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Epoxy Resin Reinforcement via Epoxidized Para-Cresol Novolac and Pendant Epoxy-Functional PDMS: A Study on Mechanical and Thermal Attributes

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Abstract

In the current study, an effort was made to enhance the performance of Diglycidyl Ether of Bisphenol A (DGEBA) epoxy resin through modification with a binary system consisting of Epoxidized Para-Cresol Novolac (p-ECN) and Pendant Epoxy Functional Polydimethylsiloxane (PEF PDMS). The modifiers were combined in various ratios and incorporated into the DGEBA resin. The resulting blends were then cured under controlled conditions. The mechanical properties of the modified DGEBA resin were evaluated through tensile, flexural, and impact tests. The results indicated a significant improvement in mechanical strength compared to the unmodified resin. Thermal behaviour was assessed using Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). Water absorption characteristics were evaluated by immersing the cured blends in water at room temperature for a specified duration. The modified resins demonstrated significantly reduced water uptake, indicating improved resistance to moisture. Overall, the incorporation of a combination of p-ECN and PEF PDMS into DGEBA resin significantly enhances its mechanical strength, thermal stability, and resistance to water uptake. These findings suggest that the binary modifier system is a promising approach for improving the performance of epoxy resins for various industrial applications.

Keywords: DGEBA, Resin, PDMS, Blending, Novolac

1. Introduction

Epoxy resins are highly regarded for their excellent mechanical strength, electrical insulation, and superior adhesive properties, which make them ideal high-performance thermosetting polymers for numerous industrial and engineering applications [1-5]. They are extensively used for encapsulating electronic components and as moulding materials, thanks to their remarkable thermal and chemical stability. However, traditional epoxy systems, especially those based on bisphenol A and epichlorohydrin (commonly known as DGEBA), tend to be inherently brittle and have limited elongation after curing. This brittleness often leads to poor resistance to crack initiation and propagation, restricting their use in structural applications that require high toughness. [6,7] Therefore, research is ongoing to modify epoxy formulations to improve toughness without sacrificing their desirable properties.

There are several approaches to modifying epoxy resins to enhance their performance. One effective method is the use of novolac resins, which are epoxidized through the reaction of phenolic hydroxyl groups

with epichlorohydrin. Novolac resins were synthesized using para-cresol, with a cresol-to-formaldehyde molar ratio of 1:0.8 to optimize property enhancement. These epoxidized novolac resins were then blended with diglycidyl ether of bisphenol A (DGEBA) resin [8].

Another method involves the synthesis of Pendant epoxy functional polydimethylsiloxanes (PEF PDMS) via hydrosilylation, which is the reaction between pendant silyl hydride-functional PDMS and allyl glycidyl ether. Incorporating these functionalized siloxanes into the epoxy matrix significantly increases the flexibility of the resulting cross-linked network. The presence of siloxane segments also enhances the thermal stability and water resistance of the cured resin systems. These improvements are due to the inherent properties of the Si–O–Si backbone, which provides superior thermal and oxidative stability as well as hydrophobicity, making PEF PDMS an effective modifier for epoxy resins.[9].

Branching in DGEBA epoxy resin can be achieved by incorporating multifunctional epoxy systems like epoxy novolac resins (EPNs)[10-12]. Branching occurs due to the reaction between the hydroxyl groups in the epoxy backbone and the epoxy functional groups in EPNs. The epoxy groups in both the epoxy novolac and the epoxy resin are opened up by the same curing agent, which initiates the cross-linking process[13].

This study focuses on modifying epoxy resin with a two-component system. The two-component system is prepared by mixing two different modifiers in various proportions. These mixtures are then blended with DGEBA, and the cured resins are tested to determine the optimal properties. The mixture of epoxidized para-cresol novolac (p-ECN) and pendant epoxy functional PDMS (PEF PDMS) is referred to as PEN.

2. Materials and Method

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) PEF PDMS(9) were synthesized in the labouratory.

Modification of DGEBA using a mixture of p-ECN and pendant epoxy functional PDMS (PEF PDMS50)

Epoxy resin was mixed with 0-20 wt% of a mixture of p-ECN and PEF PDMS50 in different proportions viz. 0/100, 25/75, 50/50, 75/25 and 100/0 (designated as PEF PDMS50, PEN1, PEN2, PEN3 and p-ECN). 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 100^0C for four hours.

Characterisations

Thermal Studies

The thermal stability of both the unmodified and modified cured resin samples was evaluated using a thermogravimetric analyzer (TGA Q50, TA Instruments). The analysis was conducted over a temperature range from ambient conditions to 600°C at a heating rate of 10°C per minute. The damping characteristics were assessed via dynamic mechanical analysis (DMA-Q800, Universal V4.0C TA Instruments) in dual cantilever mode, with a temperature range from ambient to 100°C and a frequency of 1 Hz.

Mechanical Properties

The mechanical properties of the samples were tested after post-curing. Tensile strength, modulus, and impact strength were determined, with six replicates for each property. Tensile properties were measured using a Shimadzu Autograph Universal Testing Machine (ASTM D 638-89), while Izod impact strength was evaluated using a Zwick impact tester in accordance with ASTM D 256 standards.

Water Absorption

The water absorption behavior of the samples was examined according to the ASTM D570 standard. Specimens were initially dried in an oven at 80°C for 24 hours and then cooled in a desiccator. The dry weight of the samples was recorded immediately after cooling. The specimens were subsequently immersed in water at room temperature for 24 hours. After immersion, the samples were removed, gently wiped with a lint-free cloth to remove surface moisture, and reweighed to determine the amount of water absorbed.

Morphological Analysis

The morphology of the prepared blends was analyzed using scanning electron microscopy (SEM). SEM imaging was performed on the fractured surfaces obtained from tensile testing to investigate the dispersion and interfacial interactions within the blend systems.

3. Result and Discussion

Tensile properties

As illustrated in Figure. 1, the tensile strength values achieved by incorporating 5 to 20% modifiers into the epoxy resin reveal that the inclusion of p-ECN results in a maximum enhancement of 36%. Conversely, the addition of PEF PDMS50 leads to a decline in tensile properties. This reduction can be attributed to the presence of the flexible PEF PDMS50 segments within the cross-linked networks of the epoxy resin blend. However, by employing a combination of p-ECN and PEF PDMS50 (referred to as PEN), the tensile properties can be significantly improved. Among the various three-component systems, PEN-3 demonstrates clear superiority.

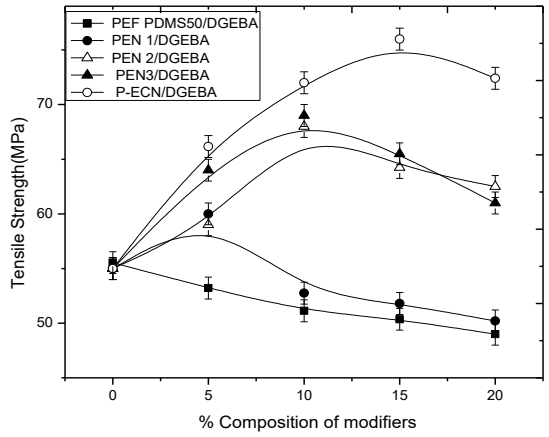

Figure. 1. Tensile strength of modified resin Vs TPN concentration

Figure 2 illustrates the impact on elongation at break. When compared to the unmodified resin, all the blends exhibit enhanced elongation. The ECN modification achieves a peak improvement of 41%, while the PEF PDMS modification results in a 23% enhancement. The PEN-1 modification shows a 25% improvement, PEN-2 modification demonstrates a 27% enhancement, and PEN-3 modification attains a 37% improvement. It is evident from these results that PEN-3 outperforms the other three-component systems.

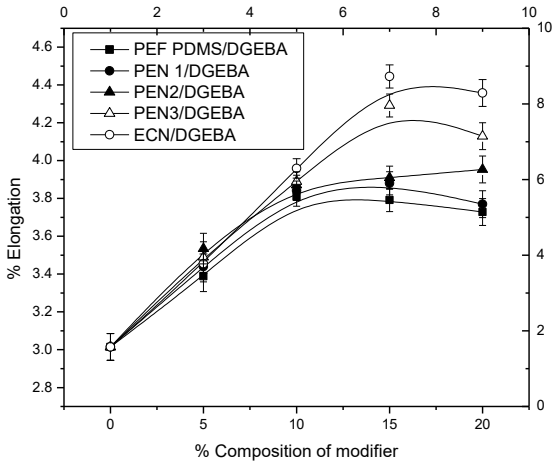

Figure. 2 Elongation (at break) of modified resin Vs modifier concentration

Figure 3 depicts the variation in energy absorbed by the blends of epoxy resin with various modifiers. At a 10% loading of the modifier, the PEF PDMS50/DGEBA blend exhibits a maximum improvement of 63%, while the ECN/DGEBA blend shows an improvement of 57%. This increase in energy absorption is attributed to the greater energy dissipation by the soft siloxane segments in the PEF PDMS50 blend. However, at higher concentrations of PEF PDMS, energy absorption decreases due to insufficient compatibilization between the components.

The p-ECN modified DGEBA achieves a maximum improvement in energy absorption of 75.5% at a 15% p-ECN concentration. This enhancement is due to the formation of a hyper-branched network structure, which also results from some degree of entanglement among the polymer chains.

Among the various mixtures, the PEN-3 modified DGEBA blend demonstrates superior properties. The PEN-3/DGEBA blend shows an improvement of 67% in energy absorption, indicating its effectiveness in enhancing the mechanical performance of the epoxy resin.

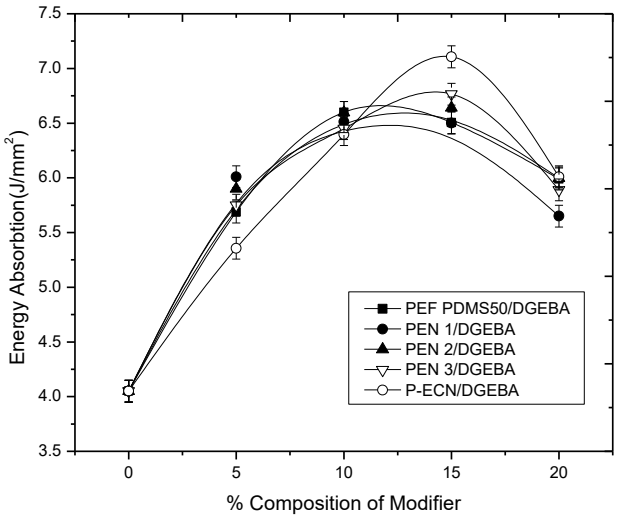

Figure. 3. Energy absorbed (to break) of modified resin Vs PEN concentration

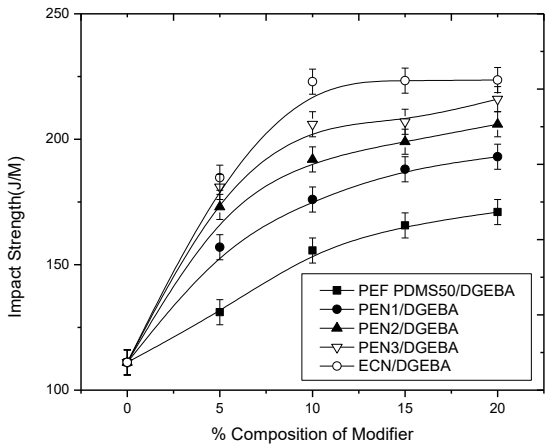

Fig. 4 Impact strength of modified resin Vs modifier concentration

Figure 4 illustrates the impact strength values obtained by blending epoxy resin with modifiers ranging from 5 to 20%. The p-ECN modified epoxy resin demonstrates a maximum improvement of 98%. This significant enhancement in impact strength is attributed to the compatibility between the components, chain entanglement, and enhanced cross-linking.

The PEF PDMS modified resin shows a maximum improvement of 44%. When considering three-component systems, the PEN-3/DGEBA blend exhibits superior properties compared to other similar systems. Specifically, the PEN-3 modified DGEBA shows an improvement of 89% over the neat DGEBA.

Thermal properties

The TGA values of the neat resin, PEF PDMS/DGEBA, PEN-3/DGEBA and p-ECN/DGEBA are given in the table (Table 1)

Table 1 TGA characteristics of DGEBA, PEF PDMS/DGEBA, pECN/ DGEBA and PEN3 /DGEBA

Resin	Onset temperature (°C)	Temperature of maximum rate (°C)	Temperature of half loss (°C)	Residue (%)
DGEBA	343	364	378	6.68
p-ECN/DGEBA	340	366	380	8.4
PEF PDMS 50/DGEBA	357.28	376.79	394.36	15.71
PEN /DGEBA	354	371	388	14.6

In contrast to neat DGEBA and ECN/DGEBA, samples modified with PEF PDMS and PEN exhibit enhanced thermal properties, largely due to the presence of siloxane segments in PEF PDMS. The superior heat resistance of silanes likely contributes to the improved thermal stability. Additionally, incorporating a higher proportion of PEF PDMS segments into the cured epoxy networks results in increased thermal stability and residual weight.

Dynamic mechanical analysis

Figure 5 presents the storage modulus values for blends of modified and neat epoxy resins. As the temperature rises, the storage modulus diminishes. At ambient conditions, the p-ECN/DGEBA blend exhibits a higher storage modulus compared to other blends and neat DGEBA, attributable to the cross-linking of the epoxide groups in ECN. The decline in storage modulus observed for PEF PDMS/DGEBA and PEN3/DGEBA blends is due to the decreased cross-link density and the plasticizing effect of siloxane within the epoxy matrix.

Figure 6 displays the tan δ (loss factor) values. The morphology of the loss spectra offers supplementary insights into the characteristics of the cross-linked networks. As the distance between cross-links shortens, the amplitude of the damping peak (tan δ max) diminishes. For neat DGEBA, blending with ECN results in a lower tan δ max, signifying heightened cross-link density. The glass transition temperature (Tg) of the epoxy-rich phase escalates with the incorporation of ECN, stemming from the augmented cross-link density in the blends. Conversely, blending neat DGEBA with siloxane leads to an elevated tan δ max, denoting reduced cross-link density. The Tg corresponding to the tan δ peak of neat DGEBA is reduced when PEF PDMS50 and PEN3 are introduced. This Tg reduction is attributed to the flexible siloxane segments in the copolymer.

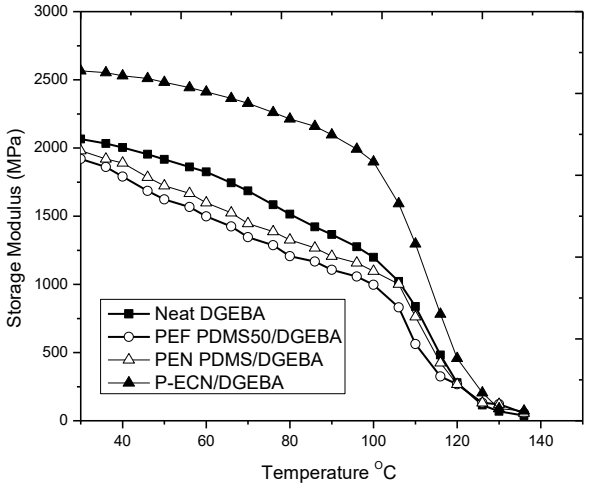

Figure 5 Storage modulus of (a) DGEBA (b) PEF PDMS/DGEBA c)pECN/ DGEBA (d) PEN/DGEBA

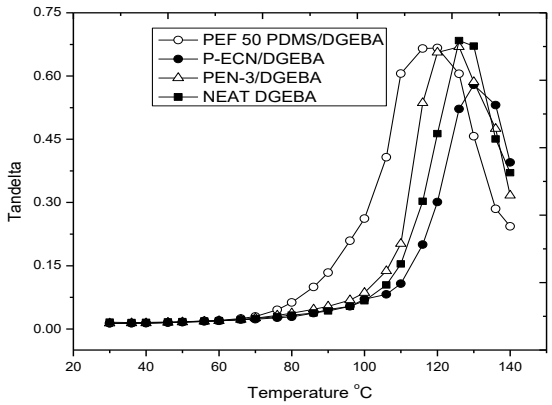

Figure. 6 Tan δ relaxations of (a) DEBA (b) p-ECN/DGEBA and (c) PEF PDMS/ DGEBA (d) PEN /DGEBA

Water absorption

Figure 7 illustrates the variation in water absorption. The incorporation of PEF PDMS and p-ECN effectively reduces water absorption. A similar trend is observed in samples modified with PEN. This reduction is likely attributed to the increased presence of methylene groups, phenolic groups, and hydrophobic siloxane molecules.

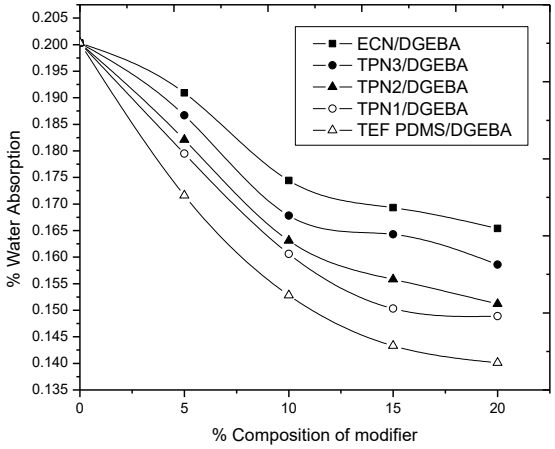

Fig. 7. Water absorption of modified resin Vs TPN concentration

Morphological studies

Figure 8 displays scanning electron micrographs of fractured surfaces at low deformation for neat DGEBA, p-ECN modified, PEF PDMS modified, and PEN modified epoxy resins. The fracture surface morphology reveals extensive crazing. In the unmodified resin (micrograph a), typical brittle fracture with pinpoint crazes is evident. For the PEF PDMS/DGEBA blend (micrograph b), the fracture surface exhibits furrows and cavitation, with circular depressions indicating rubber domain sites and significant stress whitening.

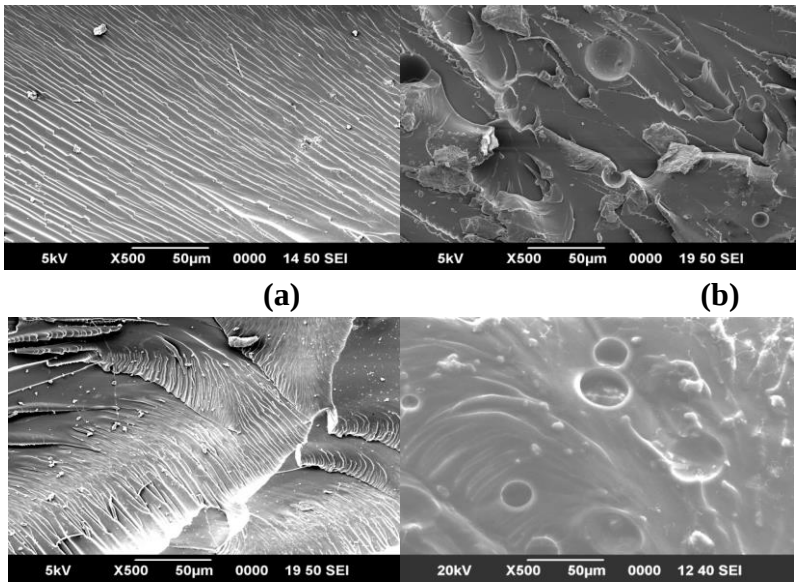

Figure. 8 Scanning electron micrographs of the fracture surfaces of a) DGEBA b) DGEBA/PEF PDMS50 c)DGEBA/pECN d) DGEBA/PEN

The p-ECN modified epoxy (micrograph c) shows fracture paths with a feathery texture and broad width. The presence of peaks and parallel fibril structures in wavy crests suggests stretching before fracture, along with stress whitening typical of crazing. The epoxy/PEN blend (micrograph d) features shallow cavities and non-uniform ridges. Holes in the stress-whitened regions likely result from the dilation and rupture of siloxane particles. These characteristics indicate enhanced toughness and load-bearing capabilities in the modified resins.

4. Conclusion

The incorporation of PEF PDMS into neat DGEBA has a modest negative effect on tensile strength, but it significantly enhances the thermal and impact properties of the resin. This improvement is attributed to the flexible nature of the siloxane segments in PEF PDMS, which can absorb and dissipate energy more effectively, thereby increasing the material's resistance to thermal and mechanical stress. Conversely, the addition of p-ECN to DGEBA leads to notable improvements in mechanical properties such as tensile strength and modulus, with only a minimal impact on thermal properties. The cross-linking density and network structure of the resin are enhanced by p-ECN, resulting in a more robust and mechanically stable material. When both modifiers are combined in the form of PEN (a blend of p-ECN and PEF PDMS), the resulting DGEBA resin exhibits a synergistic enhancement in multiple properties. The mechanical properties are significantly improved due to the reinforcing effect of p-ECN, while the thermal stability and impact resistance are bolstered by the presence of PEF PDMS. Additionally, the hydrophobic nature of the siloxane segments in PEF PDMS contributes to improved water resistance, making the modified resin more suitable for applications where moisture exposure is a concern. In summary, the addition of PEN to DGEBA not only enhances the mechanical properties but also improves thermal stability, impact resistance, and water resistance, making it a versatile and high-performance material for various industrial applications.

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