A Study Mechanical Properties of Epoxy Resin Cured at Constant Curing Time and Temperature with Different Hardeners

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Abstract

In this study, a low molecular weight epoxy resin diglycidyl ether of bisphenol A (DGEBA) is cured isothermally with an aliphatic and aromatic amine hardeners separately. (1) Triethylentetramine (TETA), (2) Diamino diphenylmethane (DDM). The samples were prepared for different hardener/resin ratios, (under stoichiometry, stoichiometry and above stoichiometry).

The mechanical Properties impact strength, tensile strength, hardness, flexural strength, compression strength and bending strength of an epoxy system has been investigated in this work. For DGEBA/TETA system the tests were done on four hardener/resin ratios (10, 13, 15 and 20) phr and for DGEBA/DDM system the hardener/resin ratios were four also; (24, 27, 30 and 34) phr. The results showed that the above stoichiometry ratio formulation (15 phr for DGEBA/TETA system and 30 phr for DGEBA/DDM system) gave the best mechanical properties, while the DGEBA/DDM system showed better mechanical properties than the DGEBA/TETA system.

Keywords: hardener, epoxy resin, curing, mechanical properties.

Introduction

In thermosetting polymers, the liquid resin is converted into a hard rigid solid by chemical cross-linking which leads to the formation of a tightly bound, three-dimensional network. The mechanical properties depend on the
molecular units making up the network and between cross-links and the length density of cross-links. [1, 2, 3]

There are different types of amine curing agents: 1) aliphatic like Triethelentetramine (TETA), 2) cycloaliphatic, 3) aromatic like (DDM), 4) polyamine adduct, etc. Numerous grades of epoxy resins and curing agents are formulated for a wide variety of applications. [4]

During cure of aliphatic amine each primary aliphatic amine reacts with an epoxy group of DGEBA, via ring opening, to form a CH₂-NH bond and a pendant hydroxyl group, the presence of which is known to accelerate subsequent ring opening reactions [5]. The resulting secondary amines react in a similar manner with remaining epoxy rings to crosslink the polymer chains, though at a slower rate.

In the aromatic amines: the amine group is separated by rigid benzene rings rather than flexible chains of molecules as in the aliphatic amines. Less reactive than aliphatic amines, require higher temperature (150-160 °C), and longer reaction times than aliphatic amines. The stoichiometric relationship between curing agents and resins has a great effect on the physical and the mechanical properties of the epoxy resin [6, 7].

Previous Works

D’Almeida and Monteiro [8] investigated the role of the resin matrix/hardener ratio on the mechanical properties of low volume fraction epoxy composites. The mechanical properties of the matrix where modified by varying the amount of hardener. Landingham et. al. [9] studied the changes in microstructure and mechanical properties as a function of epoxy-amine stoichiometry. The epoxy-amine system studied [DGEBA/Cycloaliphatic diamine bis (para-amino cyclohexyl) methane] exhibits a two-phase structure consisting of a hard microgel phase and a dispersed phase of soft, unreacted and/or partially reacted material. The fracture toughness at room temperature increases with increasing amine content. Changes in modulus values at 30°C with stoichiometry are explained by considering the effective aspect ratio of the polymer structure in the determination of sample rigidity.

D’Almeida et. al. [10] investigated 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. 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. The amine rich mixtures have the more stable structures.

Monteiro et. al. [11] investigated through mechanical tests and scanning electron microscopy observation epoxy matrix composites, with different phr (parts of hardener per hundred of resin), reinforced with 10, 20 and 30 wt.% diamond particles. The results have shown that the phr 17
epoxy; which has the highest tensile strength, is significantly stronger than the stoichiometric phr 13. Moreover, the strength of the composite is decreased with the amount of incorporated diamond.

Liu et. al. [12] studied the effects of curing agents, curing temperature, epoxy/ epoxidized soybean oil (ESO) ratio, and fiber loading on mechanical properties of fiber-reinforced epoxidized soybean oil (ESO)/epoxy resin composites. The curing agents that have been used are JeffamineD-230(polyoxypropylenediamine), Jeffamine EDR-148 (triethyleneglycoldiamine), Jeffamine T-40 (polyoxypropylenetriamine ), triethylenetetramine (TETA) and diethylenetriamine(DETA). The flexural strength and the flexural modulus for the Jeffamine curing agents was in the following order EDR-148 > T-403 > D230. By comparison of triethylenetetramine (TETA) and diethylenetriamine (DETA) to Jeffamine curing agents, TETA and DETA curing agents provide composites with better mechanical properties.

The aim of this paper is to study the mechanical properties of the DGEBA/TETA system and the DGEBA/DDM system of different hardener/resin ratios and their effect on the mechanical properties of the epoxy resin system, finding the best hardener/resin ratio formulation and the best epoxy resin system.

**Experiments work**

**The Materials**

The materials used was DGEBA-Epoxy resin and was cured using two types of hardeners, aliphatic amines which was Triethelenetetramine (TETA) and aromatic amine which was 4,4’-Diamino diphenylmethane (DDM). Samples were prepared from these materials and they were tested using the mechanical tests instruments.

**Epoxy Resin**

Epikote 828 from Shell Co. was used as epoxy resin. Epikote 828 is an unmodified liquid bisphenol A – epichlorohydrin epoxide resin of medium viscosity. Combining reasonable ease of handling with high chemical resistance and mechanical performance after cure, Epikote 828 is the standard liquid resin in many applications.

**The Hardeners**

The hardeners (curing agent) used in the experimental work was:

1. Araldite HY 951 (Triethelentetramine TETA) from Ciba Company, which is a liquid of law viscosity of an aliphatic amine basis.
2. 4, 4’-Diaminodiphenylmetane with Product No. 32950 from Fluka AG Company. It’s a solid state material of an aromatic amine basis.

The epoxy resin and the hardener were mixed together in different hardener/resin ratios. The ratio selected was depending on the stoichiometry of the epoxy resin system. The epoxy resin Epikote 828 (DGEBA) and the aromatic amine hardener 4, 4’-Diaminodiphenylmethane (DDM) were prepared in four hardener/resin ratios:

1. 24 phr (Under stoichiometry).
2. 27 phr (Stoichiometry).
3. 30 phr (Above stoichiometry).
4. 34 phr (Above stoichiometry).
These ratios were calculated based on the equivalent weight of the DGEBA and DDM used to prepare samples in order to study the effect of changing the hardener/resin ratio on the mechanical properties through applying the mechanical tests on the DDM/DGEBA resin samples’ specimens. Three test samples from each formulation were tested and the average values were reported. The hardener 4, 4’-Diaminodiphenylmethane DDM is solid at the room temperature so it must be melted in order to react with the DGEBA epoxy resin. The formulations are prepared by mixing the DGEBA in the appropriate ratio with DDM and then they were heated on a hot plate up to the DDM melting temperature (90°C), for approximately 10 minutes. The mixture was poured into the mold and was cured at 90°C for 1.5hr then post cured at 150°C for 1hr.

The DGEBA epoxy resin and the hardener HY 951 TETA were mixed in four hardener/resin ratios:
1. 10 phr (Under stoichiometry).
2. 13 phr (Stoichiometry).
3. 15 phr (Above stoichiometry).
4. 20 phr (Above stoichiometry).

These ratios were based on the equivalent weight of the DGEBA epoxy resin and the hardener TETA. Samples’ specimens were prepared in the above four ratios and they were subjected to the mechanical properties tests. Three test samples from each formulation were tested and the average values were reported.

The DGEBA epoxy resin and the hardener TETA were mixed together at the room temperature; the mixing was slowly using a disposable stirrer; to avoid making air bubbles. The mixing was carried out for about 20 minutes to ensure the homogeneity of the mixture and the two cotenants were blended well together so that the prepared sample have the same concentrations in all its part. Then the mixer was poured into the mold and it was left for 24 hours at room temperature, then it was post cured at 100°C for 1 hour.

The Mold

The mold used to manufacture the composite material is rectangular with the dimensions of 25×15 cm and 5 cm height as shown in Fig. (1). The mold is made from carbon steel.

The mold was prepared for casting the epoxy resin, it was cleaned thoroughly and a mold release wax (Meguiar’s Mirror Glaze No.8 wax) which contains carnauba wax was used as a release agent. It was applied for three times on the mold surface to ensure all the porous of surface are covered well.

Evaluation of samples

The following tests were used to evaluate the prepared samples. The summary of the mechanical tests used in this work are shown in table (1).

Table (1): Shows the summary of tests methods used in this work.

Results and Discussion

The Impact Test Results

Fig. (2) shows the variation of the impact strength of DGEBA/TETA and DGEBA/DDM systems. The epoxy rich formulation 10 phr, shows the lowest impact strength, this is due to the presence of a large number of epoxy rings
A Study Mechanical Properties of Epoxy Resin Cured at Constant Curing Time and Temperature with Different Hardeners

[13], a rigid and tight macromolecular structure is developed, were the only expected mobile group is the dimethylene ether linkage of bisphenol-A, giving way to a rigid and brittle structure [14,15].

The amino rich formulation 13,15&20 phr shows higher impact strength than the epoxy rich formulation 10 phr, this is due to the large amount of amino hydrogen groups thus more epoxy rings would be opened making the material tougher. The amino rich formulation 15 phr shows the highest impact strength of all the hardener/resin ratio formulations, which indicates that this material can absorb more energy before the break. The amino rich formulation 20 phr is showing less impact strength this behavior was associated with the presence of non-reacted points on the hardener molecule which lead to the fracture of the material [14].

For DGEBA/DDM system the amino rich formulation 30 phr shows the highest impact strength, this is due to the fact that the amino addition reaction is dominated and the crosslinking between the resin and the hardener proceed making the material flexible and stable [10]. While the epoxy rich formulation 24 phr shows the lowest impact strength, which indicates the presence of a large amount of epoxy groups which leads to the formation of a brittle and fracture material.

These results are in good agreement with those obtained by d’Almeida and Cella [17].

The DGEBA/DDM system shows higher impact strength than the DGEBA/TETA system, this is attributed to the aliphatic amines which include TETA is less stable than the aromatic amines (DDM). The (DDM) contains benzene rings which has a low potential energy making the epoxy resin system more stable [16]. In TETA molecule there are two primary amine groups at the ends of the chain and two secondary amine groups in TETA molecule. The DDM has two amine groups located on primary carbon atoms at the ends of an aliphatic polyamine chain in DDM molecule. The primary amine groups are much reactive than the secondary amine groups so that the DGEBA/DDM would show higher impact resistance than the DGEBA/TETA system [5].

### Tensile Test Results

#### Effect On The Elastic Modulus

Fig. (3) shows the elastic modulus of the DGEBA/TETA and DGEBA/DDM systems. For DGEBA/TETA system, The amino rich formulation 15 phr shows the higher elastic modulus, which means that the higher the hardener ratio in the epoxy resin the higher the Young’s modulus of it. While the stoichiometric formulation 13 phr, shows a lower elastic modulus that’s
due to the presence of a larger amount of epoxy monomers in the stoichiometric formulation which in turn leads to the epoxy ring opening reaction by the hydroxyls groups. The amino rich formulation 20 phr is showing a Young’s modulus less than the amino rich formulation 15 phr, that’s due to the presence of non-reacted hardener molecules [5]. For the 10 phr epoxy rich formulation where the epoxy ring could be opened by the hydroxyls groups leading to the formation of ether group and also homopolymerization plays a role in the formation of this material, the material is brittle and tight as observed [5].

For DGEBA/DDM system, the Young’s modulus values varied from the epoxy rich formulation to the amino rich formulation, as shown in Fig. (3) the above stoichiometric ratio 30 phr gives the highest Young’s modulus which means that it deforms linearly until the failure, giving way to the material chains to be stretched and slide on each other to the point of breaking, where the amine structure in the epoxy resin is dominated. The amino rich formulation 34 phr is showing less Young’s modulus than the amino rich formulation 30 phr, that’s due to the presence of the non-reacted hardener molecules which makes the material brittle. For the under stoichiometric formulation 24 phr the presence of excess epoxy monomer making the reaction proceed in the direction of epoxy ring reaction with hydroxyls groups introducing the ether group which is less stable than the carbon-amine nitrogen linkage so the material would be brittle and break without yielding [2,11]. For the stoichiometric formulation 27 phr the Young’s modulus is higher than that for the epoxy rich formulation 24 phr , this is due to the amino addition reaction in which it dominates the curing process rather than the homopolymerization or the epoxy ring opening by the hydroxyls groups making the material more rigid and tougher. These results agree well with the results obtained by Pandini et. al [18] and Lee [19] where they found that the Young’s modulus increase with the increase of the hardener/resin ratio.

The Young’s modulus for the DGEBA/DDM system is higher than that for the DGEBA/TETA system; this is due to the aromatic structure in the backbone which imparts better rigidity to the epoxy resin system making the material more stable and showing higher resistance to the pulling load [20].

**Effect on The Ultimate Tensile Strength**

Fig. (4) shows the relation between the ultimate tensile strength (UTS) and the hardener content (phr) for DGEBA/TETA and DGEBA/DDM systems.

For DGEBA/TETA system, the ultimate tensile strength increased with increasing the hardener content where the amino rich formulation 15 & 20 phr exhibits the higher stress at break. The higher degree of cross-linking makes the material strong and rigid in which it performs a ductile behavior in comparison with the epoxy rich formulation 10 phr that break in a brittle manner due to the presence of ether groups and homopolymerization, so the 10
phr formulation needs a lower strength to be broken than the amino rich formulation 15 and 20 phr. The stoichiometric formulation 13 phr shows a better resistance to the pulling load than the epoxy rich formulation but still 15 phr is the best [10]. While the above stoichiometry formulation 20 phr is showing less resistance to the pulling load, there is a fairly amount of non reacted hardener molecules making the material less stable.

For the DGEBA/DDM system, the above stoichiometric formulations show high ultimate tensile strength especially the 30 phr formulation due to the amino addition reaction which develops a three dimensional network [21], while the 34 phr is showing less ultimate tensile strength than the 30 phr formulation, that’s due to the presence of non reacted hardener molecules. The stoichiometric formulation 27 phr needs higher strength to be broken than the 24 phr which reveal the poor cross-linking between the DGEBA resin and the hardener DDM.

The tensile strength for the DGEBA/DDM system is higher than that for the DGEBA/TETA system, due to the aromatic structure of the DDM hardener as discussed before [16].

These results are in good agreement with the results obtained by Sulaiman et. al. [22] and Rao [23], who found that the tensile strength increased with increasing the hardener content.

**Effect On The Elongation at break**

Fig. (5) shows the elongation of DGEBA/TETA and DGEBA/DDM systems for different hardener content.

For the DGEBA/TETA system, the above stoichiometry formulations 15 phr is showing the highest elongation, that’s due to the carbon- amine nitrogen linkage which imparts better flexibility to the material thus the chains are stretched to a high extent before it breaks. The under stoichiometry formulation 10 phr is showing the lower elongation, where the ether groups and the homopolymerization reaction result making the material brittle and less flexible than the other formulations. The stoichiometric formulation 20 phr is showing less elongation than the 15 phr, that’s due to the non reacted hardener molecules which makes the material brittle [18].

For the DGEBA/DDM system, the presence of a high amount of the hardener DDM in the 30 phr enhance the material ductility so that it shows a high elongation before the failure. The 27 phr is showing higher elongation than the 24 phr which imply that the larger amount of the hardener DDM give the superiority to the epoxy ring opening by the amino-hydrogen groups rather than the epoxy ring opening by the hydroxyl groups, in which it gives the material a higher degree of cross-linking [20], while the 34 phr shows less elongation than the 30 phr formulation, that’s
indicated the presence of non-reacted molecules, which it makes the material less flexible and brittle [22].

The DGEBA/DDM system, in general, exhibits higher elongation than the DGEBA/TETA system, that’s due to the aromatic structure of the DDM hardener [16].

The results obtained here are in good agreement with the results obtained by Tricca [24] where he found that the elongation of the epoxy resin system increased with increasing the hardener/resin ratio.

The Hardness Test Results

Fig. (6) Shows the variation of hardness values with the different hardness/resin ratios for DGEBA/TETA and DGEBA/DDM systems.

For the DGEBA/TETA system the hardness values for the four hardener/resin ratios 10, 13, 15 & 20 phr indicate that the amino rich formulations 15 shows the highest values that’s due to the amino addition reaction which dominates the cross-linking process leading to the formation of a stronger material which exhibits better hardness. The formation of the three dimensional network and the high degree of cross-linking [25,26]. Fig.(6) shows that the 10 phr exhibits the lower hardness, where the epoxy ring is opened by the hydroxyl group (-OH) leading to the formation of ether group(R-CH₂-O-CH₂), [22]. These results are in good agreement with the results obtained by Sulaiman et. al. [22].

For the DGEBA/DDM system, the 30 phr shows the highest hardness that indicates the higher degree of crosslinking making the material more flexible and needs higher force to be penetrated. The lower hardness observed at the 24 phr, the more brittle the material become and easy to be scratched.

The DGEBA/DDM system shows higher hardness shore D value than that for the DGEBA/TETA system. The presence of the benzene in the DDM curing agent provides the DGEBA/DDM system with better resistance to the penetration load than the DGEBA/TETA system (27).

Flexural Strength Test Results

Fig. (7) shows the flexural strength of DGEBA/TETA system and DGEBA/DDM system.

The DGEBA/TETA system has the highest flexural strength at the hardener/resin ratio of 15 phr, which indicates the higher degree of crosslinking. It was observed that the 10 phr has the lowest flexural strength values; this is due to the large amount of epoxy groups which leads to the brittleness of the materials through the reaction with the hydroxyl groups or with each other through the homopolymerization higher flexural strength than [14,28]. While the 13 phr seems to higher flexural strength than 10 phr; that’s because more epoxy rings has been opened by the amino addition reaction which makes the material more stable and flexible, but the 20 phr, on the other hand exhibits a lower flexural strength than the 15 phr formulation, which could be related to the non reacted hardener molecules making the material less flexible and brittle [22].
For the DGEBA/DDM system, the 24 phr shows the lowest flexural strength, in which it bends and breaks under a small load indicating the brittleness of the material and the weak linkages between the hardener and the resin [5, 29]. The 27 phr; shows better resistance to the flexing load where the specimen required higher strength to be bended and finally to be broken. The 30 phr shows the best result, which indicates the high degree of crosslinking among all the formulations where the carbon-amine nitrogen linkage gives the material more rigidity and toughness than the others so that the chains would be flexed and withstand the force that tends to break it through bending it. Also the 34 phr shows lower flexural strength than the 27 phr formulation, where a fairly amount of hardener molecules still without reacting, so it will lead to the fracture of the material.

When a comparison is made between the DGEBA/TETA system and DGEBA/DDM system based on their flexural strengths, the results show that the DGEBA/DDM system formulations have higher values than those the aliphatic ones DGEBA/TETA system formulations, due to the aromatic structure of the DDM hardener as discussed before [30,31].

The results obtained here are in good agreement with those obtained by Liu et. al. [12] and Kamlesh et. al. [20], where they found that the type of the curing agent has a direct effect on the flexural strength and by using different types of curing agents.

The Compression Test Results

Fig. (8) Shows the compression strength for both the DGEBA/TETA and the DGEBA/DDM systems with different hardener/resin ratios.

For the DGEBA/TETA system the compression strength for the 15 phr is higher than the 10 phr. the failure is because of compression stresses and shear stresses. It was found that it is probable that the failure will occur in the epoxy resin material by the effect of compressive stresses, which will lead to the occurrence of buckling phenomenon in the material [32]. Where the presence of a large amount of amino groups lead to the formation of stronger material that struggles against the compressive load and inhibits the buckling. The 13 phr also demands higher compressive strength than the 10 phr, that’s due to the formation of three dimensional network and the strong chains making the material hard and tough. The 20 phr is showing less resistance to the compressive load, which indicates the brittleness of the material and that could be due to the non reacted hardener molecules [13].

For the DGEBA/DDM system, the compressive strength for the 30 and 34 phr is higher than the 24 phr, where the excess amount of epoxy groups leads to the formation of the ether groups and the homopolymerization, making the material weak and easy to be compressed. These results are in good agreement with those obtained by d’Almeida [13].

The compression strength for the DGEBA/DDM system is higher than that for the DGEBA/TETA
system, that’s due to the aromatic structure of the hardener DDM which makes the epoxy resin system more stable and stronger than the hardener TETA, where its linear structure makes the DGEBA/TETA system less strong and can’t handle a high compressive load [30].

The Bending Test Results:

Fig. (9) represents the Young’s modulus values of the DGEBA/TETA system and the DGEBA/DDM system for different hardener/resin ratios. For the DGEBA/TETA system, the Young’s modulus is increased as the hardener content TETA increased. The 15phr shows the higher elastic modulus value, that’s due to the ductility of the material in which the material is requiring high load to be bend. The 10 phr is showing lower Young’s modulus than the 13 phr, due to lower stiffness where the material is to be bend at a low load. The 20 phr is showing less Young’s modulus than the 15 phr, due to the presence of non reacted hardener molecules[33].

For the DGEBA/DDM system, the 30 and 34 phr and the stoichiometric formulation 27 phr show better results for the Young’s modulus than the 24 phr, that’s due to the higher degree of cross-linking which imparts better rigidity to the material.

The DGEBA/DDM system is showing higher Young’s modulus values than the DGEBA/TETA system, where the aromatic structure of the DDM imparts more stability to the epoxy resin system. Where the aliphatic structure of the TETA and the simple formulation of it makes the epoxy resin system less stable and less flexible, so the elasticity would be lower [27]. These results are in good agreement with the results obtained by Rao (23).

Conclusions

Higher mechanical properties was obtained when (15 phr) ratio of DGEBA/TETA was used among other hardener/resin formulation, when (30 phr) ratio of DGEBA/DDM was used also highest mechanical properties was obtained among the other hardener/resin ratio formulation . The DGEBA/DDM system exhibits a higher mechanical properties than the DGEBA/TETA system.

References


Figure (1): The mold used for casting the sample
A Study on Mechanical Properties of Epoxy Resin Cured at Constant Curing Time and Temperature with Different Hardeners

Figure (2) Impact strength of DGEBA/TETA and DGEBA/DDM systems

Figure (3) Young's modulus vs. hardener/resin ratio for the (DGEBA/TETA) system and the (DGEBA/DDM) system

Figure (4) Ultimate tensile strength vs. hardener/resin ratio
A Study Mechanical Properties of Epoxy Resin Cured at Constant Curing Time and Temperature with Different Hardeners

Figure (6) Hardness shore D value vs. hardener/resin ratio for the (DGEBA/TETA) system and the (DGEBA/DDM) system

Figure (7) Flexural strength vs. hardener/resin ratio for the (DGEBA/TETA) and (DGEBA/DDM) systems
A Study of Mechanical Properties of Epoxy Resin Cured at Constant Curing Time and Temperature with Different Hardeners

Figure (8) Compression strength vs. hardener/resin ratio for the (DGEBA/TETA) system and the (DGEBA/DDM) system

Figure (9) Young's modulus (E) vs. hardener/resin ratio for the (DGEBA/TETA) system and the (DGEBA/DDM) system