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Incorporation of Hydroxyl Terminated Polydimethylsiloxane into Dgeba Epoxy Resins via Condensation of Hydroxyl Groups: Preliminary Approach

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Abstract

We have successfully synthesised diglycidylether bisphenol-A (DGEBA)/hydroxyl-terminated polydimethylsiloxane (HTPDMS) grafting copolymer through condensation of hydroxyl groups. Diethylenetriamine (DETA) was used as a curing agent to crosslink DGEBA and DGEBA-HTPDMS. The chemical structure of the DGEBA-HTPDMS grafting copolymer was confirmed by Fourier Transform Infra-Red (FT-IR) spectroscopy. The introduction of HTPDMS in the DGEBA system slightly increase resilience properties and reduced hardness Shore-D. No phase separation was observed by Scanning Electron Microscopy (SEM). Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) showed that the thermal stability of the DGEBA system improved. While the presence of HTPDMS shows more stability towards the solvent. These results showed Si-O-Si segments can enhance the properties of the existing DGEBA.

Keywords: Diglycidylether bisphenol-A, hydroxyl-terminated polydimethylsiloxane, Diethylenetriamine, grafting copolymer

Introduction

Diglycidyl ether bisphenol A (DGEBA) epoxy is a high performance thermoset resin, which displays a unique combination of thermal and mechanical properties. This includes chain rigidity, toughness, good thermal stability, chemical resistance, and flexibility [1]. The hydroxyl and epoxy groups govern the improved adhesiveness and chemical stability, or reactivity with other chemicals. Highly cross-linked networks are formed once the resin is cured, affording a high stiffness and glass transition temperature (Tg) material [2,3].

However, the major drawback of these resins is the brittleness in the cured state [4]. Hence, modification is done to the resins to improve its brittleness. Rubber modifying epoxy resins have been studied by several researchers and successfully increase the toughness of the epoxy resins. Carboxyl-terminated butadiene-acrylonitrile rubber (CTBN) and amine-terminated butadiene-acrylonitrile rubber (ATBN) have been widely employed, with acceptable reduction of thermo-mechanical properties. However, these elastomers have a relatively high glass transition temperature which limits their low temperature flexibility. Their highly unsaturated structure also makes them unsuitable for use at elevated temperatures [5,6]. An improvement is made, which consists of the dispersion of preformed particles into the initial reactive system. However, the introduction of particles also increases the viscosity of the system, which may be unfavourable for processing. The dispersive and distributive mixing must be good to acquire the desired toughness [7,8].

The modification of epoxy system was performed by Kumar *et al.* [9] who found that the polysiloxane can function as a polymeric modifier, owing to their superior properties, such as thermal and thermo-oxidative stability, excellent moisture resistance, flexibility, excellent UV and chemical resistance [10]. This is due to the stability and flexibility of the Si-O-Si linkage. Silicone polymers have high bond dissociation energy of Si-O unit bond (443.7 kJ/mol), compared to those of C-O bond (357.9 kJ/mol) [11]. However, the effect of bleeding out of the polysiloxane during the moulding process limits its processability. To increase the compatibility of the polysiloxane with the epoxy resins, other functional groups, such as amine, hydroxyl, and epoxy have been introduced to the polysiloxane. In Ahmad *et al.* [11], the hydroxyl terminated polysiloxanes reaction with the oxirane group of epoxy with the presence of phosphoric acid (H_3PO_4), producing high performance paints. Lin *et al.* [12] and Ho *et al.* [13] incorporated the hydride-terminated polydimethylsiloxane (HTPDMS) and methyl hydrogen siloxane into polyglycidyl ether of the allyl-alkyl novolac resin through hydrosilation to produce as an encapsulated formulation to withstand the thermal stress.

Hou *et al.* incorporated the Si-H and Si-CH_3 copolymer into the epoxy resins through hydrosilation to make the epoxy resins tougher [14]. While Gong *et al.* incorporated diaminopropyl-terminated polydimethylsiloxane into oligo(hydroxyether of bisphenol A), and successfully made the resin tougher. However, no attempt has been made so far to incorporate HTPDMS into the DGEBA through condensation of the hydroxyl groups. In this work, we will incorporate HTPDMS with DGEBA with DETA acting as a curing agent. The morphology, thermal, resilience and hardness, and chemical stability properties of DGEBA-DETA and DGEBA-HTPDMS-DETA were investigated.

Materials and methods

Materials

DGEBA or epoxy resin DER 331, was purchased from Dow Chemicals (Malaysia) Sdn Bhd. HTPDMS was used as an epoxy modifier and diethylenetriamine (DETA) as a curing agent were obtained from Sigma-Aldrich (M) Sdn Bhd. Tetrahydrofuran (THF), dimethylacetamide (DMAc), acetone, chloroform, toluene, N-Methyl-2-pyrrolidone (NMP), concentrated sulphuric acid (18M) were obtained from Merck Malaysia. All materials were used as received.

Synthesis of DGEBA-HTPDMS

The DGEBA was put under vacuum for 45 min to eliminate the air bubbles. After adding HTPDMS, the mixture was then placed into a polypropylene container and mixed in ratio of 40:1 (15 g: 0.375 g) with 3 ml of acetone, which act as a solvent and dispersing agent. The compound was stirred by a mechanical stirrer under 200 rpm for 5 min. The compound was again placed in a vacuum for 1 h to eliminate the air bubbles. The curing agent (DETA) was added according to the ratio of DGEBA: DETA (15 g: 1.5 ml) and stirred using a mechanical stirrer under 200 rpm for another 5 min. The sample was then put in a vacuum for 5 min, and cured under room temperature for 24 h. The structure of DGEBA, DGEBA+HTPDMS and DGEBA+HTPDMS+DETA was further confirmed with FTIR.

Characterisation

FTIR Spectrum was obtained by using a Spectrum GX Perkin Elmer Model in accordance with ASTM E1252 between 4000-550 cm^{-1}. The sample of DGEBA was prepared in liquid form while DGEBA+DETA was prepared in powder form for FTIR characterisation. Differential Scanning Calorimetry (DSC) was performed in accordance to ASTM D3418 by using Mettler Toledo DSC 1 with a heating rate of 10 °C min^{-1} in N_2. Thermogravimetric analysis (TGA) was performed in accordance with ASTM E1131 by using Perkin-Elmer TGA7 with a heating rate of 10 °C min^{-1} under N_2. Chemical solubility and swelling tests were conducted using acetone, chloroform, toluene, dimethylacetamide, tetrahydrofuran, N-methyl-2-pyrrolidone, and concentrated sulphuric acid at room temperature. Resilience behaviour was tested in accordance with ASTM D7121 by using Dunlop Tripsometer - R2 / R2A with air compressor in room temperature. Hardness was tested by using Teclock Durometer type D model GS-743G accordance to with ASTM D2240. The surface morphology was observed using SEM; the model used was a ZEISS Supra 35VP at 1K magnifications.

$$Percentage\ \ resilience = \frac{(1\ -\ \cos\theta)}{(1\ -\ \cos 45^{o})}\ x\ \ 100$$

Results and discussion

Synthesis consideration

The DGEBA+HTPDMS resin was produced by mixing the DGEBA and HTPDMS. The DGEBA and HTPDMS undergo condensation to form an intermediate product which is still in liquid state. DGEBA and DGEBA+HTPDMS are viscous liquid resins which contains a huge amount of entrap air bubbles. The degassing process is required to get rid of the air bubbles. However, a longer degassing time would result in premature curing during the degassing process because DETA cured DGEBA resins have a short pot life. In order to prevent premature curing during degassing, the resins were put into the degassing process before the addition of DETA. Finally, the soluble 3 dimensional HPI macromolecules were obtained by thermal treatment at 160 °C. The chemical structure of DGEBA+HTPDMS (uncured) and DGEBA+HTPDMS+DETA (cured) are shown in **Figure 1**. The amine group of DETA reacts with the epoxy group, resulting in a cross-linked network structure. The FTIR spectra of the epoxy system are shown in **Figure 2**.

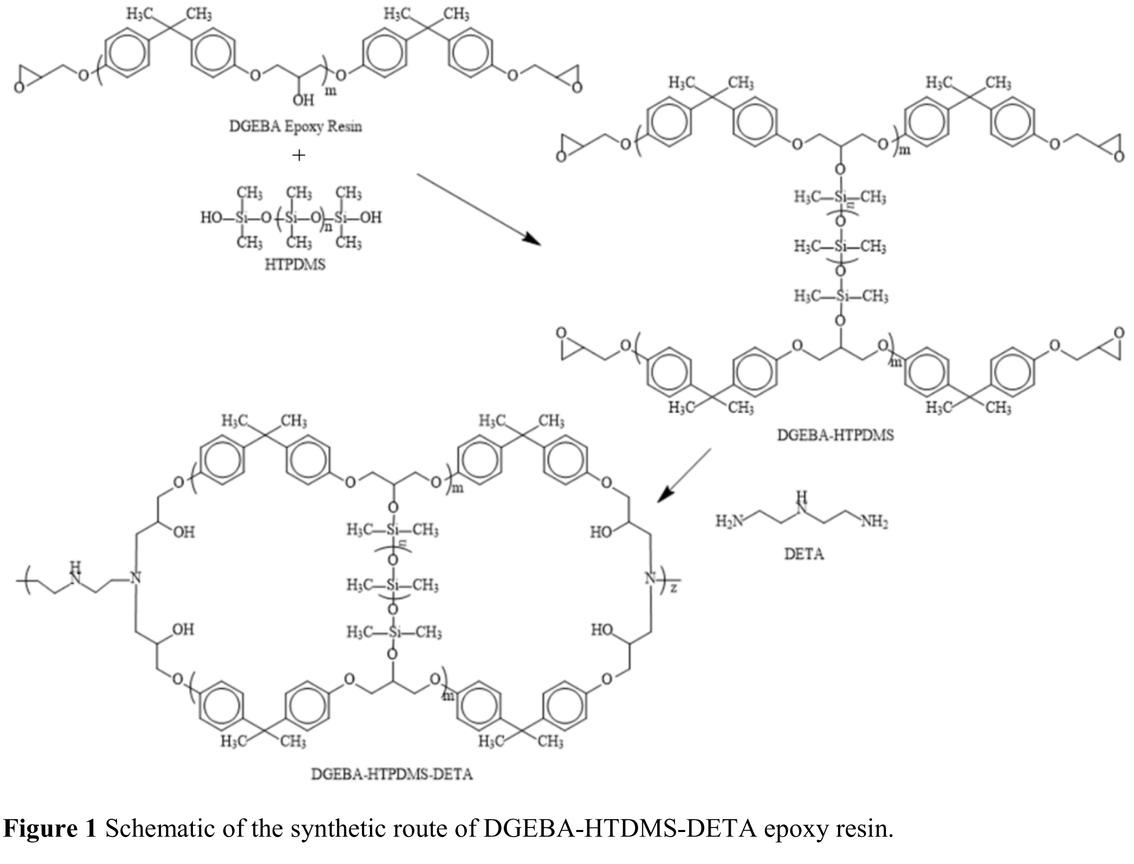

Figure 1 Schematic of the synthetic route of DGEBA-HTDMS-DETA epoxy resin.

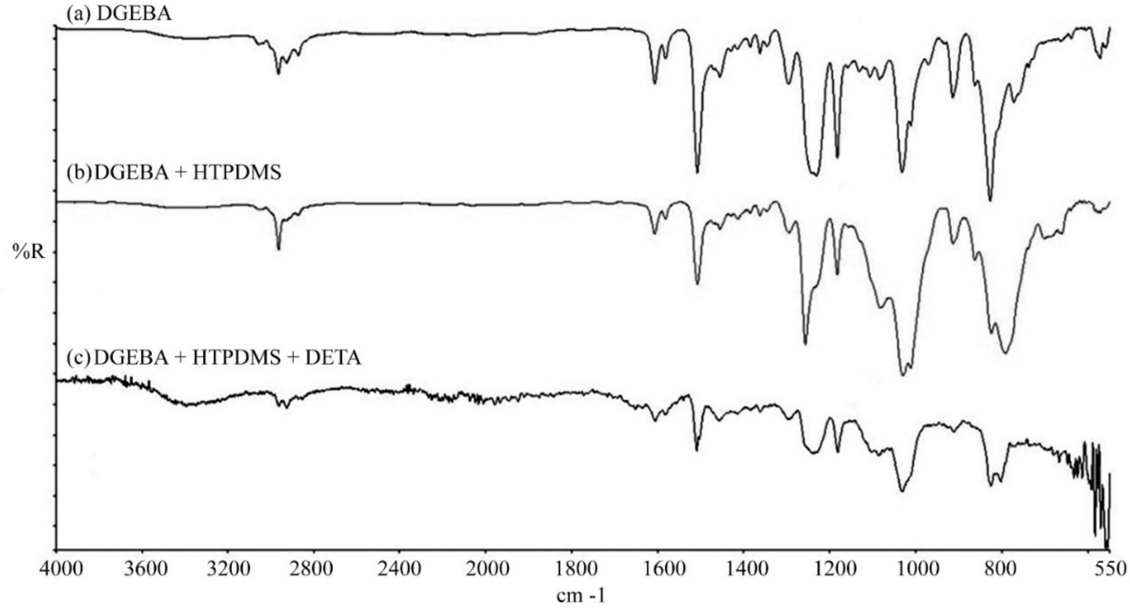

Figure 2 The FTIR spectra of the epoxy system.

The characteristics of DGEBA were respectively determined in the presence of functional groups (respective peaks) of the dimethyl group, $-C(CH_3)_2$ (3061, 2969 and 2870 cm^{-1}) and C-O-C (around 1200-1100 cm^{-1}). The reaction between DGEBA and HTPDMS involved the condensation to form an intermediate product and increase the intensity of C-O-C chemical bonds. The peak at 3350 cm^{-1} in spectra A is due to the OH group which is present in the neat DGEBA epoxy resin. When the epoxy resin is modified with HTPDMS (spectra B), it shows a considerable reduction of this peak (normalised against aromatic C=C peak at 1600 cm^{-1}) suggesting that the condensation occurs between the OH end-group of HTPDMS with the hydroxyl group of DGEBA resin with the release of water molecules. The successful incorporation of silicon units could be further substantiated by the presence of strong and broad peak at the region 1090 - 1020 cm^{-1} representing the Si-O-C and Si-O-Si bond (open chain). When DETA is added into the HTPDMS-modified DGEBA epoxy resins (spectra C), the peak at 914 cm^{-1} reduced significantly which confirmed the occurrence of oxirane ring opening by the former which affects the curing process. It was observed (not shown here) that prior to the addition of DETA that at even higher concentrations of HTPDMS in the DGEBA resin (ratio of epoxy resin to HTPDMS in 1:2), the oxirane group does not show significant reduction in peak intensity at 914 cm^{-1} (normalised against the aromatic C=C at 1600 cm^{-1}). Thus it can be safely stated that the oxirane ring opening of DGEBA was solely affected by the DETA. The occurrence of a weak band at 1140 cm^{-1} proves that the aliphatic C-N bond has been formed, due to the reaction between the oxirane groups with DETA. Substantial increase in peak at 3350-3400 cm^{-1} is shown in DGEBA+HTPDMS+DETA system, due to the formation of new hydroxyl groups during the ring opening of the oxirane ring [15].

Fracture surface morphology

The surface morphology of DGEBA+DETA and DGEBA+HTPDMS+DETA showed in **Figures 3(a)** and **3(b)** respectively. From the figures, the DGEBA+DETA surface is relatively smooth; which indicates limited plastic deformation. The DGEBA+HTPDMS+DETA system clearly shows no apparent phase separation between the HTPDMS and DGEABA moieties. The excellent homogeneity is due to the HTPDMS which is chemically incorporated into the DGEBA, in good agreement with the DSC and FTIR analyses result. **Figure 3(b)** also shows regular deformation lines with several tiny febrile pull-outs which indicate that extra energy is required to break the DGEBA+HTPDMS+DETA system. This observation is consistent with a tough but flexible material as similarly observed by several workers [16]. No discrete spherical polysiloxane particles were dispersed in the continuous epoxy resin matrix.

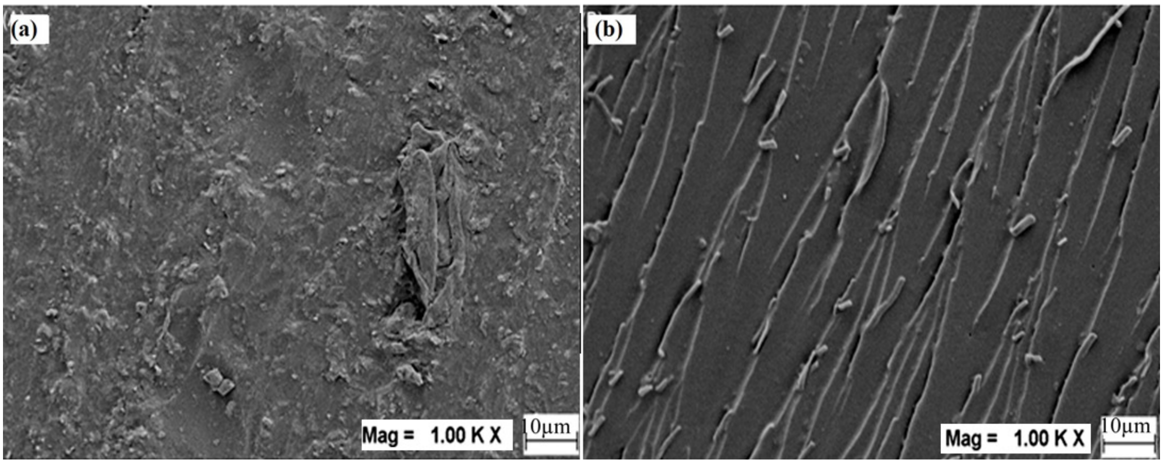

Figure 3 The surface morphology of (a) DGEBA+DETA, (b) DGEBA+HTPDMS+DETA.

Thermal properties

The DSC thermogram (second scan) of the DGEBA+HTPDMS+DETA system under nitrogen with heating rate of 10 °C min^{-1} is shown in **Figure 4(a)**. For incompatible polymer blends, it usually exhibits 2 *Tg* peaks due to inhomogeneous phases [17]. For the DGEBA+HTPDMS+DETA system, the second scan shows only a single *Tg* at 120 °C, indicating that the present system with cured DGEBA and HTPDMS exhibits a single homogeneous phase. The other work shows values of *Tg* for polydimethylsiloxane in the region of −123 to −51 °C [15]. In our work, the presence of a single *Tg* confirmed that the hydroxyl terminated polydimethylsiloxane have been successfully incorporated into the DGEBA epoxy resins.

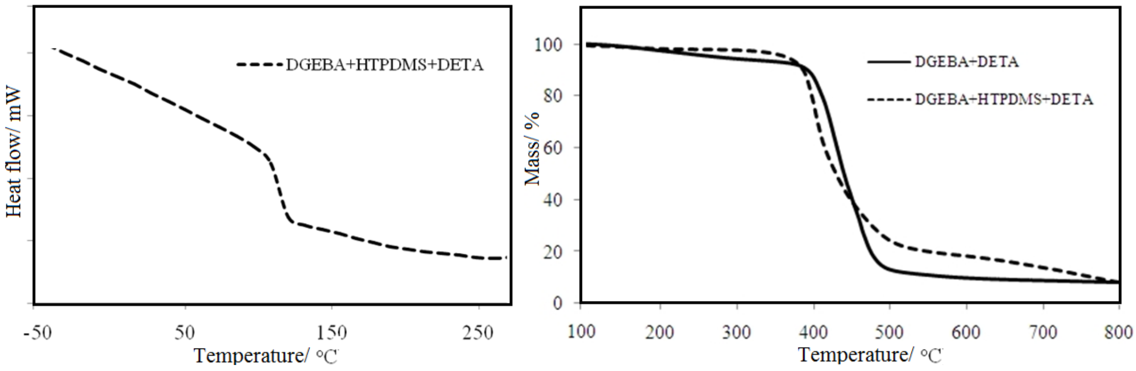

Figure 4 Thermal properties of the DGEBA+HTPDMS+DETA system (a) DSC thermogram at second heating and (b) TGA thermogram under nitrogen atmosphere.

The work of Bragg *et al*. shows that the *Tg* for DER331 cured with DETA is 108 °C [18]. In this work, the DGEBA+HTPDMS+DETA system shows an increases in *Tg* (120 °C) implying a more rigid structure. This could be attributed to the high crosslinked formation between the epoxy resins and HTPDMS as well as DETA. The thermogravimetric analysis (TGA) of the DGEBA+DETA system and DGEBA+HTPDMS+DETA system is illustrated in **Figure 4(b)**. It can be seen that the onset degradation temperature ($T_{5\%}$) for DGEBA+HTPDMS+DETA system occurs at almost 80 °C higher than the neat epoxy resin. Similarly the DGEBA+HTPDMS+DETA system displays a delay in the charring process which begins at 490 °C when compared with an unmodified epoxy system. This is mainly due to the presence of the siloxane moiety, and its partial ionic nature and high bond energy of Si-O-Si linkage. This observation is consistent with other related works [11,19,20].

Physical and chemical resistivity

Resilience behaviour has been investigated by using a Dunlop Tripsometer as reported in **Table 1**. The incorporation of HTPDMS into the DGEBA shows greater resilience than the neat DGEBA+DETA system. They indicate a higher impact resistance by incorporating the HTPDMS into the DGEBA. By incorporating a more flexible siloxane group the epoxy resins become tougher while hysteresis is inversely related to resilience. Therefore, a high resilience means low hysteresis, and this is due to less energy needed to dislodge the tough but flexible HTPDMS. The improved resilience is important for the epoxy thermoset, because they are characterised by good mechanical properties with less brittle behaviour [21,22]. Hardness has been investigated by using a Durometer type D at 3 points. The values are shown in **Table 1**. Hardness is a quick and simple method of detecting gross differences between cured properties. As shown in the results, incorporating the HTPDMS into the epoxy resins leads to a less hard material due to the flexibility of HTPDMS.

Table 1 Summary of the physical and chemical stability properties.

Physical properties			
	DGEBA+DETA	***DGEBA+HTPDMS +DETA***	**Remark**
θ	29.6	32.4	
Resilience (%)	44.56	53.15	
Hardness (Shore D)	68	59	

Chemical properties				
Solvent	**Weight change (%)**		**Appearance**	**Solubility**
Acetone	+0.4048	+0.3382	Good	--
NMP	+0.4771	+0.3487	Good	--
Toluene	+0.7108	+0.6399	Good	--
DMAc	+0.2740	+0.0911	Good	--
$CHCl_3$	+18.0060	+2.4540	Good	--
THF	+0.3231	+0.2328	Good	--
H_2SO_4 (18 mol)	-	-	Broken	++

(-- non-soluble, ++ soluble)

The chemical resistivity of the DGEBA+HTPDMS+DETA system has been investigated by using several types of solvent. The weight of the sample is controlled within the range 0.3 - 0.5 g, and are all soaked in the solvent for 3 days with a stirring speed of 400 rpm with a magnetic stirrer. Their weight change and appearances are tabulated in **Table 1**. The data obtained shows that the DGEBA+HTPDMS+DETA system shows a better swelling resistance, which may be due to the incorporation of polydimethylsiloxane between the epoxy chains leading to an increase in crosslink density. A higher cross link density would deter an efficient diffusion of solvent into the network.

Conclusions

The HTPDMS was successfully incorporated into the DGEBA epoxy resins via condensation of hydroxyl groups. FTIR, DSC and SEM verified the incorporation of the HTPDMS into the DGEBA epoxy resins. SEM shows that there is no apparent phase separation between the 2 phases. The DGEBA+HTPDMS+DETA system shows higher *Tg* and thermal stabilities while introducing flexibilities into the epoxy resins. The HTPDMS modified epoxy resins can also be cured with a conventional epoxy resin curing agent such as DETA. The swelling and solubility tests also show that the DGEBA+HTPDMS+DETA system is more resistant towards solvent compared to a conventional DGEBA+DETA system.

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