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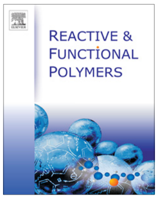

Adamantane-based epoxy resin and siloxane-modified adamantane-based epoxy resin: Characterization of thermal, dielectric and optical properties

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ABSTRACT

An adamantane-based epoxy resin (ADEP) and a siloxane-modified adamantane-based epoxy resin (Siloxane-ADEP) were synthesized, and their chemical structures were confirmed from FT-IR, ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy measurements. The morphological, thermal, dielectric and optical properties of ADEP and Siloxane-ADEP were studied. The introduction of the adamantane group into the chain of the epoxy resin resulted in improvements in the thermal, mechanical and dielectric properties. These results can be explained in terms of the tricyclic hydrocarbon of the adamantane in a diamond lattice structure and the movement of polymer chains being limited by chair-form cyclohexane rings, resulting in an immobile epoxy structure. Moreover, Siloxane-ADEP exhibited good thermal, mechanical and dielectric properties that were similar to those of epoxy resin, and its better processability may extend its application to electronic packing materials. The UV–Vis transmission spectra revealed that the adamantane-containing epoxy membranes exhibited novel ultraviolet light-filtering properties.

1. Introduction

Epoxy resins, which are one of the most important classes of thermosetting polymers, have been widely applied in surface-coating and painting materials, matrices of composites, adhesives, insulating materials, encapsulating materials, and advanced materials. With the developments in the aerospace and automobile industries in the areas of structural composites and adhesives in microelectronic devices for encapsulating electrical circuit components and electronics packaging, excellent properties are required, including good processability, thermal and chemical resistance, moisture resistance, superior electrical and mechanical properties, and good adhesion to many substrates [1–4]. However, the brittle nature and fire risk of epoxy resins restrict their application in some advanced fields. To further improve the physical properties and thermal performance of epoxy resins, researchers have developed many additives and modifiers, such as calcium carbonate, adamantane, fullerene, silica, titania and carbon nanotubes [5–10].

Adamantane (tricyclo[3.3.1.13.7]decane) is a highly symmetric tricyclic hydrocarbon with three fused chair-form cyclohexane rings in a diamond lattice structure [11,12]. The effects of incorporating adamantane into backbones or as pendant groups on the physical, thermal, and mechanical properties of a number of polymer families have been investigated [13–17]. The incorporation of adamantane led to superior thermal stability, high glass transition temperatures (T_g) and decomposition temperatures, good mechanical strength, low dielectric constants, and good transparency. Although the feasibility of incorporating adamantane into the backbone of epoxy resins has been examined [18], investigations on the relationship of siloxane modification to physical properties based on adamantane-based epoxy resins are limited. Silicon-containing compounds can migrate to the surface of the material during the course of thermal degradation because of their low surface energy. Their products are silica carbons with high thermal stability [19]. Silicon carbide can form a protective silica layer and protect the polymer residue from further thermal decomposition at high temperatures. The inorganic components could suppress the production of toxic gases [20].

Epoxy resins are widely used in many fields, such as in the manufacturing of coatings, adhesives and matrix resins for

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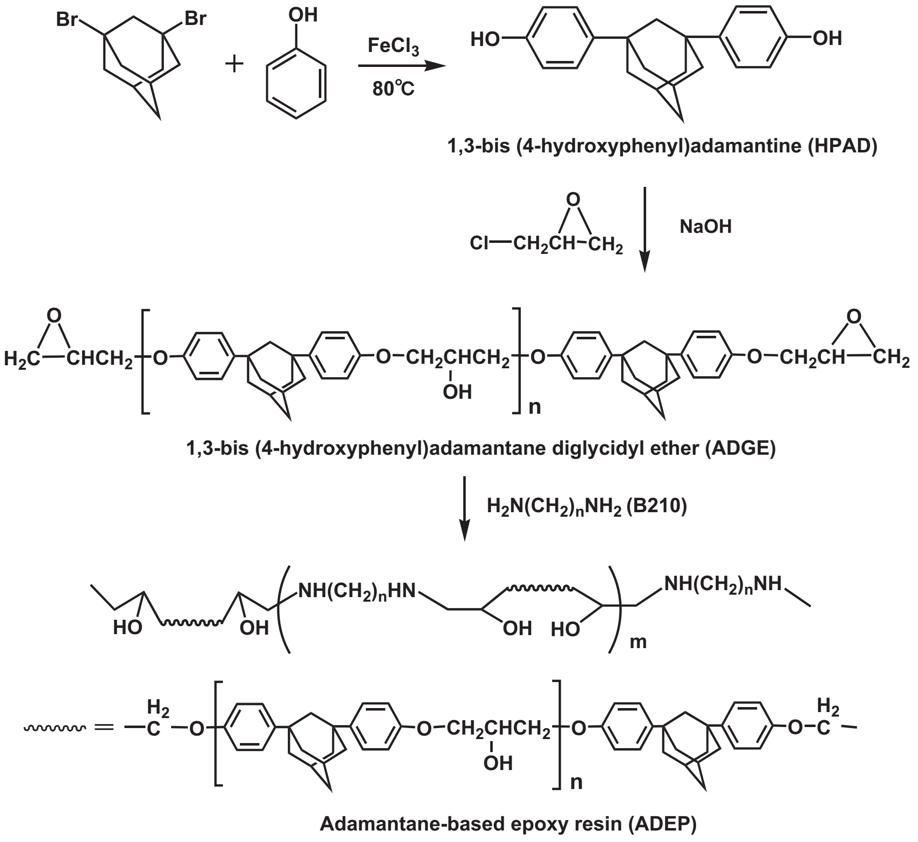


Scheme 1. Experimental procedure for the synthesis of HPAD, ADGE and ADEP.

advanced composites. Hence, the combinations of adamantane and polysiloxane with epoxy resins have broader application possibilities. To date, however, there have been few reports on adamantane-based epoxy resins with light-filtering properties. Fang et al. [7] prepared fullerene-containing epoxy membranes with tunable ultraviolet light-filtering properties. However, the thermal, dielectric and optical properties of siloxane-modified adamantane-based epoxy resins have not been investigated in detail. In this study, 1,3-dibromoadamantane and phenol were used as the starting materials to prepare 1,3-bis(4-hydroxyphenyl)adamantane (HPAD). Then, HPAD was reacted with epichlorohydrin to synthesize 1,3-bis(4-hydroxyphenyl)adamantane diglycidyl ether (ADGE). The synthesized adamantane-based epoxy resin (ADEP) was produced by curing ADGE with diamine (B210). A novel siloxane-modified adamantane-based epoxy resin (Siloxane-ADEP) was synthesized from 3-isocyanatopropyltriethoxysilane (IPTES), phenyltriethoxysilane (PTEOS) and ADGE using the sol–gel copolymerization technique. The chemical structures of ADEP and Siloxane-ADEP were confirmed using Fourier transform infrared, ^{1}H NMR, ^{13}C NMR and ^{29}Si NMR spectroscopy measurements. The morphological, thermal, dielectric and optical properties of ADEP and Siloxane-ADEP were studied and compared with those of the diglycidyl ether of bisphenol-A epoxy.

2. Experimental

2.1. Synthesis of 1,3-bis(4-hydroxyphenyl)adamantane (HPAD)

HPAD was prepared using a modification of a previously reported procedure [18]. A 150-mL round-bottom flask was filled with 1,3-dibromoadamantane (6.00 g), phenol (60.00 g) and iron(III) chloride (1.10 g). The flask was equipped with a reflux condenser and an outlet to a beaker containing a solution of NaOH to capture the HBr released from the reaction. The solution was stirred at 80 °C for 16 h under nitrogen. The excess phenol was removed by stirring the product in 500-mL portions of hot water 3 times, followed by drying under vacuum. The crude product was crystallized from methanol to afford 3.04 g (50.7 wt% yield) of white crystals of HPAD. The experimental procedure is shown in Scheme 1. Fig. 1 presents the ^{1}H and ^{13}C NMR spectra of HPAD. ^{1}H NMR (500 MHz, DMSO-d$_6$), δ 1.72 (s, 2H, H-3), 1.80 (m, 10H, H-1), 2.22 (s, 2H, H-2), 3.43 (s, HOD in DMSO-d$_6$), 6.75 (m, 4H, ArH), 7.22 (m, 4H, ArH), 9.18 ppm (s, 2H, H-6); ^{13}C NMR (500 MHz, DMSO-d$_6$), δ 29.58 (C-4), 35.83 (C-5), 36.36 (C-2), 42.28 (C-3), 49.70 (C-1), 115.21 (C-8), 125.78 (C-7), 141.41 (C-6), 155.50 ppm (C-9).

2.2. Synthesis of 1,3-bis(4-hydroxyphenyl)adamantane diglycidyl ether (ADGE) and ADEP

A 100-mL round-bottom flask was filled with 1 g of HPAD, 3.0 mL of isopropyl alcohol and 4.34 g of epichlorohydrin. The reaction temperature was controlled at 80 °C, and 0.625 g of 40 wt% aqueous NaOH was added dropwise over the course of 1 h. The mixture was reacted at this temperature for 6 h. After the reaction reached completion, the salt was filtered, and then the filtrate was washed three times with water. Then, the organic phase was separated from the mixture. Excess epichlorohydrin and the solvent were distilled using a rotary evaporator to afford 1.97 g of a yellow liquid of 1,3-bis(4-hydroxyphenyl)adamantane diglycidyl ether (ADGE). The mixture of ADGE and 10 wt% B210 diamine as a curing agent was homogeneously dissolved in THF as a solvent. The reaction solution was stirred for 12 h, evacuated for 5 min to remove the solvent from the solution, and then aged at 60 °C for 48 h to

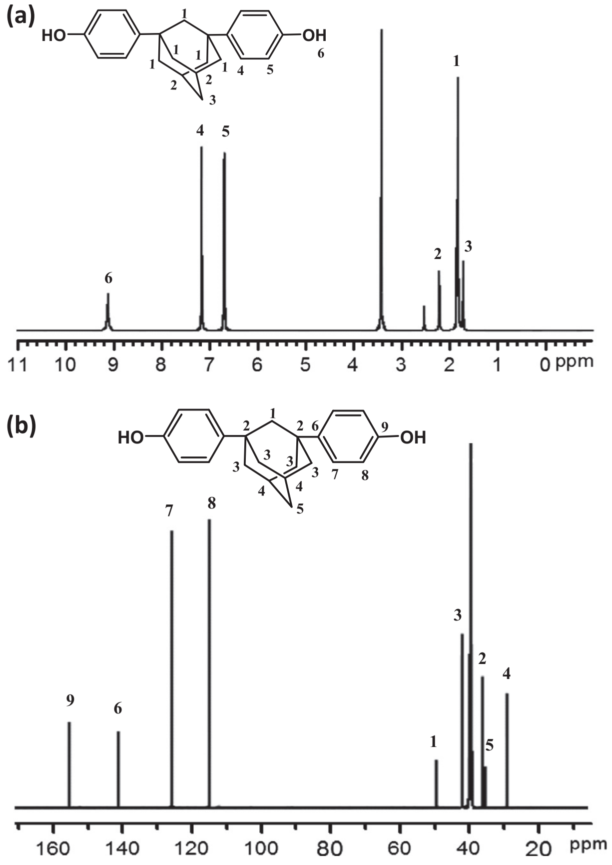


Fig. 1. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of HPAD in DMSO-d$_6$.

obtain ADEP. The experimental procedure is shown in Scheme 1. Fig. 2 presents the ^{1}H and ^{13}C NMR spectra of ADGE. ^{1}H NMR (500 MHz, DMSO-d$_6$), δ 1.78 (s, H-3), 1.90 (m, H-1), 2.26 (s, H-2), 2.68,2.84 (m, H-11), 3.19 (m, H-7), 3.52 (m, H-10), 3.80 (s, H-9), 3.83 (s, H-6), 4.27 (m, H-8), 6.92 (m, ArH, H-5), 7.34 ppm (m, ArH, H-4); ^{13}C NMR (500 MHz, DMSO-d$_6$), δ 29.58 (C-4), 35.83 (C-5), 36.55 (C-2), 42.50 (C-3), 44.20 (C-A), 47.67 (C-1), 49.58 (C-B), 67.72 (C-C), 69.64 (C-E), 69.86 (C-D), 115.21 (C-8), 126.78(C-7), 144.31 (C-6), 157.20 ppm (C-9). The ^{1}H NMR integration ratio of H-10 and H-11 was higher than that of H-4 and H-5, as shown in Fig. 2(a). This result may be due to the purification of ADGE being insufficient and the excess epichlorohydrin not being sufficiently distilled from the product.

2.3. Synthesis of siloxane-ADEP resin

ADGE (3.0 g) and tetrahydrofuran (THF; 10 mL) were stirred in a 100-mL three-neck round-bottom flask at 60 °C to obtain the epoxy solution. Then, IPTES (0.25 g) was added with THF to the epoxy solution. The entire mixture was homogeneous and was stirred at 60 °C until the characteristic peak of the NCO group (2270 cm^{-1}) in the FT-IR spectrum disappeared. The reaction time was approximately 12 h. A quantitative amount of PTEOS (molar ratio of 1:1 with respect to IPTES) was placed in a beaker with 0.05 M HNO$_3$ and deionized water. The resulting solution was added to the above-described sol solution, and stirring was continued under an inert atmosphere at room temperature for an additional 24 h. Then, B210 diamine was used as the curing agent for the modified epoxy resin. THF was removed from the siloxane-modified epoxy in a vacuum oven at room temperature for 1 h, and then the siloxane-modified epoxy was cast on a polytetrafluoroethylene plate to gel at room temperature for 24 h. The samples were placed in a drying oven at 60 °C for 24 h to obtain the clear Siloxane-ADEP. The experimental procedure is shown in Scheme 2. Ep904 resin was prepared in the same way. The diglycidyl ether of bisphenol-A epoxy used in this work was supplied by Nan Ya Plastics Co., Ltd., Taiwan, and it possessed an epoxide equivalent weight of 807 g/eq (Eporite-904). Epoxy resin and THF were stirred in a 500-mL three-neck round-bottom flask at 40 °C to obtain the epoxy solution. Then, B210 diamine was used as the curing agent, and the resulting resin was abbreviated as Ep904.

2.4. Experimental techniques

The chemical structures were confirmed by Fourier transform infrared (FTIR) spectral analysis (Tensor 27) of samples prepared using the KBr pellet technique. ^{1}H and ^{13}C NMR spectra were recorded on Bruker MSL-500 NMR spectrometers using DMSO-d$_6$ as the solvent and tetramethylsilane as the internal standard. The ^{29}Si NMR spectrum of the solid-state sample (MSL-400, Bruker) was obtained using the cross-polarization/magic-angle spinning (CP–MAS) technique. The morphologies of the samples were observed using a scanning electron microscope (SEM, Hitachi S-800) equipped with an energy-dispersive X-ray (EDX) microanalysis system. A PerkinElmer thermogravimetric analyzer (TGA-7) was used to investigate the thermal stabilities of the samples. The samples (~5 mg) were heated in a N$_2$/air atmosphere from

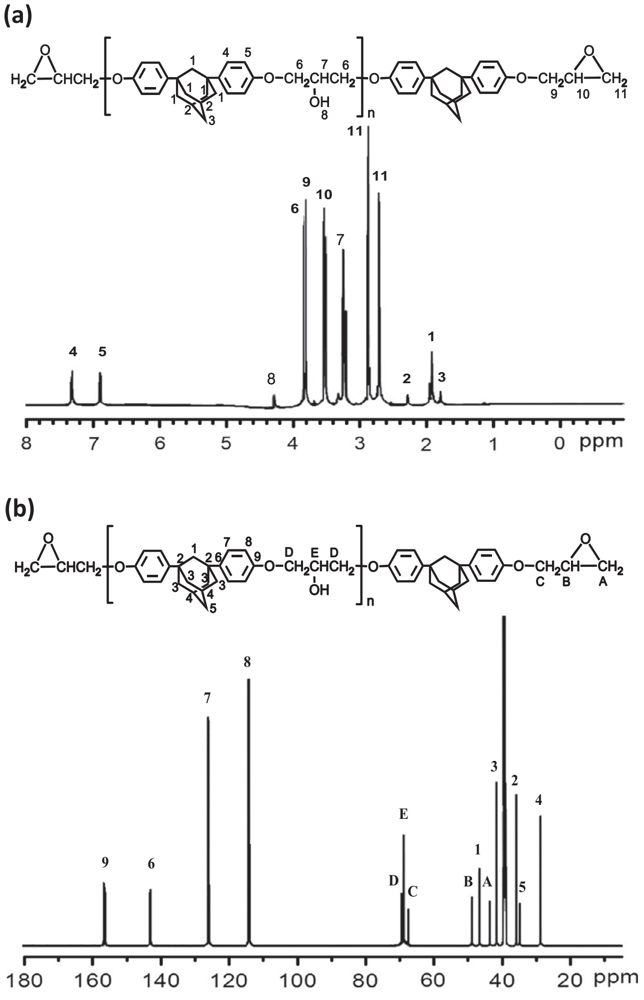
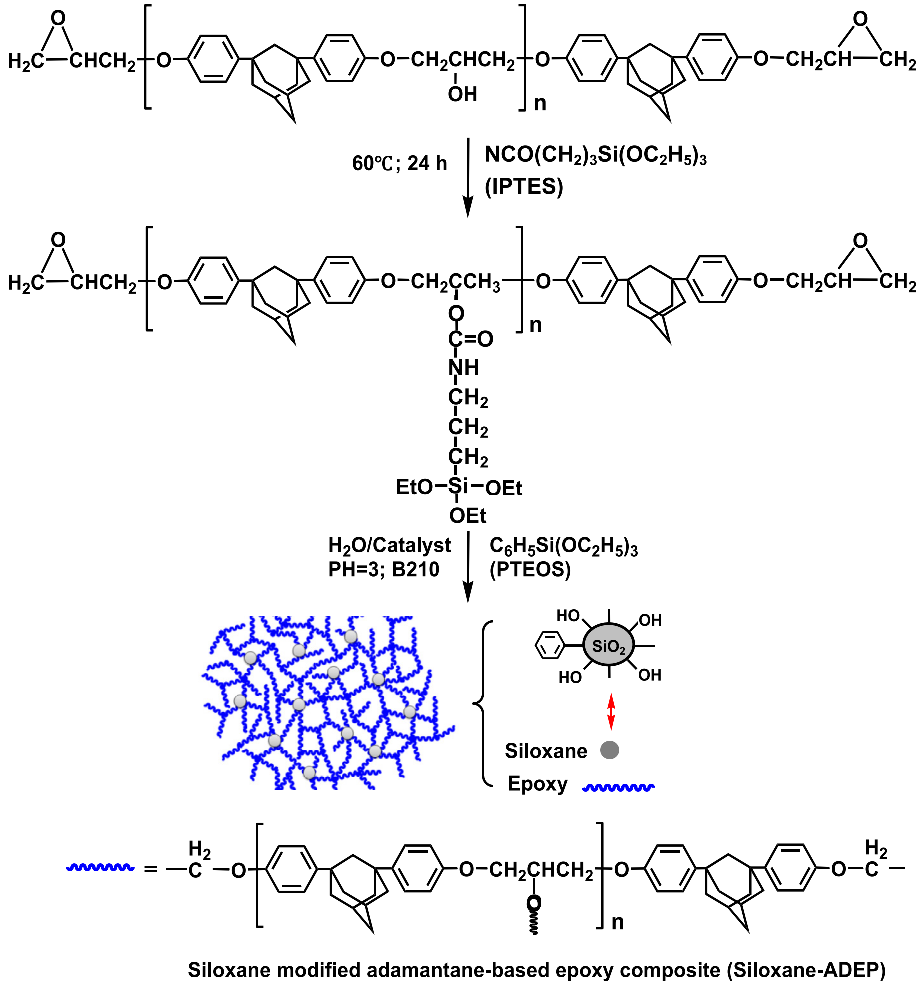


Fig. 2. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of ADGE in DMSO-d$_6$.



Scheme 2. Experimental procedure for the synthesis of Siloxane-ADEP.

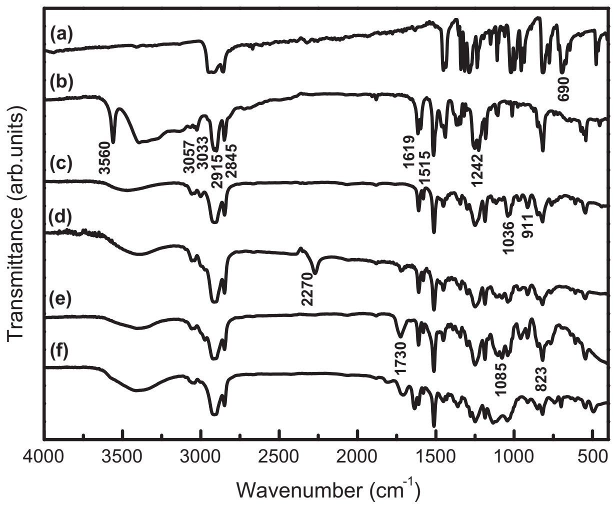


Fig. 3. FTIR spectra of (a) DBAD, (b) HPAD, (c) ADGE, (d) ADGE + IPTES, (e) ADGE + IPTES/24 h and (f) Siloxane-ADEP.

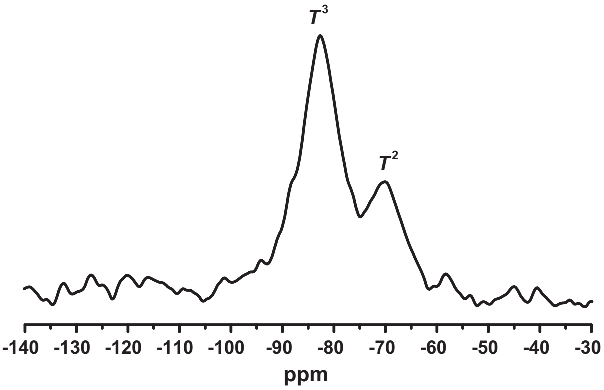


Fig. 4. ^{29}Si NMR spectrum of Siloxane-ADEP composite.

ambient temperature to 800 °C at a heating rate of 10 °C/min, and the gas flow rate was maintained at 50 mL/min. Storage modulus (E') tests were performed using a dynamic mechanical thermal analyzer (PerkinElmer DMA-7) with a temperature range from ambient temperature to 200 °C. A PerkinElmer TMA-7 thermal analyzer was used to determine the coefficients of thermal expansion of the samples. The samples were heated in an air atmosphere from ambient temperature to 100 °C at a heating rate of 5 °C/min.

The dielectric constants of the various epoxy systems were determined using a Novocontrol GmbH (Germany) dielectric spectrometer at room temperature from 100 to 900 MHz. Samples with a diameter of 10 mm and a thickness of 1 mm were dried *in vacuo* at 100 °C until the moisture had been expelled. After cooling to

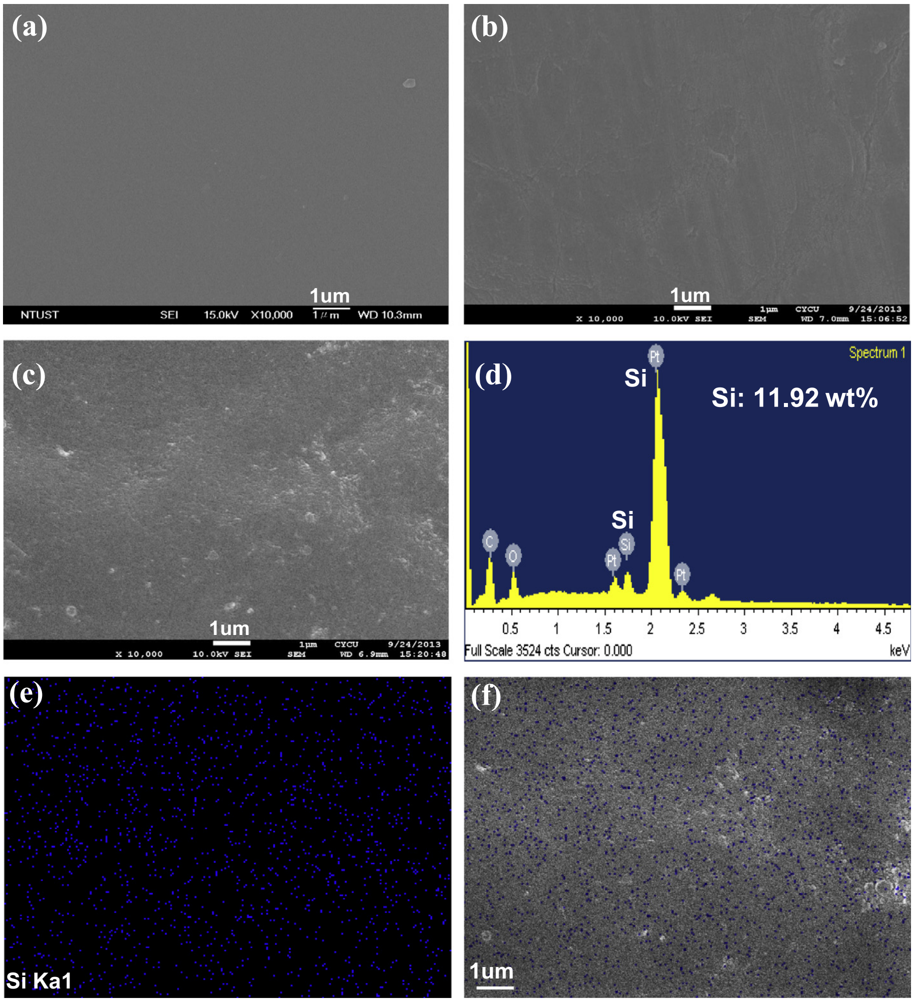


Fig. 5. SEM images of (a) EP904, (b) ADEP, (c) Siloxane-ADEP; (d) EDX, (e) Si-mapping and (f) SEM + Si-mapping images of Siloxane-ADEP.

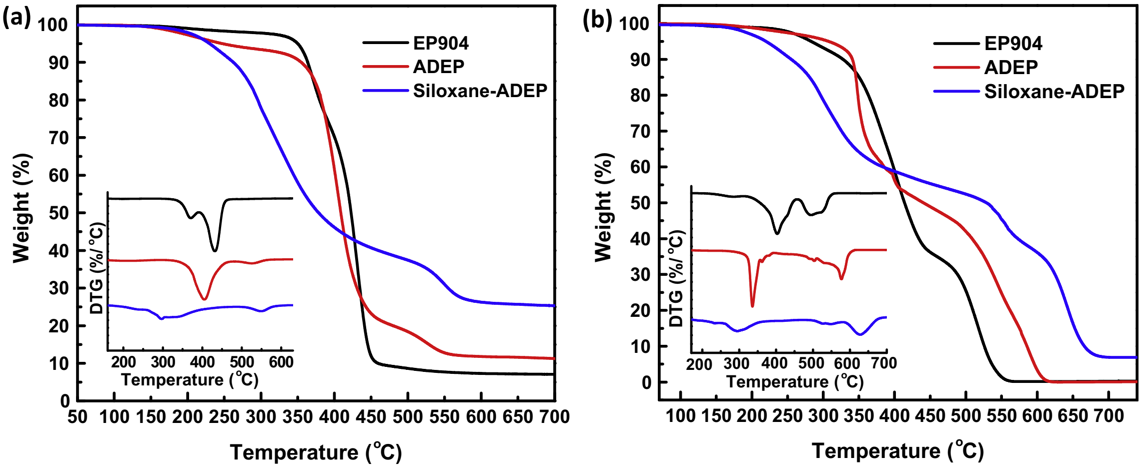


Fig. 6. TGA thermograms of various epoxy systems in (a) N_2 and (b) air.

room temperature, the samples were weighed, placed in 25 °C/100 °C water for 24 h/2 h, and weighed again according to ASTM D-570. The moisture absorption was calculated as follows: weight gain (%) = $(W/W_o - 1) \times 100$, where W is the weight of the sample after being placed in water for a certain period and W_o is the weight of the sample before being placed in water. Light transmittance measurements of the samples before and after thermal aging were performed using a UV–Vis spectrophotometer (UV3101PC, Shimadzu, Kyoto, Japan) over the wavelength range of 300–800 nm.

Table 1
Physical properties of various epoxy systems.

Sample	Storage modulus E' (GPa)	CTE (10^{-6}/°C)	Dielectric constant (MHz)				% H_2O absorption	
			200	400	600	800	100 °C 10 h	30 °C 168 h
Ep904	0.24	782	3.63	3.61	3.64	3.85	2.23	1.99
ADEP	2.10	24	3.07	3.06	3.08	3.07	1.96	1.68
Siloxane-ADEP	0.94	522	4.54	4.39	4.34	4.32	2.42	2.08

3. Results and discussion

3.1. Structural and morphological characterization

Fig. 3 presents FT-IR spectra that provide evidence for the formation of HPAD, ADGE monomer, and Siloxane-ADEP. The characteristic absorption bands of HPAD appeared at 3560 cm^{-1} (free Ar—OH), 3200–3500 cm^{-1} (Ar—OH), 3057/3033 cm^{-1} (aromatic C—H), 2915/2845 cm^{-1} (C—H), 1619/1515 cm^{-1} (aromatic C—C), and 1242 cm^{-1} (alkyl–aryl C—C), and the characteristic peak of the C—Br group (690 cm^{-1}) disappeared. The FTIR spectrum of ADGE exhibited characteristic absorption bands at 1036 cm^{-1} (aromatic C—O—C) and 911 cm^{-1} (oxirane ring), and the characteristic absorption peaks at 3200–3500 cm^{-1} became weak, whereas aromatic C—O—C formation and the epoxy group were apparent. This result indicated that the epichlorohydrin had reacted with the —OH in HPAD.

The characteristic absorption bands of ADGE + IPTES appeared at 3200–3700 cm^{-1} (Si—OH) and 2270 cm^{-1} (N=C=O). Moreover, the intensity and width of the absorption band at approximately 3500 cm^{-1} significantly increased after the epoxy derivatives were modified with IPTES oligomer. After condensation (Fig. 3e), the intensity of the absorption band at approximately 3500 cm^{-1} (Si—OH) decreased and the absorption band of the NCO group disappeared. In addition, the intensities of the absorption bands at 1730 cm^{-1} and 1085/823 cm^{-1} increased due to C=O and Si—O—Si stretches. This result indicated that the NCO group in IPTES had reacted with the —OH in ADGE and that the condensation reaction of Si—OH occurred to form a Si—O—Si bond. Siloxane-ADEP was synthesized from ADGE, IPTES, PTEOS, and curing agent B210. Siloxane-ADEP presented the characteristic siloxane and ADEP peaks. This formed connections between the organic and inorganic phases. There are covalent bonds between the organic and inorganic moieties. In addition, the O—H stretching vibrations of the Si—OH and C—OH groups absorb in the region of 3200–3700 cm^{-1}. The absorption characteristics in that region depend on the degree of hydrogen bonding. Therefore, the intensity and width of the absorption band at approximately 3500 cm^{-1} significantly increased after the epoxy derivatives were modified with siloxane.

^{29}Si NMR provided structural information regarding the type of silicon present in the resin network. Fig. 4 presents the ^{29}Si solid-state NMR spectrum of Siloxane-ADEP. Distinct peaks of the silica network units in the siloxane were observed at −69.8 (T^2) and −83.6 ppm (T^3). T^2 and T^3 denote $R—Si(OSi)_2(OH)$ and $R—Si(OSi)_3$, respectively. The results revealed that T^3 were the major microstructures, and formation of the network structure enhanced the thermal stability and mechanical properties of the epoxy resin.

The compatibility of the organic polymer and siloxane greatly affects the thermal and optical properties. The morphology of the fractured surfaces was observed by SEM, and the EDX mapping technique was used to determine the distribution of silica and the separation of the microphase in the epoxy matrix. Fig. 5 presents SEM, EDX and Si-mapping images of the morphologies of the various epoxy systems. As observed from the SEM images, the cured Ep904 and ADEP exhibited very dense and smooth surfaces. As siloxane was introduced, the surfaces become rougher and exhibited a heterogeneous morphology in the matrix. Moreover, the EDX spectrum of Siloxane-ADEP indicated the presence of a significant amount of silicon in the ADEP matrix. As indicated by the SEM and Si-mapping images (Fig. 5(e) and (f)), the siloxane was uniformly dispersed throughout the ADEP matrix. This result revealed that Siloxane-ADEP exhibited good miscibility between the organic and inorganic phases.

3.2. Thermal and mechanical properties

The thermal stabilities of the various epoxy systems were investigated using TGA/DTG. The weight loss, as well as various pyrolysis steps up to 700 °C in N_2 and air, are shown in Fig. 6(a) and (b). It was observed that the TGA curves of Ep904 and ADEP exhibited similar degradation profiles in N_2, implying a similar mechanism. The incorporation of adamantane into the epoxy resulted in a retarded mass loss rate and an enhanced char yield. This effect was attributed to the fact that the rigid and bulky adamantyl element increased the rigidity of the epoxy chain, which could improve the inherent thermal stability of the thermoset substance. It was observed that the initial thermal decomposition temperatures (250–400 °C) were decreased for Siloxane-ADEP. The initial mass loss was attributed to the decomposition of aliphatic amine segments linking the ADEP units to the silica network. The thermal stability of the graft aliphatic amine segments in Siloxane-ADEP was lower than that of the backbone aliphatic amine segments in ADEP, potentially due to hydrogen-bonding effects. This result may be due to the enhanced heat transfer resulting from the hydrogen-bonding interaction, which leads to a decrease in the scission of aliphatic amine segments in ADEP. The weight loss over the interval of 450–600 °C was attributed to the decomposition of the adamantane moiety and silica network. A higher char yield indicated that the introduction of the siloxane favored the formation of char residue because of the existence of silica in the epoxy matrices.

The TGA/DTG curves, recorded in air, of the various epoxy systems are shown in Fig. 6(b). The major mass loss of epoxy can be attributed to the breakdown of the hydrocarbon soft segment phase (300–450 °C) and the hard segment phase (450–550 °C). It was observed that the thermo-oxidative decomposition temperatures were enhanced for ADEP and Siloxane-ADEP over the interval of 400–650 °C. This relatively high thermo-oxidative stability can be explained by the presence of cyclohexane rings and a —Si—O—Si— inorganic network because the bond dissociation energy of Si—O is higher than that of C—C and C—O. Consistent with the literature on neat resin systems, the Siloxane-ADEP in this study was typically more thermally stable than the adamantane-based epoxy due to the formation of highly crosslinked networks in the former.

The storage modulus (E') and coefficient of thermal expansion (CTE) were used to evaluate the thermo-mechanical stabilities of the various epoxy systems, and the results are summarized in Table 1. The E' and CTE results were of the order ADEP > Siloxane-

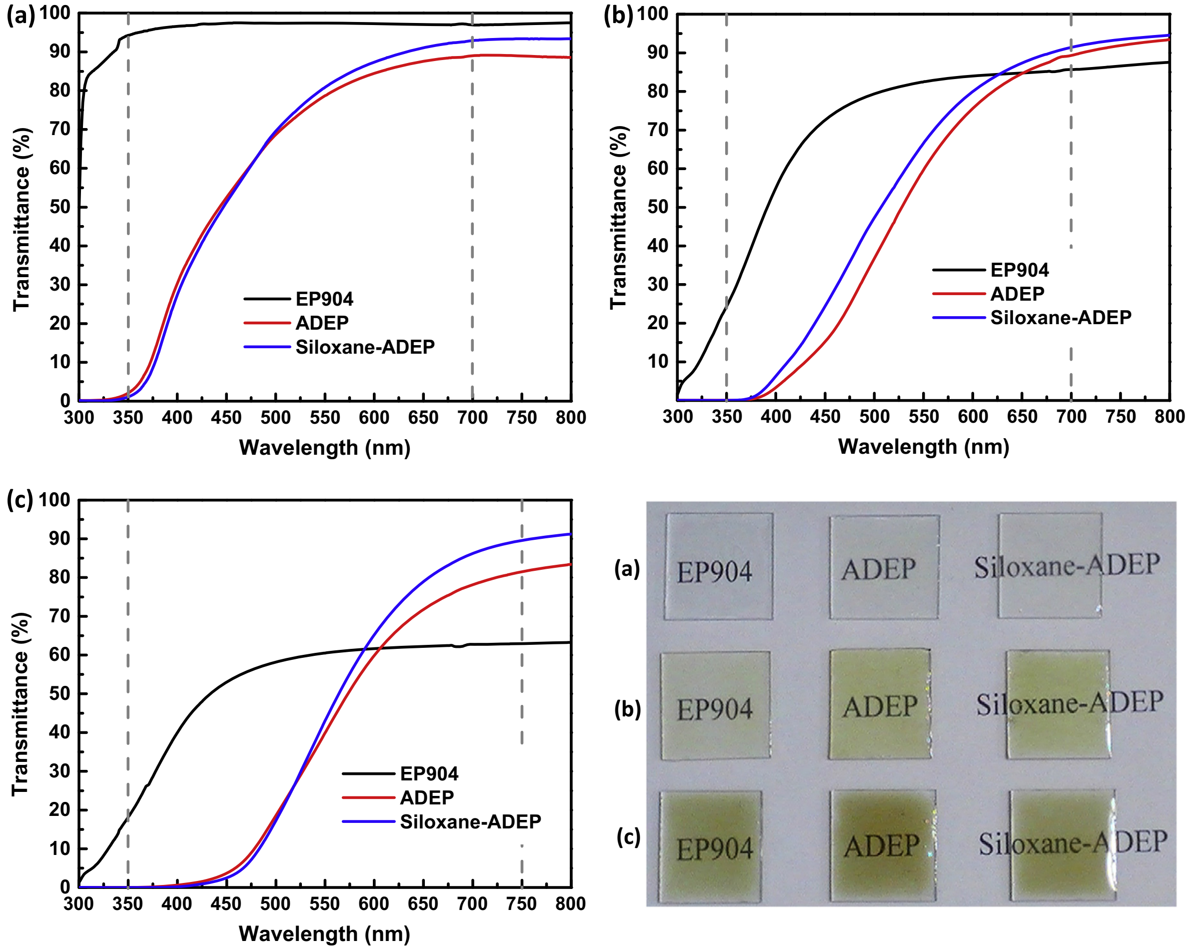


Fig. 7. Transmittance spectra and photographs of the various epoxy systems before/after thermal aging at (a) 90 °C for 24 h (before), (b) 120 °C for 72 h and (c) 120 °C for 168 h.

Table 2
The transmittance on 350 and 700 nm wavelength of various epoxy systems before and after thermal aging.

Samples	Before		90 °C, 168 h		120 °C, 72 h		120 °C, 168 h	
Transmittance (%)	350	700	350	700	350	700	350	700
Ep904	94	97	62	96	24	86	18	63
ADEP	1.9	90	0	86	0	89	0	82
Siloxane-ADEP	1.0	93	0	89	0	91	0	90

ADEP > Ep904 and ADEP < Siloxane-ADEP < Ep904, respectively. These results were generally interpreted on the basis of reinforcement of the adamantane cage diamond-like skeleton in the epoxy matrices, which is able to restrict the motion of the macromolecular chains. After introducing siloxane into ADEP, the steric hindrance in Siloxane-ADEP increased, thereby reducing the dimensional stability. Moreover, Siloxane-ADEP contains bulky pendants, which might increase the free volume and reduce the crosslinking density.

3.3. Dielectric and moisture absorption properties

A lower dielectric constant is one of the most desirable properties for the next generation of electronic devices. The various epoxy systems exhibited similar dielectric constants in the frequency range of 200–800 MHz at room temperature. Table 1 shows the variations in the dielectric constants as a function of the frequency. The dielectric constants of ADEP and Siloxane-ADEP were 3.06–3.08 and 4.32–4.54, respectively. The lower dielectric constants of ADEP are attributed to the fact that adamantane is a fully aliphatic hydrocarbon, thus leading to low hydrophobicity and polarity [21]. On the other hand, the steric hindrance of adamantane decreased the activity of the main chain, and this went against the orientation polarization of polar groups in the cured epoxy polymer. It can be observed that the dielectric constants of Siloxane-ADEP were higher than those of Ep904 and ADEP at all frequencies. This phenomenon was attributed to the lone pair electrons of the Si—OH group of the siloxane, which resulted in the molecule being easily polarized under an electrical field.

Moisture absorption will ionize ionic impurities (e.g., Cl^-) and consequently corrode integrated circuits. Moisture absorption will also increase an encapsulating material's dielectric constant. Therefore, lower moisture absorption is favorable for encapsulating materials. Table 1 summarizes the final moisture absorptions of the three resin films at 100 °C for 10 h and 30 °C for 168 h. Clearly, ADEP had a lower water absorption (%) compared to Ep904. Siloxane-ADEP also had excellent moisture resistance (2.42%/100 °C and 2.08%/30 °C), but under the same conditions, the water absorption of ADEP was only 1.96% (100 °C) and 1.68% (30 °C). It is possible to conclude that the waterproofing effect of the adamantane moiety improved the moisture resistance of the cured ADEP resin. The higher water absorption of Siloxane-ADEP compared with Ep904 and ADEP is likely due to the interaction of the Si—OH group and H_2O (Si—OH···OH_2), which results in increased water absorption (%). However, the moisture resistance properties of Siloxane-ADEP were, in general, satisfactory.

Siloxane-ADEP is soft, resulting in a bendable sample, which means that it can sufficiently protect encapsulated devices from external shock.

3.4. Optical and thermal resistance properties

Fig. 7(a) presents light transmission spectra and photographs of the three resin films after thermal aging at 90 °C in air for 24 h. Discoloration was barely distinguishable by the naked eye for all of the samples. The light transmittance of Ep904 at 350 and 700 nm was greater than 90%. The light transmittance of ADEP and Siloxane-ADEP at 350/700 nm was 1.9/90% and 1.0/93%, respectively. The cutoff wavelengths λ_c of ADEP and Siloxane-ADEP were 327 and 343 nm, respectively. Here, λ_c was defined as the wavelength at which the light transmittance was 0.5%. It can clearly be observed that the spectra ranging from 300 to 350 nm of ADEP and Siloxane-ADEP showed strong absorptions, and there was almost no large change in transmittance at 700 nm (>90%). Interestingly, ADEP and Siloxane-ADEP exhibited novel ultraviolet light-filtering properties when adamantane was introduced.

Fig. 7(b) and (c) and Table 2 present light transmission spectra and photographs of samples aged at 90 and 120 °C for 72–168 h under an air atmosphere in comparison with those of the initial sample before aging. After thermal aging for 120 °C/168 h, the transmittance of the Ep904 epoxy decreased with increasing thermal aging temperature and time. However, when the thermal aging temperature and time were increased, the spectra ranging from 300 to 400 nm of ADEP and Siloxane-ADEP showed a stronger absorption and little change in transmittance at 700 nm. Furthermore, the λ_c of ADEP and Siloxane-ADEP exhibited an almost horizontal bathochromic shift with little change in shape. When the thermal aging temperature and time were varied from 90 °C/24 h to 120 °C/168 h, λ_c ranged from 327 to 420 nm. As indicated by the photographs in Fig. 7, the samples showed good transparency and little yellowing upon thermal aging at 120 °C for 168 h under air, but the UV absorption and visible light transmittance properties were not affected.

It has been reported that electron donor–acceptor interactions may play an important role in UV-filtering properties [22]. There are plentiful strong polar groups, such as amines or hydroxyls, in an epoxy–amine crosslinked system, thus allowing charge-transfer complexes to form between the fullerene derivatives and the epoxy–amine complex, which may enhance the UV light-filtering properties [7]. From a literature study, fullerene derivatives are easily aggregated into crystalline clusters in the solid state and in solution. These nanoaggregations may also be responsible for the light-filtering phenomenon [23]. In the present study, the ADEP and Siloxane-ADEP resins possessed conjugated phenyl chain and polar groups such as carbonyl, amines or hydroxyls in an epoxy crosslinked system. However, no such UV light-filtering properties were observed for Ep904 resin; thus, we hypothesize that the rigid adamantane structure with crystalline clusters as inserted backbone units may enhance the UV light-filtering properties [23].

4. Conclusion

An adamantane-based epoxy resin (ADEP) and a siloxane-modified adamantane-based resin (Siloxane-ADEP) were successfully prepared using the sol–gel copolymerization technique. The adamantane and siloxane moieties were successfully incorporated into the epoxy resin system without phase separation. The cured ADEP and Siloxane-ADEP were superior to epoxy resin in terms of their thermal and mechanical properties. ADEP and Siloxane-ADEP had low dielectric constants and low moisture absorption, and they exhibited little yellowing upon thermal aging at 120 °C for 168 h under air. The UV–Vis transmission spectra revealed that ADEP and Siloxane-ADEP exhibited novel ultraviolet light-filtering properties, and the cutoff wavelength λ_c of these adamantane-containing epoxy membranes can be changed simply by varying the thermal aging temperature. The rigid adamantane structure with crystalline clusters and charge transfer complexes between the adamantane derivatives and the epoxy–siloxane composite are responsible for the UV light-filtering behavior of the adamantane-containing epoxy membranes.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.reactfunctpolym.2015.04.002.

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