i.e., the 7 and 9 phr mixtures, were more strongly affected by ageing. For these systems two main structural characteristics were so far determined. First, there remains a great number of unreacted epoxy rings, as shown by infrared analysis[18]. Second, a rigid and tight macromolecular structure is developed, were the only expected mobile group is the dimethylene ether linkage of bisphenol-A[20,27,30]. These characteristics are a direct consequence of the complete exhaustion of all the reactive sites on the hardener molecule, giving way to a rigid and brittle structure[30]. The existence of a more closely packed structure for these epoxy rich formulations was recently confirmed by solid state nuclear magnetic resonance measurements[31].

The brittleness of these formulations could be inferred directly from the shape of their engineering stress *vs.* strain curve, Fig. 3a. As one can see, the overall macroscopic behaviour of these formulations under uniaxial tensile stress was an almost entirely linear curve until the fracture stress is reached. The topographic aspects observed at the frac-
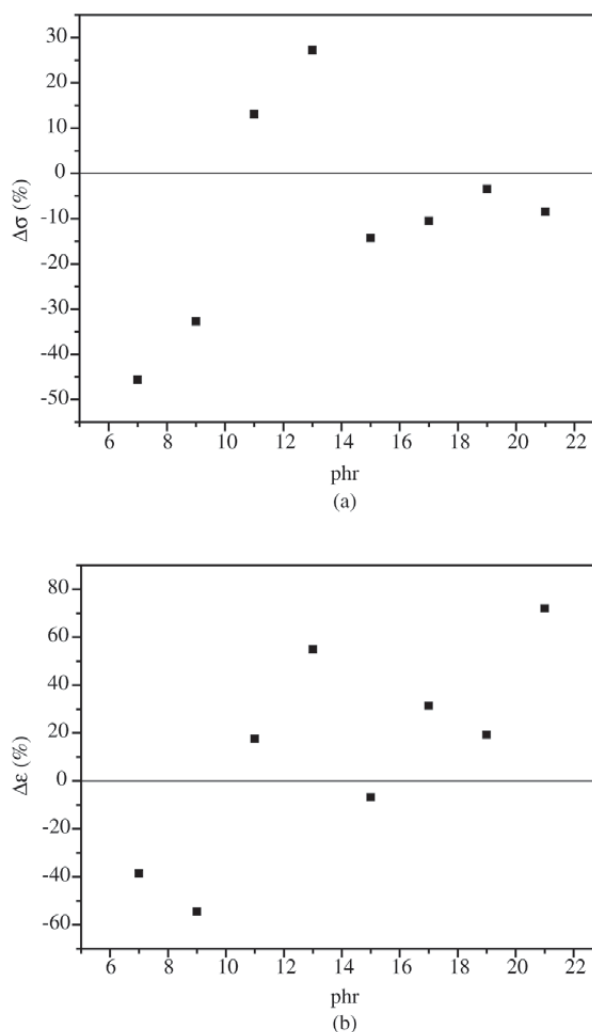
Figure 2. Percent variation of the tensile mechanical properties between the as fabricated epoxy formulations and the aged formulations. a) Tensile strength; b) Strain at rupture.
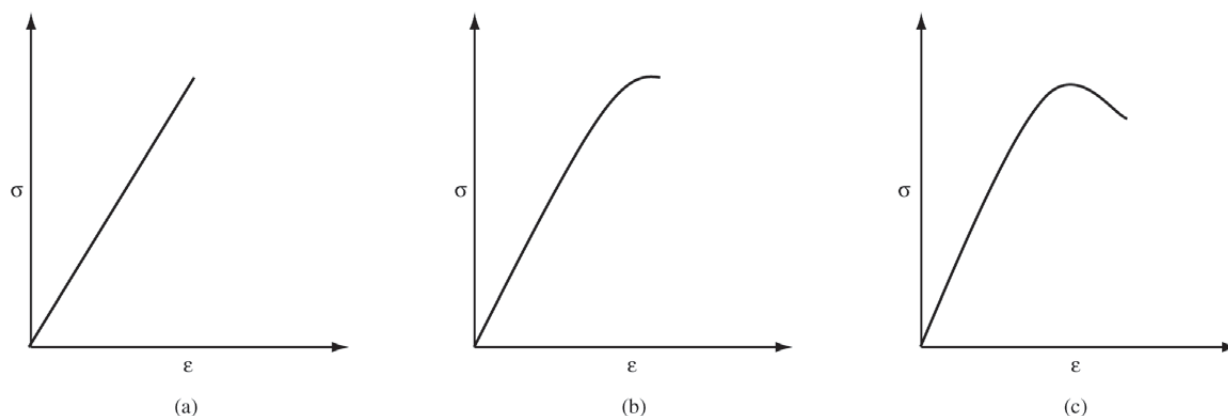
Figure 3. Schematic of the engineering stress-strain curves for the different epoxy formulations analysed. a) Brittle behaviour common to epoxy rich formulations; b) Quasi- brittle behaviour shown by the amine rich and the aged stoichiometric formulations; c) Ductile behaviour shown by the as fabricated and aged amine rich formulations.

ture surface of the epoxy rich formulations also indicate that these hardener to epoxy formulations have a very brittle behaviour. The fracture surface of thermoset polymers is characterised by the presence of three different regions[32,33]: (a) a flat featureless mirror zone surrounding the crack initiation point; (b) a transition zone, where the surface roughness steadily increases; (c) a final propagation zone with conical marks. The overall aspects of the fracture surface morphology of a thermoset polymer is shown in Fig. 4. Of particular relevance for this study is the size of the mirror zone, which has been correlated with the toughness of polymers and particulate composites[34]. The smaller the mirror zone, the more brittle the material is. And, as shown in Fig. 5, the mirror zone of the epoxy rich formulations is smaller than that of the stoichiometric or amine-rich formulations.

The presence of a large fraction of unreacted epoxy rings, up to 29% for the 7 phr formulation as shown by the previous FTIR analysis performed[18], could give way to homopolymarization of these epoxy rich mixtures through epoxy ring opening by secondary OH groups[1,12,35]. Nevertheless, this reaction proceeds at a much slower rate than the amine-epoxy addition reaction[35-37] and it is not considered as a main reaction for room temperature cured systems. Unreacted DGEBA epoxies can, however, recrystallize in ambient cured epoxies, thus causing embrittlement[38]. Therefore, recrystallization can play an important role whenever ageing of the epoxy rich formulations could take place. This is, in fact, the experimental behaviour observed, where a strong reduction on the values of the strain and stress at rupture are observed for the 7 and 9 phr formulations, as shown in Fig. 2.

An intermediate behaviour between that shown by 7 and 9 phr formulations and the one from amine rich formula-
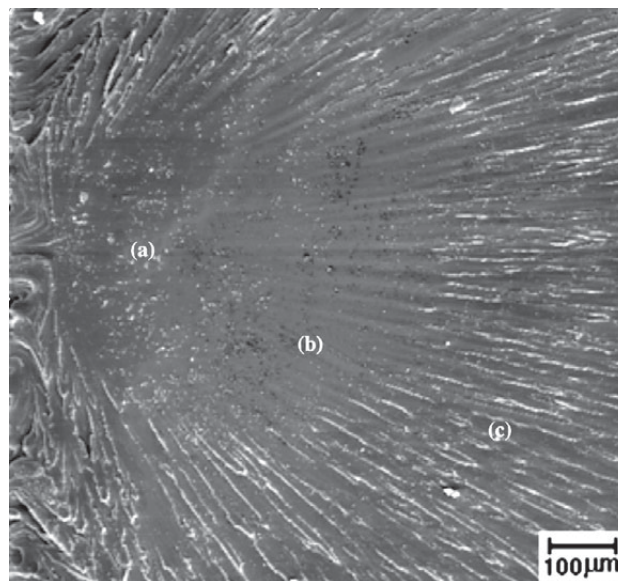
Figure 4. Surface features for a 13 phr specimen, showing the three regions present at the fracture surface of a thermoset polymer: a) the mirror zone; b) the transition zone; c) the final propagation zone.

tions was observed for the variation of the stress at rupture of the 11 and 13 phr formulations. For these mixtures, a fairly large amount of unreacted epoxy rings still exists[18]. Therefore, one could expect that recrystallization still occurs. However, as shown by solid state nuclear magnetic resonance experiments, more open macromolecular structures were developed on these two formulations during the first, and amine addition dominated, steps of the cure reaction[31]. This picture is particularly true for the stoichiomet-
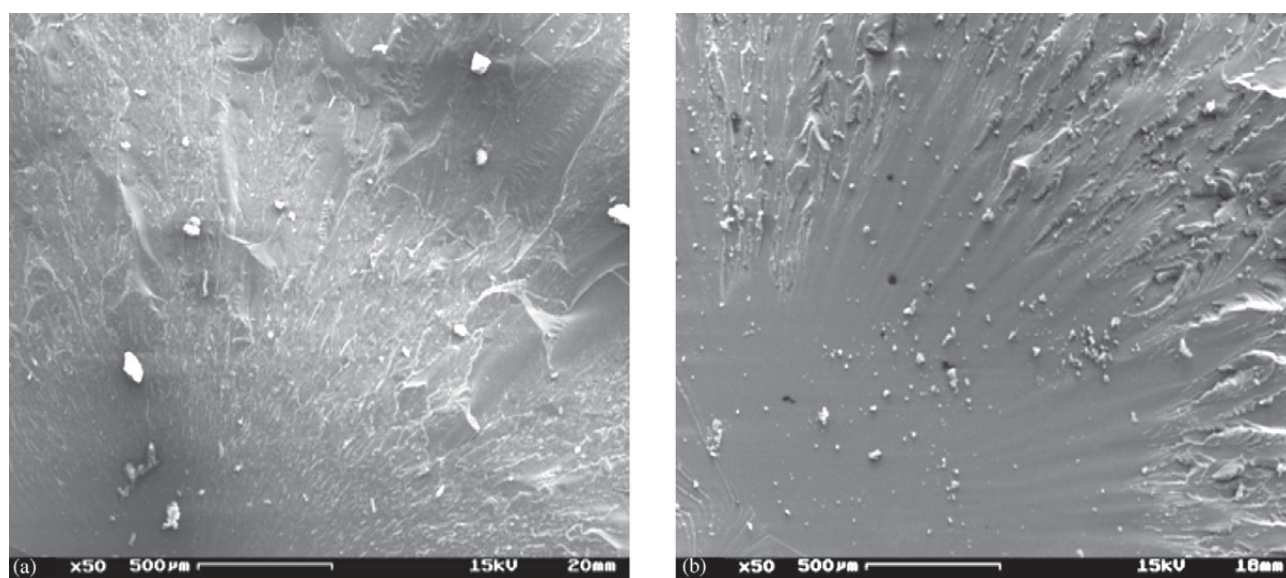
Figure 5. Fracture surface aspects. a) Common fracture surface for the brittle epoxy rich mixtures showing a small and not well defined mirror zone. Micrograph taken from a specimen of the 7 phr formulation; b) The fracture surface of the amine rich formulations dominated by a very large mirror zone. Micrograph from a 21 phr specimen.

ric 13 phr formulation, which structure is significantly less tight than the ones from the epoxy rich formulations[31]. The net result observed is that, although recrystallization could still be occurring in some significant amount, better mechanical properties were obtained. One can note, nevertheless, that the strain at rupture has a huge increase. This behaviour cannot be associated to the embrittlement behavior of recrystallization or be attributed to the completion of the cure process due to homopolimerization. Therefore, plasticization of the material due to absorption of humidity from the surroundings must be accounted for. In fact, it is well known that epoxy resins readily absorb water from the surrounding environment and the absorbed water could increase their toughness[22,24,39,40].

The shape of the tensile curve for the as fabricated 11 and 13 phr formulations was also almost linear to rupture, as schematically shown at Fig. 3a. For the aged specimens a slight deviation from linearity was observed for the 11 phr mixture. For the 13 phr material the tensile curve shows a large deviation from linearity, as shown at Fig. 3c. This aspect and the increase of the mirror like zone observed at the fracture surface, shows that the deformation capacity of the 13 phr formulation is modified by the exposure of the material to ambient room temperature ageing.

For the amine rich mixtures, only the strain values showed relevant changes and, within the experimental error, the 15 phr formulation has its properties virtually unchanged. In fact, it is relevant here to say that the structure

developed for this particular hardener to epoxy ratio was shown to have a higher degree of organisation in respect to heat conduction[41]. From the results shown in Fig. 2, it seems that this macromolecular structure is the more stable also in respect to ageing at room temperature.

The increase observed on the values of the strain at rupture could also be related to plasticization of the epoxy network due to water absorption. On the other hand, since for these amine rich mixtures homopolymerization or recrystallization of unreacted DGEBA will play only a minor effect as their degree of cure is high[18], the stress at rupture is not strongly affected. The minor variations observed in the tensile properties of these mixtures could, therefore, be ascribed only to plasticization effects.

The overall shape of the stress-strain curve of the amine rich formulations showed always deviations from linearity, Figs. 3b and c, both for the as fabricated and the aged materials. On the same way, the fracture surfaces of these formulations are dominated by larger mirror zone, as shown in Fig. 5b. These aspects are also clear evidences that the amine rich formulations have a larger deformability and, the more important, are, within the range of time analysed, more stable than the epoxy rich or stoichiometric formulations. Therefore, one could expect that the good mechanical properties of these amine rich formulations with respect to fracture toughness[19] and impact resistance[21] will also be maintained. Works on these topics are now being carried out at our laboratories.

4. Conclusions

The mechanical performance of the DGEBA/TETA epoxy formulations fabricated with different hardener to epoxy ratios is affected by room temperature ageing. The way the tensile properties vary is, nevertheless, dependent on the hardener to epoxy ratio, because this ratio produces macromolecular networks with very different characteristics.

The epoxy rich formulations with large excess of epoxy monomer have their brittleness increased by the ageing treatment. This behaviour was mainly attributed to recrystallization of the unreacted epoxy monomers, although homopolymerization through epoxy ring opening by OH groups could also play a minor role.

For the stoichiometric hardener to epoxy ratio, and for the 11 phr formulation where the excess of epoxy monomer is not so high, the macromolecular structure developed at the first amine addition dominated reaction steps dominates the mechanical performance. This different behaviour is a direct consequence of the more open macromolecular structure of these formulations, in their as fabricated condition. The sharp increase observed for the deformability of these formulations, was attributed to plasticization due to humidity absorption from the surroundings.

The performance of the amine rich mixtures under room temperature ageing was very promising, because they showed to be much more stable with respect to the tensile properties and only their deformability was significantly enhanced. The increase of the toughness of these amine rich mixtures was also attributed to plasticization.

Acknowledgments

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