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# **Mechanical and Thermal Properties of Epoxy Resin Modified by A Mixture of Epoxidised Para Cresol Novolac and Terminal Epoxy Functional PDMS**

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# Abstract

In the present study, Diglycidyl Ether of Bisphenol A (DGEBA) was modified using a binary modifier system consisting of Epoxidised Para Cresol Novolac (p-ECN) and Terminal Epoxy Functional Polydimethylsiloxane (TEF PDMS). These two modifiers were combined in various ratios and incorporated into the DGEBA resin. The resulting blends were cured and evaluated for their mechanical performance, thermal behavior, and water absorption characteristics. The findings indicate that incorporating a combination of p-ECN and TEF PDMS into DGEBA significantly enhances its mechanical strength, thermal stability, and resistance to water uptake.

Keywords: DGEBA, Resin, Modification, Siloxane, Novolac

# 1. Introduction

Epoxy resins are widely recognized for their outstanding mechanical strength, electrical insulation, and excellent adhesive properties, making them a preferred choice as high-performance thermosetting polymers in a variety of industrial and engineering applications [1-5]. Their utility extends to encapsulating electronic components and serving as molding materials due to their superior thermal and chemical stability. However, conventional epoxy systems, particularly those derived from bisphenol A and epichlorohydrin (commonly referred to as DGEBA), tend to exhibit intrinsic brittleness and limited elongation after curing. These limitations often result in poor resistance to crack initiation and propagation, which restricts their use in structural applications where high toughness is required [6,7]. As such, ongoing research continues to focus on modifying epoxy formulations to enhance toughness without compromising their desirable properties.

Epoxy resins can be modified using a variety of approaches to enhance their performance characteristics. One effective method involves the use of novolac resins, which are epoxidised via the phenolic hydroxyl groups through reaction with epichlorohydrin. In the present study, novolac resins were synthesized using para-cresol, maintaining a cresol-to-formaldehyde molar ratio of 1:0.8 to optimize property enhancement. The resulting novolac resins were subsequently epoxidised and blended with diglycidyl ether of bisphenol A (DGEBA) resin.[8].



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In another method Terminal epoxy functional polydimethylsiloxanes (TEF PDMS) were synthesized via hydrosilylation, involving the reaction between terminal silyl hydride-functional PDMS and allyl glycidyl ether. The incorporation of these functionalized siloxanes into the epoxy matrix significantly enhances the flexibility of the resulting cross-linked network. Additionally, the presence of siloxane segments contributes to improved thermal stability and water resistance of the cured resin systems. These enhancements are attributed to the inherent properties of the Si–O–Si backbone, which offers superior thermal and oxidative stability along with hydrophobicity, making TEF PDMS an effective modifier for epoxy resins[9].

Branching in DGEBA epoxy resin is achieved by the incorporation of multifunctional epoxy systems like EPNs[10,11]. Branching takes place due to the reaction of the hydroxyl groups in the epoxy back bone with the epoxy functional group in EPN [12]. The epoxy groups in both epoxy novolac and epoxy resin are opened up by the same curing agent which triggers the cross-linking process. This study deals with modification of epoxy resin with a two-component system. The two-component system is prepared by mixing two different modifiers in different proportions. The mixtures in different proportions were blended with DGEBA and the cured resins were tested for optimum properties. The mixture of p-ECN (epoxidised para cresol novolac) and) TEF PDMS [Terminal epoxy functional PDMS] is represented as as TPN.

#### 2. Materials and Methods

# Materials

Epoxy resin GY 250 (WPE 188) and amine hardener HY951 were sourced from Petro Araldite Pvt. Ltd., Chennai., Epoxidized p-cresol novolac (p-ECN) (8) TEF PDMS(9) were synthesized in the labouratory.

# Modification of DGEBA Using a Mixture of p-ECN and TEF PDMS

DGEBA was modified using varying weight ratios (0–20 wt%) of p-ECN and TEF PDMS mixtures in proportions of 0/100, 25/75, 50/50, 75/25, and 100/0. The formulations are designated as TEF PDMS, TPN1, TPN2, TPN3, and p-ECN respectively. A 10 wt% hardener was incorporated into each blend. The mixtures were stirred, degassed, and then poured into Teflon molds. Curing was carried out at ambient temperature for 24 hours, followed by post-curing at 100°C for four hours.

# Characterisations

#### Thermal studies

Thermal stability of the neat and modified cured resin samples was assessed using thermo gravimetric analyser (TGA Q50, TA Instruments) over a temperature range from room temperature to 600 °C at a heating rate of 10°C/min. The damping qualities were measured by dynamic mechanical analysis (DMA-Q800, Universal V4.0C TA Instruments) using dual cantilever mode over a temperature range from min and a frequency of 1 Hz.

#### **Mechanical properties**

The samples, after post curing, were tested for tensile strength, modulus and impact strength, taking six trials in each case. The tensile properties were determined on a Schimadzu Autograph Universal Testing Machine (ASTM D 638-89) and Izod impact strength was measured on a Zwick impact tester as per ASTM D 256 specifications.

#### Water Absorption

The water absorption behaviour of the samples was evaluated following the ASTM D570 standard. Initially, specimens were dried in an oven at 80°C for 24 hours, then allowed to cool in a desiccator. Once cooled, the samples were immediately weighed to determine the dry weight. Subsequently, the specimens



were immersed in water maintained at ambient temperature for 24 hours. After immersion, they were removed, gently wiped using a lint-free cloth to eliminate surface moisture, and then reweighed to assess water uptake.

#### **Morphological Analysis**

The morphology of the prepared blends was examined through scanning electron microscopy (SEM). SEM imaging was carried out on the fractured surfaces obtained from tensile testing in order to investigate the dispersion and interfacial characteristics within the blend systems.

#### **3.** Results and Discussions

#### **Tensile Properties**

Tensile strength decreases with increase in concentration of TEF PDMS. This is due to the presence of flexible siloxane segments in the cross linked networks of the epoxy resin blend. Referring to Fig.1, tensile strength values obtained by blending epoxy resin with 5 to 20% modifiers show that a mixture of p-ECN and TEF PDMS considerably improves the tensile properties. The improvement in tensile strength over that of the neat DGEBA is due to a higher degree of cross-linking as well as chain extension. This can also be attributed to some amount of entanglement among the polymer chains. Three component systems show improved properties but they are still less than that of pECN modified DGEBA. Among three components TPN3/DGEBA shows superior properties. TPN3 shows a maximum improvement of 13% in tensile strength.



Fig.1 Tensile strength of modified resin Vs modifier concentration

The effect on elongation at break is shown in Fig.2 Compared to unmodified resin all the blends show an increase in elongation. At 5% concentration of modifier TEF PDMS modified system shows maximum elongation. But after 5%, elongation decreases for TEF PDMS modified DGEBA due to lower compatibility. At 15% concentration of modifier ECN modified sample shows a maximum improvement of 41%. Three component systems show improved elongation than neat resin. In this case TPN-3 enjoys clear superiority over the other three component system. TPN-3 modified DGEBA shows a maximum improvement of 36% in elongation.





Fig. 2 Elongation (at break) of modified resin Vs modifier concentration

Fig. 3 gives the variation of energy absorbed (to break) by the blends of epoxy resin with modifiers. This can be taken as a measure of the toughness. While TEF PDMS/DGEBA shows a maximum improvement of 56% the ECN/DGEBA shows only 30% improvement at 5% loading of the modifier. The increase is due to greater energy dissipation by the soft siloxane segments. At higher concentrations of TEF PDMS energy absorption decreases due to lack of compatibilisation. The maximum improvement in energy absorption by the p-ECN modified DGEBA is 75.5% at 15% p-ECN concentration. The improvement in energy over that of the neat DGEBA is due to the formation of hyper branched network structure. This can also be attributed to some amount of entanglement among the polymer chains. Among the mixtures, TPN-3 modified DGEBA shows maximum improvement in energy. TPN-3/DGEBA shows an improvement of 68.5% in energy absorption.



Fig. 3. Energy absorbed (to break) of modified resin Vs TPN concentration



#### **Impact Strength**



Fig. 4 Impact strength of modified resin Vs modifier concentration

Impact strength values obtained by blending epoxy resin with 5 to 20% modifiers are shown in (Fig.4.). p-ECN modified epoxy resin shows a maximum improvement of 98%. The improvement in impact strength of epoxy novolac modified resins is a direct consequence of compatibility, chain entanglement and enhanced cross-linking. TEF PDMS modified resin shows a maximum improvement of 66%. In the case of three component system increase in concentration of ECN improves the impact strength and TPN3/DGEBA shows superior properties over other three component systems.

#### **Thermal properties**

The TGA values from thermogram (Fig. 5) of the neat resin, TEF PDMS/DGEBA, TEN-3/DGEBA and p-ECN/DGEBA are given in Table 1. There is slight improvement in thermal properties of DGEBA by the addition of modifier resin. Residue values indicate slight improvement in charring properties. TEF PDMS and TPN modified samples shows better properties due to presence of TEF PDMS. The siloxane segments improve thermal stability probably due to better heat dissipation by the siloxane chains, thus reducing the temperature at the epoxy networks.



Fig 5.Thermogram of neat and modified DGEBA

International Journal for Multidisciplinary Research (IJFMR)



# Table 1 TGA characteristics of DGEBA, TEF PDMS/DGEBA ,p ECN/ DGEBA and TPN/DGEBA

Resin	Onset temperature (°C)	Temperature of	Temperature of	Residue
		maximum rate	half loss	(%)
		(°C)	(°C)	
DGEBA	343	364	378	6.68
p-ECN	340	366	380	8.4
TEF	350	369	382	10.43
PDMS/DGEBA				
TPN3 /DGEBA	349	367	381	10.4

#### Dynamic mechanical analysis

The storage modulus values of blends containing the modified as well as neat epoxy are shown in Fig.6. The storage modulus decreases with increase in temperature. At room temperature p-ECN/DGEBA showed a higher value compared to other blends and neat DGEBA due to the cross linking of the epoxide groups of ECN. The decrease in the storage modulus for TEF PDMS/DGEBA and TPN3/DGEBA is due to the reduced crosslink density and plasticization effect of siloxane in the epoxy matrix.



Fig 6 Storage modulus of (a) DGEBA (b) TEF PDMS/DGEB (c) pECN/DGEBA (d) TPN/DGEBA

The tan  $\delta$  (loss factor) values are shown in Fig.7. The shape of the loss spectra can give additional information about the nature of the cross linked networks. The amplitude of the damping peak (tan  $\delta_{max}$ ) becomes lower as the distance between the crosslinks decreases. The tan  $\delta_{max}$  for neat DGEBA decreases on blending with ECN indicating increased crosslink density. The Tg of the epoxy rich phase increased with the addition of ECN. This is due to the increase in crosslink density of the blends on addition of ECN. The tan  $\delta_{max}$  for neat DGEBA increases on blending with siloxane indicating reduced crosslink density. The glass transition temperature Tg corresponding to tan  $\delta$  peak of neat DGEBA decreases when TEF PDMS and TPN3 are incorporated. The lowering of Tg is due to the flexible siloxane segments in the copolymer.





Fig.7 Tan δ relaxations of (a) DEBA (b) pECN/DGEBA and (c) TEF PDMS/ DGEBA (d) TPN3/DGEBA

#### Water absorption

The variation in water absorption is given in Fig. 8. The water absorption can be reduced by adding TEF PDMS and p-ECN. The same trend can be seen in TPN modified samples also. This is possibly due to a greater extent of methylene groups, phenolic groups and hydrophobic siloxane molecues .



Fig. 8. Water absorption of modified resin Vs TPN concentration

#### **Morphological studies**

Scanning electron micrographs of neat DGEBA, p-ECN modified, TEF PDMS modified and TPN modified epoxy resins fractured at low deformation are shown in Fig. 9. The fracture surface of the blend is characterised by a morphology indicating extensive crazing. The Micrograph (a) of the unmodified resin shows typical brittle fracture with pinpoint crazes.

The fracture surface shows furrows and cavitation in the case of terminal epoxy functional PDMS (TEF PDMS/DGEBA) modified epoxy resin, (b). The circular depressions represent the sites of rubber domains. Considerable stress whitening is also observed. Referring to pECN modified sample (c), the



fracture paths have a feathery texture with large breadth. Peaks and parallel fibril structures in pulled up wavy crests indicate the stretching that takes place prior to fracture. Stress whitening characteristic of crazing is also observed. Micrograph (d) representing epoxy/TPN blend is characterised by shallow cavities as well as non-uniform ridges. The holes in the stress-whitened regions presumably result from dilation and rupture of siloxane (TEF PDMS) particles. These features point to improved toughness and load bearing characteristics of modified resin.



Fig. 9 Scanning electron micrographs of the fracture surfaces of a) DGEBA b) DGEBA/TEF PDMS c)DGEBA/pECN d) DGEBA/TEN

# 4. Conclusion

The addition of TEF PDMS can improve the thermal properties and impact properties with slight reduction in tensile properties. p-ECN can improve the mechanical properties without much deterioration in thermal properties. So addition of mixture of p-ECN and TEF PDMS to DGEBA can lead to improvement in mechanical properties, thermal properties and water resistance.

Modification of DGEBA with siloxanes (TEF PDMS) improves the water resistance, impact strength and marginally, the thermal properties with slight reduction in tensile strength. Addition of a mixture of p-ECN and siloxane shows improvement in tensile properties, impact strength, thermal properties and water resistance.

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