# AGEING STUDIES OF DGEBA MODIFIED WITH MIXTURE OF EPOXIDISED CARDANOL AND EPOXIDIED NOVOLAC FROM P-CRESOL

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***ABSTRACT:*** *Diglycidyl ether of Bisphenol A (DGEBA) resins are generally exposed to harsh environment and this leads to aging of resin. In this study, novolacs were prepared from para cresol. The Cresol-formaldehyde ratio in the novolacs was maintained at 1:0.8 for maximum property enhancement. Epoxidised cardanol can be used as a low cost modifier since it is an agro-by product from cashew nut shell liquid. The two component system is prepared by mixing epoxidied novolac from p-cresol and epoxidised cardanol. The mixture was blended with DGEBA and the cured resins were tested for optimum properties. These blends were subjected to ageing studies and the results compared with those of the neat resin. The post-cured samples of the neat DGEBA, DGEBA/p-ECN blend (15 wt %) and DGEBA/EC blend (10 wt%) DGEBA and two component DGEBA blends were aged in a temperature controlled air oven kept at 100 0C for 24, 48, 72, 96 and 120 hours successively. The aged samples were tested for tensile properties, impact strength and water absorption*

***Key Words:*** *DGEBA, Ageing, Resin, Novolac, Cardanol,*

## I. Introduction

Epoxy resins constitute a class of thermosets containing more than one epoxide groups per molecule which are very reactive to many substrates (Collyer AA, 1994). The first, and still the most important, commercial epoxide resins are reaction products of bis-phenol A and epichlorhydrin (Brydson , 1999). DGEBA resins are widely used as a high performance thermosetting material in many industrial and engineering fields (Lee and Neville, 1967;Lubin,1982; Jenish et al 2015). Epoxy resins are generally exposed to harsh environment and this leads to aging of epoxy resin (delor et al 2006, Ravari et al 2012) . Cardanol has the advantages of low cost and renewable supply, since it is an agro-by product [Lubi et al 2000;Mary et al 2006]. Cardanol on reaction with epichlorohydrin under alkaline conditions to synthesise epoxidised cardanol (Unnikrishnan et al 2008, Natrajan et al 2013) . Novolacs can be prepared from Cresol , and formaldehyde (Sandler SR and Karo W, 1992). EPNs can be prepared by glycidylation of novolacs using epichlorohydrin (Unnikrishnan et al 2005, Cherian et al 2006). Being low cost epoxidised cardanol (EC) can be used as a good modifier. By the addition of EC to DGEBA increases the water absorption and improvement in properties are marginal. Additon of a mixture of EC and p-ECN to DGEBA resin not only reduces water absorption it also improves the mechanical properties without much deterioration in thermal properties(Jenish et al 2019). In this study the mixture was blended with DGEBA and the cured resins were tested for optimum properties. These blends were subjected to ageing studies and the results compared with those of the neat resin. The post-cured samples of the neat DGEBA, DGEBA/p-ECN blend (15 wt %) and DGEBA/EC blend (10 wt%) DGEBA two component blends were aged in a temperature controlled air oven kept at 100 0C for 24, 48, 72, 96 and 120 hours successively. The aged samples were tested for tensile properties, impact strength and water absorption

## II Experimental

### 2.1 Materials

Epoxy resin GY 250(WPE 188) and amine hardener HY951 were procured from Petro Araldite Pvt. Ltd. Chennai. p-cresol, (MW=108.14, BP=202$^0$C, 98% assay), formaldehyde (37-41% w/v, $d^{20}$=1.08), sodium hydroxide (M.W= 40, 97% assay) and oxalic acid (M.W=126.07, 99.8% assay) were supplied by Merk, India. Cardanol was recovered from cashew nut shell liquid by distillation.

### 2.2 Blending of DGEBA with Epoxidised phenolic novolacs from p-cresol (p-ECN)

The novolacs were prepared by reacting cresol with formaldehyde in the molar ratio 1:0.8 in presence of oxalic acid catalyst in a 3-necked flask fitted with a mechanical stirrer, water condenser and thermometer (Brydson,1999) 1 mole of the novolac resin (1:0.8) was dissolved in 6 moles of epichlorohydrin and the mixture heated in a boiling water bath. The reaction mixture was stirred continuously for 16 hours while 3 moles of sodium hydroxide in the form of 30 % aqueous solution was added drop wise. The rate of addition was maintained such that the reaction mixture remains at a pH insufficient to colour phenolphthalein (Unnikrishnan et al 2005). It is denoted as p-ECN. DGEBA is mixed with 15 weight % Epoxidised cresol novolac resins prepared from p-cresol and was cured at room temperature by adding 10 weight % of the amine hardener and stirring the mixture. The resin was then poured into appropriate moulds coated with a releasing agent. Curing was done at room temperature for 24 h, followed by post curing at 120°C for 4 hours.

**2.3 Blending of DGEBA with monoglycidyl ether of cardanol**

Cardanol was reacted with ECH under alkaline conditions to give the monoglycidyl ether. In a typical experiment, 10 g of cardanol was heated to 95 $^0$C in a 500-ml round bottomed flask fitted with a mechanical stirrer, thermometer and dropping funnel. The required quantity of ECH (30.4 g, 0.32 mol) was then added drop wise at the above mentioned temperature for 2–3 hr. Then, a stoichiometric amount of sodium hydroxide (4 g /10 ml water) was added drop wise to the reaction mixture, and the temperature was increased to 100 $^0$C and heating continued for 2–3 hr. The product was separated and washed with excess water to remove the by-product sodium chloride and other unreacted materials. The product was obtained with 80–85% yield. **(**.(Natrajan et al. 2013)

It is denoted as EC. DGEBA is mixed with 10 weight % Epoxidised cardanol and was cured at room temperature by adding 10 weight % of the amine hardener and stirring the mixture. The resin was then poured into appropriate moulds coated with a releasing agent. Curing was done at room temperature for 24 h, followed by post curing at 120°C for 4 hours.

**2.4 Modification of DGEBA using a mixture of p-ECN and EC**

Epoxy resin was mixed with 15 wt% of a mixture of p-ECN and EC in 75/25 ratio (EEN) , 10w% hardener was added, stirred and degassed in vacuum. The mixture was poured into Teflon moulds and cured for 24 hrs at room temperature. Post curing was done at 100$^0$C for four hours.

**2.5 Ageing studies on epoxy resin modified by a mixture of p-ECN and EC**

The post-cured samples of the neat DGEBA, DGEBA/p-ECN blend (15 wt %), DGEBA/EC blend (10 wt %) and DGEBA/EEN blend (15 wt%) were aged in a temperature controlled air oven kept at 100 $^0$C for 24, 48, 72, 96 and 120 hours successively. The aged samples were tested for mechanical properties and water absorption

**2.6 Testing of Cast Samples**

The samples after post curing were tested for tensile strength, elongation-at-break, toughness, impact strength and water absorption taking six trials in each case.

## III Results and discussion

### 3.1 Tensile properties

The effect of variation of ageing time with tensile strength is shown in Fig.1. Tensile strength decreases during ageing due to the stiffening and thermal degradation of polymer chains. After ageing for 120 hrs the neat resin shows a reduction of 37% in tensile strength while the reduction is 35% in the case of DGEBA/EC, 28% in DGEBA/p-ECN and 30% in DGEBA/EEN blends.

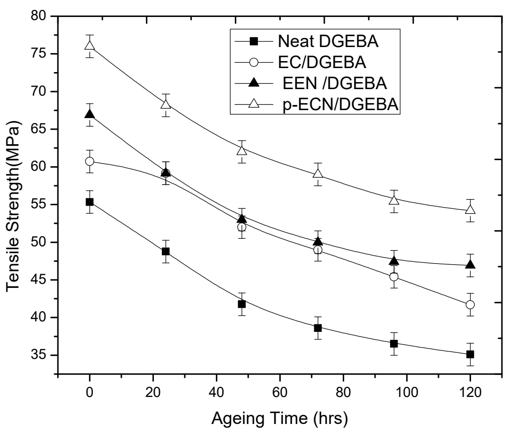


Fig. 1 Tensile strength of modified resin Vs ageing time

Fig.2 depicts the decrease in elongation at break with ageing time, which is attributed to the reduction in flexibility due to increased stiffening of polymer chains. After ageing for 120 hrs the neat resin shows a reduction of 45.5 % in elongation while the reduction is 35% in the case of DGEBA/EC, 23% in DGEBA/p-ECN and 23% in DGEBA/ EEN blends.

The variation in toughness of cured resin (measured as the energy absorbed to break) with ageing time is given in Fig. 3. The energy absorbed (to break) decreases with ageing time mainly due to reduced flexibility of the chains. While the neat resin shows a reduction of 41% in energy absorption at break and DGEBA/EC shows a reduction of 37%, the p-ECN and EEN blends show a reduction of only 27-30%. This suggests the superiority of these p-ECN resins in improving the ageing characteristics.

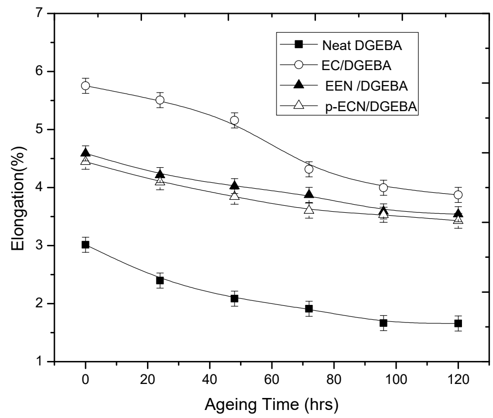


Fig. 2 Elongation at break of modified resin Vs ageing time

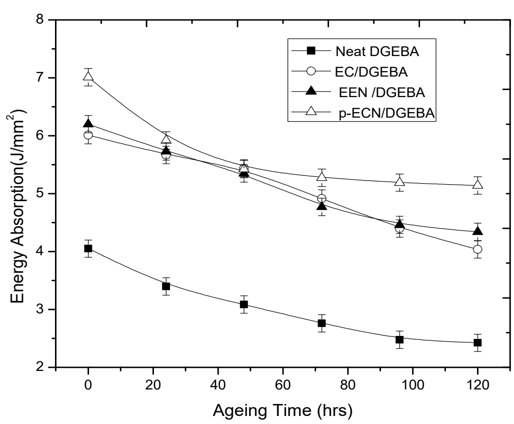


Fig. 3. Energy absorbed (to break) of modified resin Vs ageing time

## 3.2 Impact strength

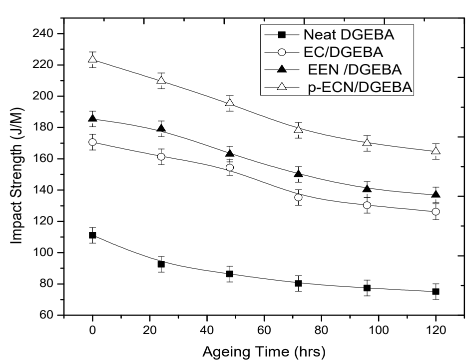


Fig. 4 Impact strength of modified resin Vs ageing time

The variation in impact strength of the modified resin during ageing is given in Fig.4. Impact strength decreases sharply during ageing due to stiffening of the polymer chains. However the extent of decrease is less in the blends (p-ECN 26.5% and EEN 26.4%) compared to the unmodified (33%) and EC modified DGEBA (29.4%) samples. This confirms the ability of p-ECN to improve the ageing properties.

### 3.3 Water absorption

DGEBA/p-ECN and DGEBA/EEN blends show better water resistance (Fig.5) than neat DGEBA resin and EC modified DGEBA after ageing. This is also due to additional cross-linking accompanying the ageing process.

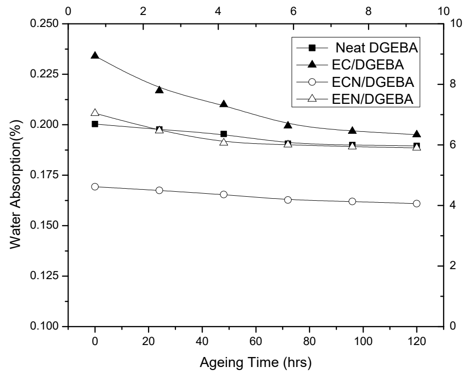


**Fig. 5. Water absorption of modified resin Vs ageing time**

## IV Conclusion

The study reveals that modification using p-ECN and EEN improves the ageing behaviour of the neat resin. Being low cost epoxidised cardanol (EC) can be used as a good modifier. By the addition of EC to DGEBA increases the water absorption and improvement in properties are marginal. Additon of EEN (a mixture of EC and p-ECN) to DGEBA resin not only reduces water absorption it also improves the mechanical properties without much deterioration in thermal properties. So by using EEN we can reduce the cost and improves the mechanical properties and water resistance. The modified resin retains the mechanical properties to a greater extent than the unmodified resin after ageing.

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