Evaluating the Thermal and Mechanical Properties of Siloxane-Enhanced Epoxy Resins in Adhesive Formulations

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Abstract

This study investigates the impact of siloxane modification on the thermal and mechanical properties of epoxy resins used in adhesive formulations. Siloxane-enhanced epoxy resins were synthesized and characterized to assess improvements in adhesive performance, including thermal stability, mechanical strength, and durability. In this study, highly epoxidized polysiloxanes were synthesized using diglycidyl ether of bisphenol-A (DGEBA). Two different siloxanes were employed: ether-terminated polydimethylsiloxane (PDMS-DGE) and 3-glycidoxypropyl trimethoxysilane (GPTMS). The thermal and mechanical properties of the resulting composites were assessed, and a comparative analysis was conducted. Detailed discussion on the reaction mechanisms is provided. Structural analysis was performed using FT-IR, while thermal properties were evaluated through TGA and DSC. Mechanical properties were assessed using flexural test measurements. Understanding the effects of siloxane modification on epoxy resins will provide insights into developing adhesives with superior thermal and mechanical properties, expanding their applications in various industries.

Keywords: Epoxy resins, siloxanes, adhesives

1. Introduction

Epoxy resins are a class of thermosetting polymers known for their strong bonding capabilities, durability and versatile applications. Epoxy resins are widely utilized in adhesive formulations due to their excellent adhesion, chemical resistance, and mechanical properties [1]. They are widely used in various industries, including automotive, aerospace, electronics, and construction. Epoxy based adhesives are formulated by mixing epoxy resins with hardeners or curing agents to create a durable, high-performance adhesive. Nevertheless, improving their performance for specialized applications—such as high-temperature environments or those subject to significant mechanical stress—continues to be a major research focus. Epoxy adhesives are well-regarded for their exceptional bonding strength and durability, which makes them a preferred choice for demanding applications across various industries [2,3]. However, these resins are typically brittle and exhibit low impact resistance [4-6]. This brittleness often intensifies as thermal stability is enhanced [7]. Consequently, enhancing the toughness of epoxy resins is an urgent priority and efforts have been directed towards enhancing their toughness by incorporating elastomers. The search of epoxy formulations with resistance to high temperatures or moisture for long periods of time has led to the investigation of functional silanes, polysiloxanes, silsesquioxanes, and nanosilicas as possible reinforcers of epoxy resins [8-11].

Polysiloxane is regarded as one of the most effective toughening agents for epoxy resins due to its flexible Si-O-Si backbone, low glass transition temperature, excellent thermal and oxidative stability, as well as its low surface tension and good weather resistance [12,13]. Despite these advantages, pure poly(dimethylsiloxane) (PDMS) has had limited use as a toughening agent because of its poor compatibility with the polar hard segments of epoxy resins [14]. This incompatibility arises largely from the absence of hydrogen bonding, leading to issues with adhesion strength, particularly on polar or untreated surfaces. PDMS adhesives often exhibit lower adhesion strength and may require surface treatments or primers to enhance bonding. Additionally, PDMS can be relatively soft, lacking the mechanical strength necessary for high-load applications, and may deform or lose structural integrity under stress [15,16].

To improve the compatibility of polysiloxane with epoxy matrices, extensive research has been undertaken. Strategies have included using silane coupling agents, introducing polar functionalities into polysiloxanes (such as hydroxyl [17], amino [18], epoxide [19], carboxyl [20] and isocyanate [21] groups), adding block or graft silicone to achieve homogeneous dispersion in the matrix, and chemically incorporating PDMS into the epoxy main chain. Notably, our preliminary studies have shown that introducing a high number of epoxide groups into polysiloxane through hydrolysis and condensation reactions can enhance the compatibility of polysiloxane with epoxy resin. This modification not only improves the dispersion of polysiloxane in the epoxy matrix but also boosts the toughness and thermal properties of the resulting material. However, there is a lack of extensive research on the production of highly epoxidized polysiloxane via hydrolysis and condensation reactions for achieving uniform dispersion in epoxy matrices.

This research has focused on using siloxanes with functional end groups to refine the thermal and mechanical properties of epoxy resins. The goal is to enhance the toughness of composites and nanocomposites for more demanding applications. In this study, highly epoxidized polysiloxanes are obtained with with diglycidyl ether of bisphenol-A (DGEBA). Two different siloxanes are used, that are ether-terminated polydimethylsiloxane (PDMS-DGE) and 3-glycidoxypropyl trimethoxysilane (GPTMS). The thermal and mechanical properties are evaluated for both types of composites and a comparative study is also perfomed. The reaction mechanisms are also discussed elaborately. The structure is studies through FT-IR, the thermal properties are evaluated using TGA, DSC and the mechanical properties are evaluated using flexure test measurements.

2. Experimental

2.1 Materials

The epoxy resin used was diglycidyl ether of bisphenol-A (DGEBA), characterized by an epoxy equivalent weight of 170.2 g/eq, a functionality of 2, a molecular weight of 340.41 g/mol, a density of 1.16 g/ml (at 25°C), and a viscosity ranging from 4000 to 6000 cP. The hardener employed was 1,2-diaminocyclohexane (1,2-DCH), with an epoxy equivalent weight of 28.5 g/eq, a functionality of 4, a density of 0.931 g/ml (at 25°C), and a molecular weight of 114.19 g/mol. The liquid rubber used was poly(dimethylsiloxane) diglycidyl ether terminated (PDMS-DGE), featuring an epoxy equivalent weight of 490 Eq./g, a functionality of 2, an approximate molecular weight of 800 g/mol, a density of 0.99 g/ml (at 25°C), and a viscosity of 15 cSt (at 25°C). The molecular weight and viscosity values of the reactants are provided by the supplier, Sigma-Aldrich (St. Louis, MO, USA; sigma-aldrich.com). The other curing agent used was 4, 4-diaminodiphenylmethane (DDM), sourced from Shanghai SSS Reagent Co., Ltd.,

China. The 3-glycidoxypropyl poly(methylsilane) (GPPMS) was supplied by Shanghai Sili Industry & Trade Co., Ltd., China. γ-Aminopropyl triethoxysilane (APTES) and 3-glycidoxypropyl trimethoxysilane (GPTMS) were obtained from Silicone Co., Ltd., China. Dibutyltin dilaurate was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd., China.

2.2 Synthesis of Epoxidized Polysiloxane using ether-terminated polydimethylsiloxane (PDMS-DGE)

Initially, PDMS-DGE was subjected to a pre-reaction with the hardener 1,2-diaminocyclohexane (DCH). During this stage, the oxirane groups in PDMS-DGE were consumed through the reaction with DCH, leaving only the amine groups of DCH available for subsequent interactions. Once this pre-reaction was complete, the resulting mixture was combined with diglycidyl ether of bisphenol-A (DGEBA). The final blend was then cured, resulting in nanocomposites with significantly improved flexural mechanical properties. The reaction mechanism is shown in the schematic representation in **Figure 1**.

It is important to note that both the epoxy resin DGEBA and the PDMS-DGE elastomer feature oxirane rings as their functional end groups. Consequently, during the curing process, the curing agent DCH is expected to react with both the DGEBA epoxy system and the PDMS-DGE elastomer. This reaction involves the opening of the oxirane rings, and any unreacted rings will interact with other diamine molecules to form a molecular network. It is proposed that this network chemically bonds the elastomer to the resin, effectively integrating the elastomer within the polymeric matrix.
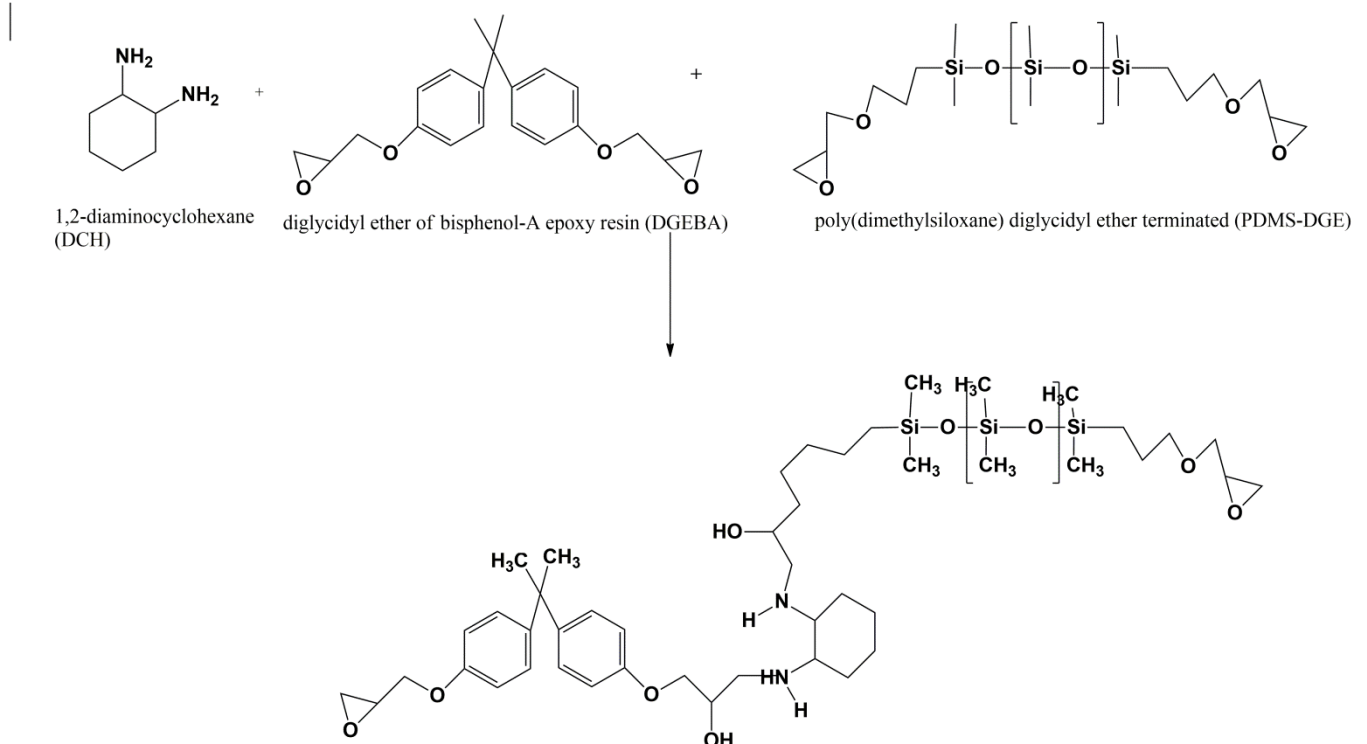
Chain Propagation
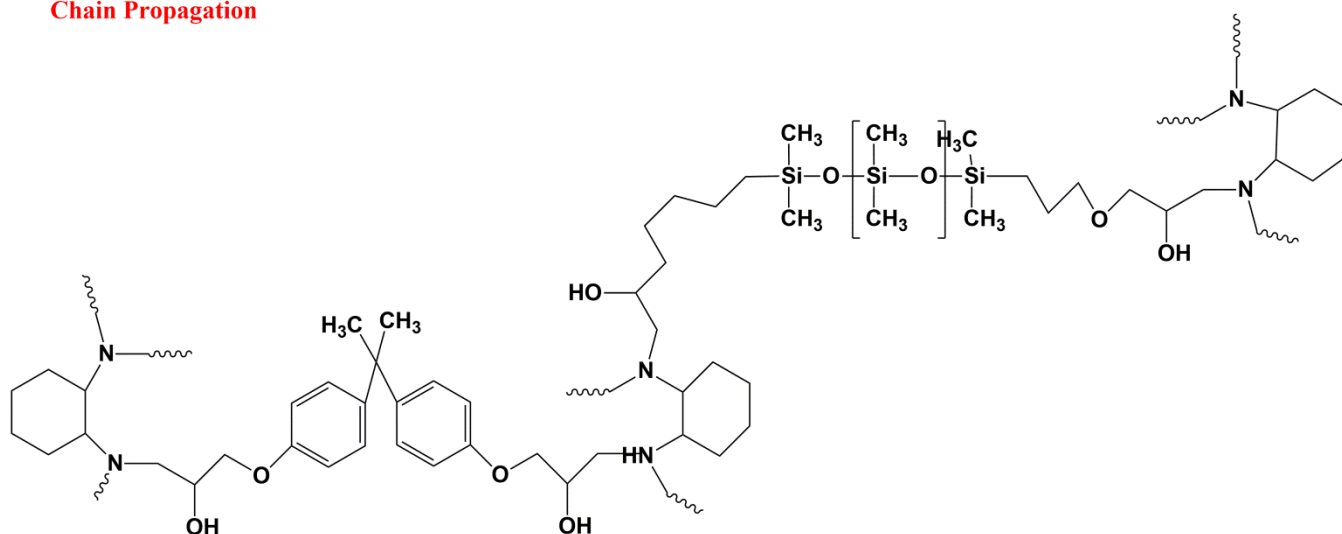
Figure 1. The schematic representation of reaction mechanism for synthesis of epoxidized polysiloxane using ether-terminated polydimethylsiloxane (PDMS-DGE)

2.2 Synthesis of Epoxidized Polysiloxane using 3-glycidoxypropyl trimethoxysilane (GPTMS)

This synthesis involves the following steps:

Step 1: Preparation of APTES bearing 3-glycidoxypropyl poly(methylsilane) (AGPMS)

APTES-bearing 3-glycidoxypropyl poly(methylsilane) (AGPMS) was synthesized via the ring-opening reaction of 3-glycidoxypropyl poly(methylsilane) (GPPMS) with γ-aminopropyl triethoxysilane (APTES). In a three-necked round-bottom flask equipped with a magnetic stirrer, thermometer, and reflux condenser, 100 g of GPPMS, 11.1 g of APTES, and 111 g of toluene were combined. The mixture was purged with nitrogen at room temperature for 1 hour, then heated to 110°C and reacted for 6 hours under nitrogen. The solvent was removed using a rotary evaporator. The resulting AGPMS was light yellow, transparent oil.

Step 2: Preparation of epoxidized polysiloxane

Epoxidized polysiloxane was prepared by hydrolyzing and condensing AGPMS with 3-glycidoxypropyl trimethoxysilane (GPTMS) using dibutyltin dilaurate as a catalyst. In a three-necked round-bottom flask with a magnetic stirrer, thermometer, and reflux condenser, the calculated amounts of AGPMS, GPTMS, distilled water, dibutyltin dilaurate, and tetrahydrofuran were combined. After vigorous stirring for 10 minutes, the mixture was heated to 65°C and reacted for 5 hours. The solvent and water were then quickly removed using a rotary evaporator. The resulting polysiloxane was a colorless, transparent, viscous liquid. This compound was mixed with diglycidyl ether of bisphenol-A (DGEBA) in an oil bath at 90°C with continuous stirring until homogeneous. A stoichiometric amount of DDM relative to DGEBA was then added, and the mixture was stirred vigorously until uniform. The mixture was degassed in a vacuum oven. The entire process took approximately 20 minutes. The ternary mixtures were poured into preheated stainless steel molds and cured at 90°C for 3 hours, followed by 150°C for 2 hours, and 180°C for 2 hours in a vacuum to ensure complete curing. The reaction mechanism is shown in the schematic representation in **Figure 2**.

Step 1: Preparation of APTES bearing3-glycidoxypropyl poly(methylsilane) (AGPMS)
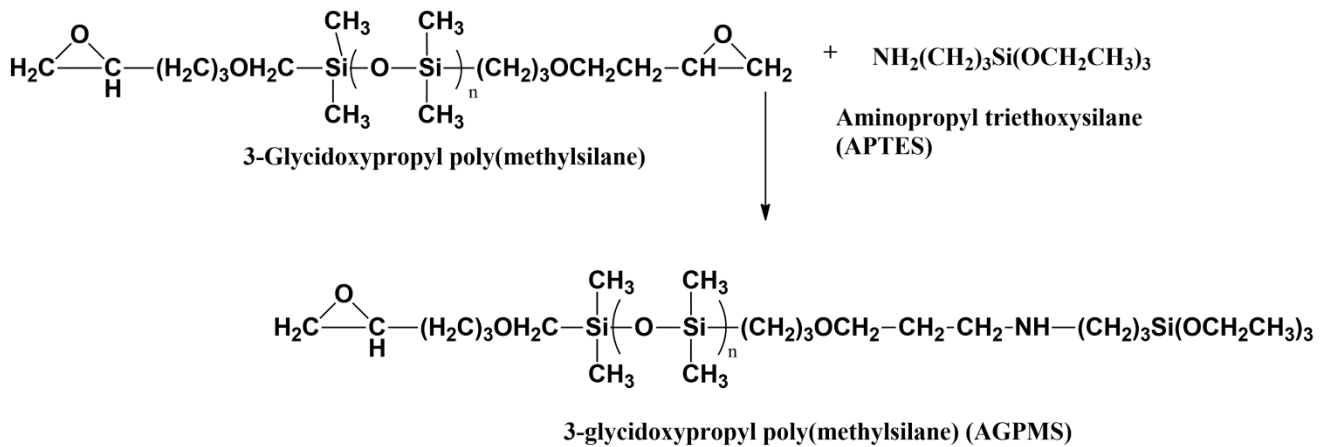
Step 2: Preparation of epoxidized polysiloxane
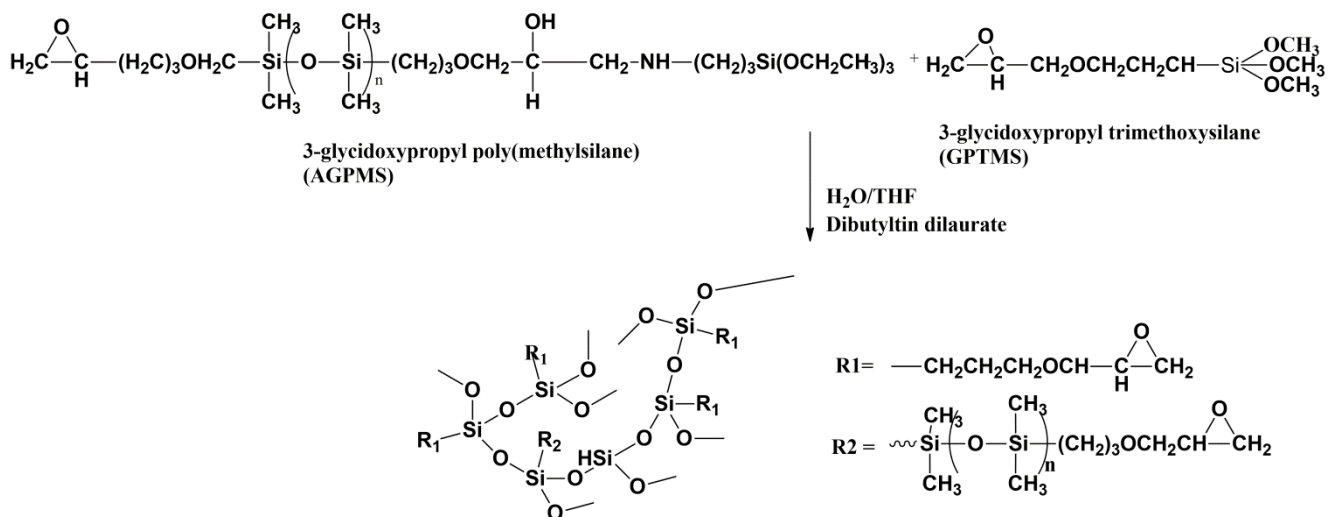

Figure 2. The schematic representation of reaction mechanism for synthesis of epoxidized polysiloxane using 3-glycidoxypropyl trimethoxysilane

2.3 Characterization

2.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

Structural characterization was performed using a Shimadzu FTIR 8400S equipped with a MIRacle™ ATR accessory.

2.3.2 Thermogravimetric Analysis (TGA)

The thermal stability of polymer nanocomposites and neat epoxy was analyzed using a Q-500 thermogravimetric analyzer from TA Instruments Inc. (DE). Samples weighing approximately 10-12 mg were used for the tests. TGA scans were conducted at a rate of 10 °C/min over the temperature range of 0 to 800 °C under a nitrogen atmosphere, with a purge flow rate of 60 mL/min

2.3.3 Differential Scanning Calorimetry (DSC)

DSC measurements were conducted using a Pyris-1 thermal analysis apparatus (Diamond DSC, Perkin-Elmer, USA) under a dry nitrogen atmosphere. The instrument was calibrated with standard indium.

Samples, approximately 13 mg each and cut into small pieces, were initially heated to 200°C and maintained at this temperature for 3 minutes to eliminate any thermal history. The samples were then rapidly cooled to 50°C and reheated from 50 to 200°C at a rate of 20°C/min. The glass transition temperature (Tg) was determined as the midpoint of the heat capacity change.

2.2.4 Flexure Test

A three-point bending flexure test was performed following ASTM D790-02 standards using a Zwick-Roell Z 2.5 machine. The test was conducted in displacement control mode with a crosshead speed of 1.2 mm/min.

3. Results and Discussion

3.1 FT-IR Studies

The FT-IR studies were performed to understand the chemical structure of the epoxidized polysiloxane. **Figure 3** shows the FT-IR spectrum of the epoxidized polysiloxane synthesized using ether-terminated polydimethylsiloxane (PDMS-DGE). The important peak observed is around 2,958 cm-1 which can be attributed to the CH_2 groups of the elastomers relative to the neat epoxy resin. On the other hand, the peaks at about 1262, 1073, 896 cm^{-1} are assigned to the Si–O bond in the elastomers.
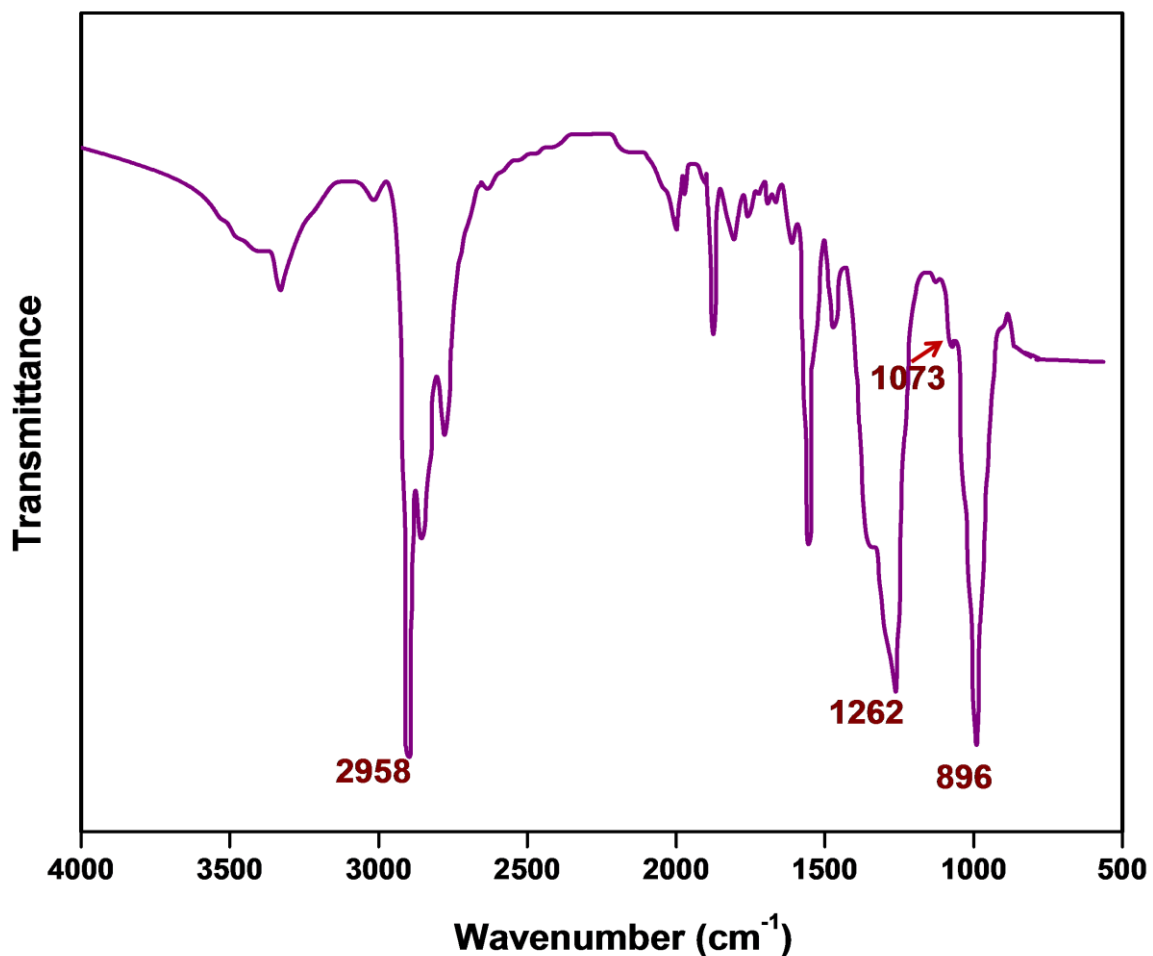
Figure 3. FT-IR spectrum of the epoxidized polysiloxane synthesized using ether-terminated polydimethylsiloxane (PDMS-DGE)

Figure 4 presents the FTIR spectra for GPPMS, AGPMS, and its epoxidized polysiloxane. The FTIR spectrum of AGPMS (Figure 4b) closely resembles that of GPPMS (Figure 4a), likely due to the low N-H and O-H ratio in AGPMS, which makes their absorption peaks less detectable. In contrast, the FTIR spectrum of epoxidized polysiloxane (Figure 4c) shows distinct peaks at 3420 cm^{-1} (O-H of Si-OH), 1204 cm^{-1} (Si-OH), and 910 cm^{-1} (oxirane group), indicating the hydrolysis and condensation reactions between AGPMS and GPTMS. The prominent peak at 3420 cm^{-1} suggests that the condensation reaction was not fully completed, which could also explain the liquid state of epoxidized polysiloxane. Additional characteristic peaks for its epoxidized polysiloxane are observed at 1260 cm^{-1} (Si-C), 1100-1000 cm^{-1} (Si-O-C, Si-O-Si), and 800 cm^{-1} (C-H of Si-CH$_2$ and Si-CH$_3$).
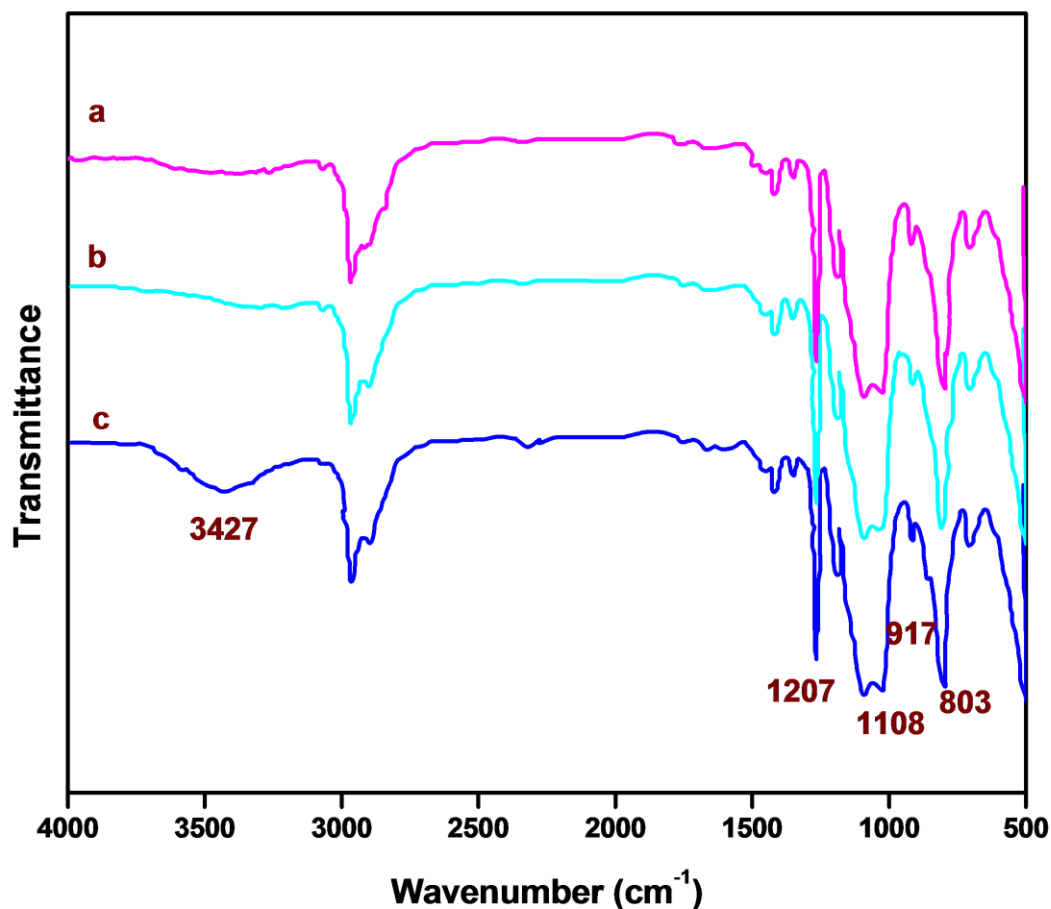
Figure 4. FTIR spectra for (a) GPPMS, (b) AGPMS and its (c) epoxidized polysiloxane

TGA Studies

The thermal stability of the composites was assessed using thermogravimetric analysis (TGA) in both modulated mode and high resolution. Figure 5 illustrates the mass loss traces as a function of temperature for (a) neat epoxy, (b) epoxidized polysiloxane with ether-terminated polydimethylsiloxane (PDMS-DGE), and (c) epoxidized polysiloxane with GPTMS.

The results reveal that neat DGEBA (Figure 5a) shows a 5% mass loss at approximately 280°C. As the temperature increases, there is a sudden mass loss around 300°C, followed by a slower rate of mass loss until all the material is burnt up by 520°C, where the mass loss stabilizes.

In contrast, composites with PDMS-DGE (Figure 5b) start to lose mass at about 280°C. This composite experiences a 10% mass loss before reaching a second thermal decomposition onset at 310°C. After this point, the nanocomposites initially exhibit a rapid mass loss, but the rate slows down compared to the neat resin.

Composites with GPTMS demonstrate a 5% weight loss at 320°C, 10% weight loss at 380°C, followed by a sudden 40% weight loss at 412°C, and then a gradual plateau region. These results suggest an improvement in thermal stability with the incorporation of siloxane components into the cured networks. This enhanced stability is likely due to the high thermal stability of the silicone compound and the protective effect of the silica layer formed during decomposition, which significantly reduces oxidation and weight loss of the polymeric materials, resulting in a higher residual weight at 800°C [22,23]

Overall, thermal studies indicate that epoxidized polysiloxane with GPTMS exhibits better thermal stability compared to the one with PDMS-DGE.
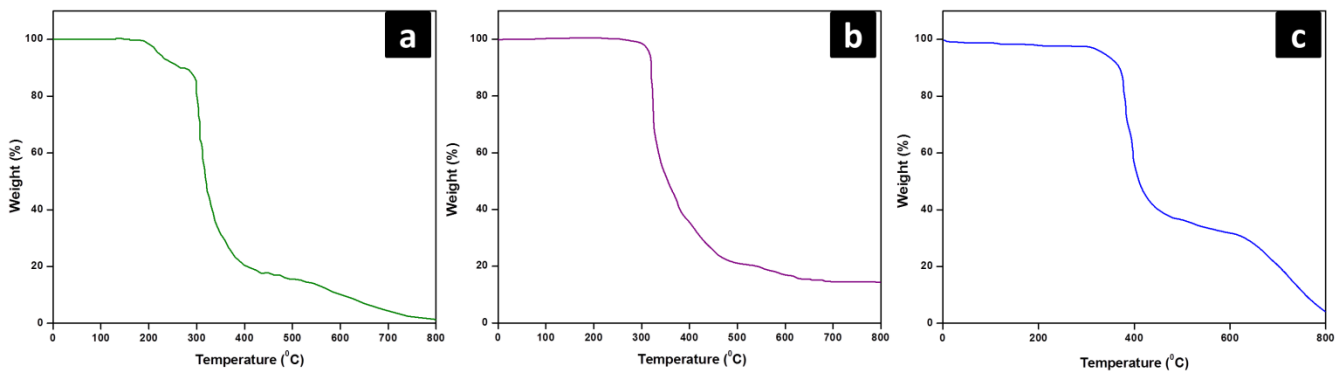
Figure 5. TGA analysis of (a) neat epoxy, (b) epoxidized polysiloxane using ether-terminated polydimethylsiloxane (PDMS-DGE) and (c) epoxidized polysiloxane using GPTMS

DSC Studies

The glass transition temperature (Tg) is a key indicator of the thermal stability of epoxy-based samples. The DSC analysis of epoxidized polysiloxane using ether-terminated polydimethylsiloxane (PDMS-DGE) and GPTMS are shown in Figures 6a, 6b.

Notably, composites containing PDMS-DGE show two distinct glass transitions: a lower Tg in the range of 50-60°C and a higher Tg at 105°C. Conversely, composites with GPTMS exhibit two glass transitions as well, with a lower Tg around 140°C and a higher Tg at 180°C. The higher glass transition temperatures in the composites can be explained as follows: the dissolution of PDMS into the epoxy matrix tends to lower its Tg due to a plasticizing effect. For the GPTMS composites, the higher Tg values suggest less disruption and better integration of the epoxy phase.

The low glass transition temperatures (~50°C) for PDMS-DGE composites indicate some degree of interaction and interpenetration of the ether-terminated PDMS into the epoxy phase. This interaction suggests that PDMS may disrupt or interpenetrate the epoxy network to some extent, a phenomenon also seen in epoxy resins blended with various functional polymers, such as epoxy-rubbers and epoxy-thermoplastic blends [24].

During the curing process, phase separation of PDMS occurs, creating heterogeneity in the composite. Even a small amount of PDMS can contribute to toughening and the presence of oxirane functionality in PDMS likely facilitates covalent bonding at the epoxy interface, resulting in a lower temperature Tg.

This lower Tg can be attributed to incomplete phase separation due to plasticization effects, which leads to some degree of interpenetration between phases—a behavior observed in several rubber-modified epoxy formulations [25].
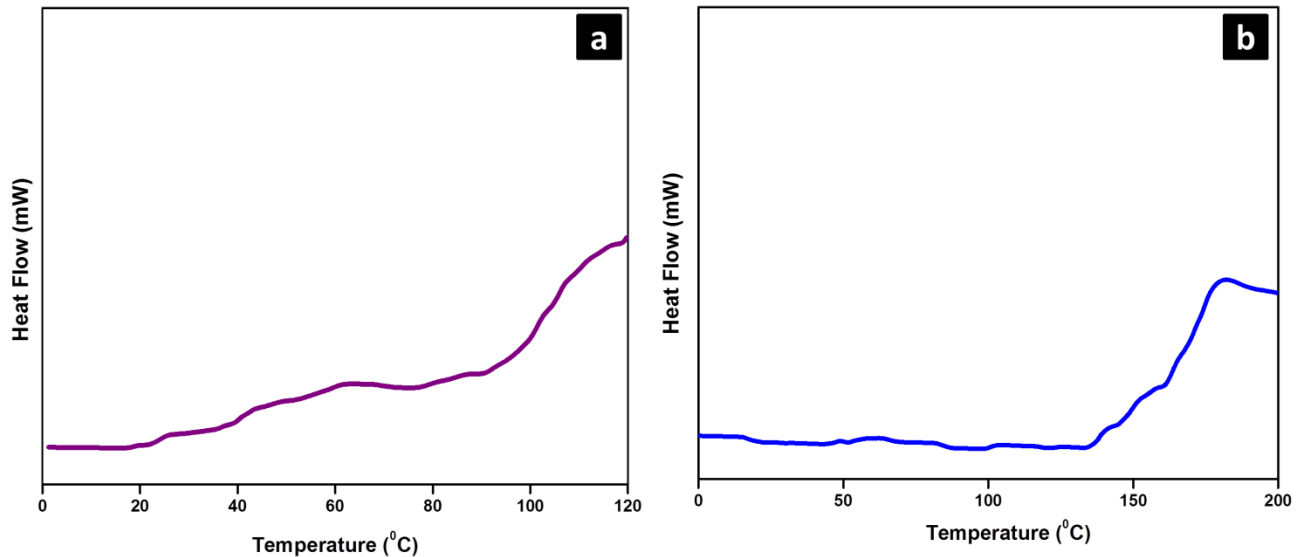
Figure 6. DSC analysis of (a) epoxidized polysiloxane using ether-terminated polydimethylsiloxane (PDMS-DGE) and (b) epoxidized polysiloxane using GPTMS

Flexure Test

Flexure properties of nanocomposites are characterized by subjecting neat epoxy and CNFs reinforced nanocomposites under three point bending load. The stress-strain curves as shown in the Fig. 4, Flexure Test

Flexure Test

Flexure properties of nanocomposites are characterized by subjecting neat epoxy and epoxidized polysiloxane PDMS-DGE and epoxidized polysiloxane GPTMS under three point bending load. The stress-strain curves as shown in the **Figure 7**.

The trace for the neat epoxy shows a linear, elastic behavior up to approximately 2% strain and fractures at around 6.1% strain. In contrast, the composites with PDMS-DGE and GPTMS demonstrated significantly greater flexural deformation compared to DGEBA. The fractures occurred at around 8.3 and 9.2 %. representing a profound increase compared to the neat epoxy. This enhancement can be attributed to the increased cross-linking between epoxy molecules and PDMS leading to an interlocking structure within the matrix, which reduces the mobility of the epoxy polymer chains throughout the system. The chemically interlocked structure of the enhances the stress transfer.
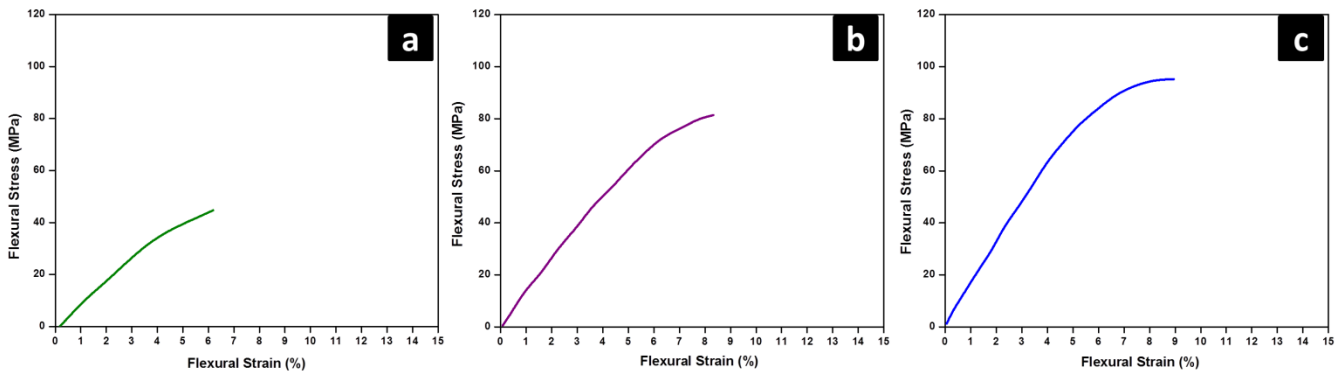
Figure 7. Flexural stress-strain curves of (a) neat epoxy, (b) epoxidized polysiloxane using ether-terminated polydimethylsiloxane (PDMS-DGE) and (c) epoxidized polysiloxane using GPTMS

4. Conclusions

Siloxane-enhanced epoxy resins were synthesized through a facile route using two different siloxanes, that are ether-terminated polydimethylsiloxane (PDMS-DGE) and 3-glycidoxypropyl trimethoxysilane (GPTMS). The structure, thermal and mechanical properties were examined. The TGA and DSC studies indicate that epoxidized polysiloxanes exhibit improved thermal stability compared to neat epoxy. Similarly, flexural tests demonstrate that epoxidized polysiloxanes offer enhanced mechanical durability. Among the two types of epoxidized polysiloxanes, the one with GPTMS shows the greatest performance. This highlights the potential of siloxane modifications for advanced adhesive applications. Gaining a deeper understanding of how siloxane modifications affect epoxy resins could lead to the development of adhesives with superior thermal and mechanical properties, thereby broadening their applications across various industries.

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