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# PEG-based epoxy and epoxy/silica networks: Thermal, mechanical, and thermo-mechanical investigations

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ABSTRACT

A diglycidyl ether resin and an amine hardener, both based on polyethylene glycol (PEG) were synthesized and utilized for preparing new epoxy thermosetting materials. Two popular monomers, i.e. diglycidyl ether of bisphenol A (DGEBA) and/or isophorone diamine (IPDA) were also utilized. Three transparent and rubber-like films were fabricated through one combinational and two non-combinational manners. In the combinational manner, diglycidyl ether of PEG (DGEPEG) and DGEBA with equal moles were cured with equal moles of amine-functionalized PEG (APEG) and IPDA. In the non-combinational manners, at one time, the PEG-based resin was cured with IPDA hardener, and at the other time, DGEBA resin was cured with PEG-based amine hardener. Stoichiometric amounts of epoxy resin and amine hardener were used in all of the curing processes. Three epoxy/silica nanocomposites with silica-loading of 5.0 wt%, and with the same epoxy matrices were also synthesized similarly. Silica nanoparticles were organically modified and amine-functionalized prior to use. The neat epoxy networks and their silica-loaded nanocomposites were characterized by FT-IR, and FE-SEM techniques. The structure and composition of the six networks obtained significantly affect their thermal, mechanical, and thermo-mechanical behaviors. These influencing factors were fully investigated by thermogravimetric analysis, tensile testing, and dynamic mechanical analysis.

## 1. Introduction

Due to their outstanding thermal and mechanical properties, cured epoxy resins are extensively used in various industries as adhesives, coatings, and composite materials [1–4]. Among various kinds of cured epoxy resins, epoxy-amine networks based on diglycidyl ether of bisphenol A (DGEBA) and aliphatic/aromatic amine hardeners have attracted the most attention in recent two decades [5–9]. These glass-like thermosetting materials offer good thermal stability as well as high tensile strength and modulus. Nevertheless, the fracture toughness of DGEBA-amine systems is quite low, and these epoxy networks generally have high brittleness and low elasticity. This drawback significantly restricts their widespread applications, especially if high toughness is required. In the literature, many epoxy additives have been reported in order to improve their toughness, such as reactive rubbers [10,11] and inorganic fillers [12,13]. One other approach to reduce the brittleness of epoxy networks is to utilize glycidyl ethers with more flexible structures [14–16]. Undoubtedly, polyoxyalkylene-based glycidyl ethers are the best choice to fabricate epoxy sheets with lower brittleness and higher elasticity. Among them, diglycidyl ether of polyethylene glycol (PEG) seems to be a unique epoxy resin due to its biocompatibility and the low price of PEG. Networks of this resin have been widely used to produce different types of epoxy-based hydrogels as well [17,18]. On the other hand, in order to enhance the toughness of epoxies, common amine hardeners, such as isophorone diamine (IPDA) and diaminodiphenylsulfone (DDS), can be replaced by ether-containing macrodiamines such as the various kinds of Jeffamines [19–21]. If both epoxy resin and amine hardener are based on polyoxyalkylene chains, even in their low molecular weights, the resulting epoxy networks seems not to have adequate dimensional stability. Therefore, to fabricate epoxy sheets with high mechanical strength, employing well-known DGEBA resin and IPDA hardener along with polyoxyalkylene-based resins and hardeners is unavoidable.

The thermal and thermo-mechanical behaviors of epoxy thermosetting materials can be also reinforced by loading inorganic nanoparticles into the polymer matrix [22–24]. Among them, silica nanoparticles (SNP) are one of the best choices for this purpose [25–28]. Recently, some DGEBA-based epoxy sheets loaded with SNP were fabricated in our laboratory [29]. In this study, the thermal and thermo-mechanical properties of the sheets obtained clearly revealed that the presence of this nanofiller can significantly reinforce these properties. Nevertheless, the obtained glassy sheets were fully brittle due to the rigid structure of their

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initial monomers. Therefore, in this work, we tried to fabricate some other sheets of epoxy networks and epoxy/silica nanocomposites starting from two structurally flexible monomers. Herein, epoxy resin and amine hardener, both, were based on the chemical structure of PEG. However, two popular monomers including DGEBA resin and IPDA hardener were also used in all of the curing processes. One combinational and two non-combinational manners led to epoxy networks with the codes of DGEPEG:DGEBA/APEG-IPDA (A), DGEPEG/IPDA (B), and DGEBA/APEG (C). In addition, silica-loaded nanocomposites of each of these epoxies were also prepared by the same manners. The loading content of the nanofiller was 5.0 wt%, which led to the corresponding nanocomposites encoded with DGEPEG:DGEBA/APEG-IPDA 5.0 (D), DGEPEG/IPDA 5.0 (E), and DGEBA/APEG 5.0 (F). To characterize the resultant epoxies and epoxy/silica nanocomposites, Fourier transform infra-red spectroscopy (FT-IR), field emission-scanning electron microscopy (FE-SEM), thermogravimetric (TG) analysis, tensile testing, and dynamic mechanical analysis (DMA) were used.

## 2. Experimental

### 2.1. Materials

The polyoxyethylene used was purchased from Sigma-Aldrich with a molecular weight of *ca* 600 g mol$^{-1}$ (PEG-600), and dried at 60 °C under vacuum for 24 h. Epichlorohydrin (ECH, 98%) was obtained from Merck, and used as received. DGEBA epoxy resin (D.E.R. 332) was supplied from Sigma-Aldrich with an epoxide equivalent weight of 170.20 g.eq$^{-1}$. Isophorone diamine (IPDA) was obtained from Merck. Both the epoxy resin and the amine hardener were used without further purification. 3-Aminopropyltriethoxysilane (APTES) was obtained from Sigma-Aldrich, and used as received. Silica nanopowder with particle size of 10–20 nm (BET), 99.5% trace metals basis was purchased from Sigma-Aldrich, and dried in a vacuum oven at 120 °C for 1 h prior to use. APTES-modified silica nanoparticles were prepared according to our previous work [29]. Dimethylformamide (DMF) and dichloromethane (DCM), both purchased from Merck, were distilled from calcium hydride. Other chemicals and solvents such as magnesium sulfate, tetrahydrofuran (THF) and diethyl ether (DEE) were purchased from Merck, and used as received.

### 2.2. Synthesis of epoxide-functionalized PEG

Into a round-bottom flask fitted with a dropping funnel, PEG (24 g, 0.04 mol), NaOH (8.0 g, 0.20 mol), and $H_2O$ (1.0 mL) were poured. The mixture was heated to 40 °C, and then ECH (21.6 g, 0.24 mol) was added dropwise, while stirring magnetically. Stirring was continued at this temperature for a period of 1 h. After filtration under reduced pressure, the filtrate was fully washed with DCM solvent. The viscous liquid obtained was eventually dried with $MgSO_4$ and concentrated in vacuum to give the epoxide-functionalized PEG (DGEPEG). In addition, the concentration of epoxide groups in DGEPEG epoxy resin determined by titration was found to be $2.81 \times 10^{-3}$ mol g$^{-1}$ [30].

### 2.3. Synthesis of amine-functionalized PEG

Amine-functionalized polyoxyethylene (APEG) was synthesized according to our previous work [30]. The specific synthetic route employed was identical to that reported, except that herein polyethylene glycol-600 was used instead of polybutylene glycol-1000. Moreover, the concentration of amino groups of APEG hardener determined by titration was found to be $3.21 \times 10^{-3}$ mol g$^{-1}$ [31].

### 2.4. Preparation of epoxy networks

Three neat epoxy networks designated DGEPEG:DGEBA/APEG:IPDA (A), DGEPEG/IPDA (B), and DGEBA/APEG (C) were prepared as follows: Stoichiometric amounts of epoxy resin (DGEPEG and/or DGEBA) and amine hardener (APEG and/or IPDA) were homogeneously mixed with each other using a mechanical stirrer at 80 °C for 10 min. Next, the viscous mixtures of resin/hardener were gently poured into polytetrafluoroethylene (PTFE) molds. The curing process was carried out in a vacuum oven at 80 °C for 48 h.

### 2.5. Preparation of epoxy/silica networks

Three epoxy/silica networks designated DGEPEG:DGEBA/APEG:IPDA 5.0 (D), DGEPEG/IPDA 5.0 (E), and DGEBA/APEG 5.0 (F) were prepared as follows: Firstly, to soften the epoxy resin, it was heated to 40 °C for a few minutes. APTES-modified silica nanopowders (5.0 wt% relative to the weight of the resulting epoxy networks) were gradually added to the heat-softened resin, while vigorously stirring using a mechanical stirrer. After complete addition of silica, the mixture was stirred at the same temperature for another 0.5 h. To achieve a uniform mixture, it was sonicated in an ultrasonic bath for 15 min. Subsequent steps were the same as those described for the neat counterparts.

### 2.6. Characterization

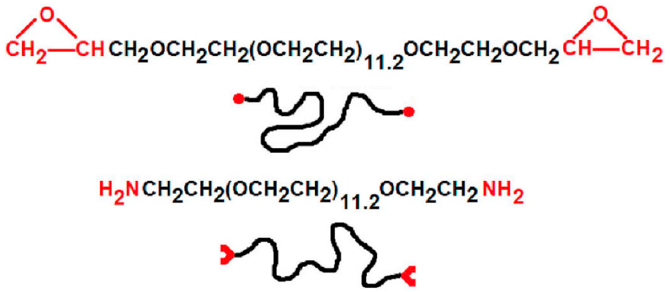
A Parsonic 2600 s ultrasonic water bath with a capacity of 2.6 L was used for homogeneous dispersion of the nanoparticles in the epoxy matrix. FT-IR spectra of the products obtained were recorded on a PerkinElmer RX I FT-IR spectrometer using KBr pellets. A MIRA3 LM TESCAN FE scanning electron microscope was used for FE-SEM analysis. Prior to the capturing, the samples were attached to double-sided carbon tape and coated with 100 nm gold using a DC sputtering coater. Thermogravimetric (TG/DTG) analyses were performed on a BAHR-Thermoanalyse GmbH-Simultaneous Thermal Analyzer STA 503 under an inert argon atmosphere by increasing temperature from 25 °C to 725 °C at a heating rate of 10 °C/min with $Al_2O_3$ as a reference. Dynamic mechanical analysis (DMA) was conducted using a TT DMA, Triton Technology instrument. Rectangular specimens with dimensions of $2 \times 12 \times 40$ mm$^3$ were used. Temperature sweeps were performed at a rate of 3 °C/min and a frequency of 1 Hz, between −50 and + 50 °C. The temperature of the main mechanical relaxation, $T_\alpha$, was evaluated at the temperature of the maximum of the peak of loss factor. $^1$H NMR spectra were recorded on a Bruker Avance 500 spectrometer in DMSO-$d_6$ at 25 °C with tetramethylsilane as an internal standard. Tensile tests were performed according to ASTM D-638 (Type 1) standard dumbbell shaped specimens with 7 mm thickness using a Santam STM-50 test machine at a crosshead speed of 1 mm min$^{-1}$.

## 3. Results and discussion

### 3.1. PEG-based resin and hardener

PEG-600 was used for the synthesis of both epoxy resin and amine hardener. Scheme 1 shows the chemical structures of these two synthesized materials. In an alkaline medium, activated hydroxyl groups of PEG simply attack methylene groups of the ECH molecules during preparation of the corresponding diglycidyl ether. The concentration of epoxide groups of DGEPEG was determined by titration, and the value obtained clearly indicated that nearly all of the hydroxyl end groups of the initial glycol (PEG-600) reacted with ECH. On the other hand, to reach the amine hardener, three consecutive reactions were carried out via two intermediates, i.e., chlorine-capped and phthalimide-capped polyoxyethylenes. Synthetic details are similar to those reported previously for preparing amine-terminated polyoxybutylene [32].

Chemical structures of the PEG-based epoxy resin and amine hardener were fully verified by FT-IR and $^1$H NMR techniques. In the FT-IR spectrum of DGEPEG resin (Fig. 1, top), the absence of an O–H stretching peak at about 3500 cm$^{-1}$ and the presence of the peak



**Scheme 1.** Chemical structures of PEG-based epoxy resin (upper) and amine hardener (lower).

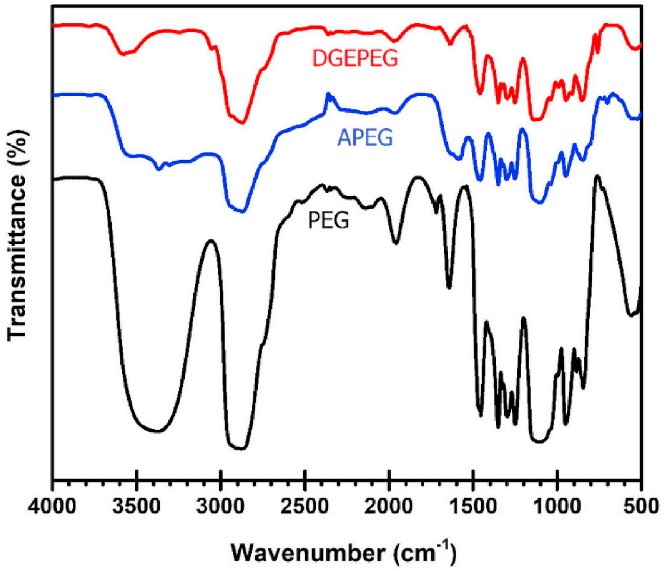


**Fig. 1.** FT-IR spectra of DGEPEG resin (top), APEG hardener (middle) and PEG (bottom).

related to oxirane ring at about 915 cm$^{-1}$ demonstrate the success of the reaction progress. In the FT-IR spectrum of the APEG hardener (Fig. 1, middle), the strong peak associated with the O–H vibration of PEG (Fig. 1, bottom) was replaced by a weak peak within the same region. This peak can be attributed to the stretching vibration of N–H end groups in the amine hardener. Fig. 2 shows the $^1$H NMR spectra of DGEPEG resin (upper) and APEG hardener (lower). The peaks related to the oxirane rings of the DGEPEG resin (peaks attributed to hydrogens "c" and "d") appeared at lower chemical shifts relative to the peaks of the other hydrogens. The diastereotopic hydrogens (hydrogens "$b_1$ and $b_2$" and "$d_1$ and $d_2$") were split by the hydrogen attached to the chiral center (hydrogen "c"). In addition, in the spectrum of the APEG hardener the peaks related to the amine hydrogens did not appear due to fast proton exchange in the solution. As the figure shows, all the peaks which appeared in these two spectra were fully assigned to the corresponding hydrogens in their chemical structures. The number of peaks, the values of the chemical shifts, and the surfaces under the peaks are thoroughly in accordance with the type and the number of attributed hydrogens.

### 3.2. Epoxy and epoxy/silica networks

Three neat epoxy networks and three silica-loaded epoxy nanocomposites, all based on PEG polyether were prepared using combinational and non-combinational manners. Two epoxy resins, i.e. DGEPEG and/or DGEBA, and two amine hardeners, i.e. APEG and/or IPDA, were used. The stoichiometric ratio of amino and epoxide groups was 1.00 for the neat networks ($r = 2[NH_2]_0/[E]_0 = 1.00$, where $[NH_2]_0$ and $[E]_0$ are the initial concentrations of amino and epoxide groups, respectively). This stoichiometric ratio of amino and epoxide groups for epoxy/ASNP networks was not exactly 1.00. The reaction between the amino groups of the functionalized silica and a number of epoxide groups of the epoxy resin somewhat disarranged the balance between amino and epoxide groups in the curing process. However, since the number of amino groups on silica is so low, the disbalancing which occurred was fully negligible. Table 1 presents some information regarding the networks obtained such as the formula of the network, molar ratios of the initial substances, and the manner utilized to obtain the network.

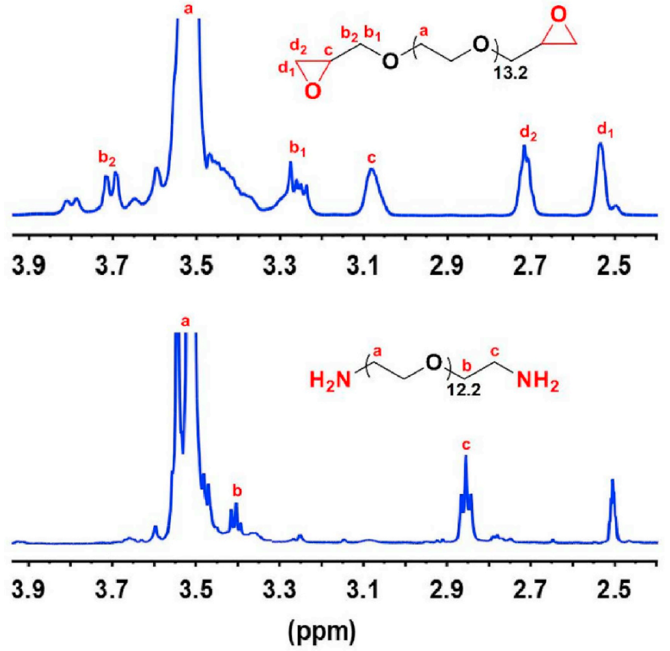


**Fig. 2.** $^1$H NMR spectra of DGEPEG resin (top) and APEG hardener (bottom).

In the combinational manner a two-resin/two-hardener system was stoichiometrically used in the curing process. In this manner equal moles of the resins (DGEPEG and DGEBA) as well as equal moles of the hardeners (APEG and IPDA) were used. In the non-combinational manners, however, stoichiometric amounts of only one resin and one hardener were used. In one of the non-combinational manners the epoxy resin was based on PEG (DGEPEG), and conversely in the other one, the amine hardener was derived from PEG (APEG). Undoubtedly, IPDA with an alicyclic microstructure will be a stronger hardener than APEG with a polyoxyethylene macrostructure. Normally, accessibility of amine groups decreases with increasing size of the hardener molecules. The curing temperature and time used in this study were based on the reactivity of the weaker hardener, i.e., APEG. An amine hardener

**Table 1**
Some information regarding the networks obtained.

| Cods | Formula | Molar rations | Synthesis manner |
|---|---|---|---|
| A | DGEPEG:DGEBA/APEG:IPDA | 1:1/0.5:0.5 | Combinational |
| B | DGEPEG/IPDA | 1/0.5 | Non- Combinational |
| C | DGEBA/APEG | 1/0.5 | Non- Combinational |
| D | DGEPEG:DGEBA/APEG:IPDA/5.0 wt% $SiO_2$ | 1:1/0.5:0.5 | Combinational |
| E | DGEPEG/IPDA/5.0 wt% $SiO_2$ | 1/0.5 | Non- Combinational |
| F | DGEBA/APEG/5.0 wt% $SiO_2$ | 1/0.5 | Non- Combinational |

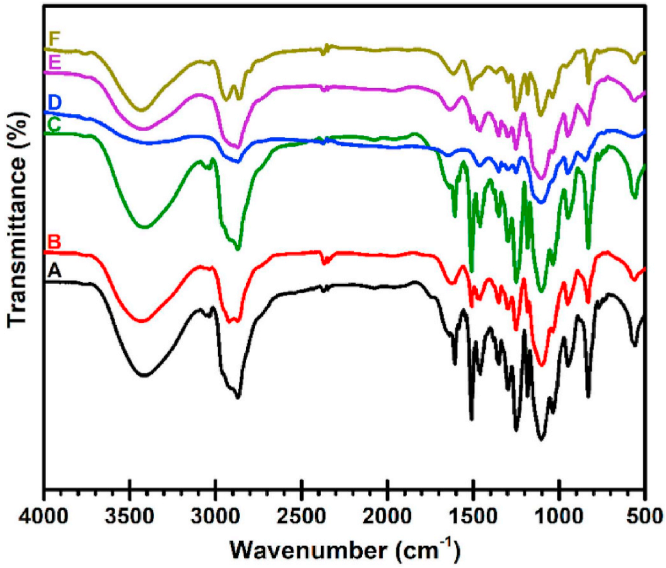


**Fig. 3.** FT-IR spectra of the epoxy and epoxy/silica networks.

with a structure similar to that of APEG takes about two days at 80 °C for complete curing of a DGEBA epoxy resin [33]. Furthermore, to reach the gel point, resin and hardener need to mix with each other, homogeneously, before the main curing process. Herein, in all cases, due to the long molecular size of resin or hardener (or both) a unique curing protocol was used.

Fig. 3 illustrates the FT-IR spectra of the resultant epoxy and epoxy/silica networks. Due to the presence of polyoxyethylene segments as well as linkages such as O–H and N–H in all of the structures, the general pattern of the spectra obtained is similar to each other. In these spectra, the wide and strong peak which appeared over the range 3200–3650 cm$^{-1}$ is related to an O–H stretching vibration. This linkage is formed after the attack of amino groups of hardener to oxirane rings of epoxy resin during the curing process. The stretching vibration of the N–H bond, which must lead to a peak arround 3400 cm$^{-1}$ overlaps with the mentioned peak of O–H. The peaks which appeared at about 2950 and 1100 cm$^{-1}$ are attributed to the stretching vibration of C–H and C–O bonds, respectively.

To investigate the quality of dispersion of ASNP filler within the resulting epoxy matrices, the FE-SEM technique was used. Fig. 4 displays the images taken from the surfaces of neat and silica-loaded epoxy films. The upper row images (A-C), which are related to the neat epoxy networks, have almost similar morphology. In these images, a crack-free and continuous texture can be seen. Instead, the lower row images (D-F), which are related to the silica-loaded epoxy networks, obviously show a heterogeneity in the textures compared to the former images. Nevertheless, no continuous bulks of nanoparticles are observed in these micrographs. Amine-functionalization of the loaded nanoparticles gave them an efficient role in the course of the curing process. In this condition, the functionalized nanoparticles could covalently link to their epoxy matrices. As a result, a better dispersion of the silica nanoparticles can occur. Indeed, the clusters present in these micrographs have been formed from many nano-sized particles of silica.

### 3.3. Heat stability and thermal degradation

Silica nanoparticles were organically modified and amine-functionalized by APTES coupling agent prior to use. This amine-functionalization allowed the nanoparticles to be covalently bonded to the resulting PEG-based epoxy network during the cure process. More filler-matrix compatibility, and consequently better dispersion of the nanoparticles within the polymer matrix occurs in this condition. Fig. 5 shows TG thermograms of the silica nanoparticles used before and after surface modification. The weight residues of SNP and ASNP at 725 °C were ~95% and ~83%, respectively. Hence, about 12% of the weight of ASNP must be organic moiety resulting from the modification process.

Stability towards heat and thermo-degradation behavior for all epoxy networks including the neat ones (A, B, and C) and the ASNP-loaded composites (D, E, and F) were investigated by TG/DTG measurements. Among the neat networks, the heat stability order was found to be B > A > C. The hardener used in the synthesis of network B, i.e. isophorone diamine, has a rigid microstructure. Instead, to reach network C, a flexible macrostructure, i.e. amine-terminated polyoxyethylene, is used as the reaction hardener. In general, heat stability of an epoxy network increases with increasing crosslink density. On the other hand, the crosslink density increases with decreasing molecular size of the hardener used. Accordingly, IPDA hardener led to an epoxy network with more heat stability than that obtained from the APEG hardener. Moreover, incorporation of organically modified silica nanoparticles (ASNP) into the prepared epoxy networks significantly affected the heat stabilities. When the networks loaded by silica nanoparticles (networks D, E, and F) are compared with their neat counterparts (networks A, B, and C), the outstanding effect of these nanoparticles can be easily understood. Fig. 6 displays TG/DTG thermograms of the resulting PEG-based epoxy networks in the thermal range of 25–725 °C. A one-step thermal degradation occurred for all of them at temperatures above 325 °C. Some thermal data such as temperatures of 5% and 10% weight loss (Td5% and Td10%), temperature of maximum weight loss (Td max), and the amount of carbonized residue (char yield) are also tabulated in Table 2.

### 3.4. Tensile strength investigation

Ultimate tensile strength (UTS), often shortened to tensile strength, is measured by the maximum stress that a material can withstand while being stretched or pulled before breaking. Also, elongation at break is the ratio between increased length and initial length after breakage of the tested specimen at a controlled temperature. In general, the combination of ultimate tensile strength and elongation at break can be a good estimation for the toughness of a polymeric material. These two mechanical characteristics were measured for four films prepared (films A, B, C, and D). Herein, the presence of oxyethylene flexible units in the structure of the networks obtained lead to relatively low tensile strength values. Instead, the values of elongation at break significantly increased due to these units. Among the silica-unloaded films, the film obtained from the combinational manner (film A) showed the most value of tensile strength. The other two neat networks also did not show equal amounts of tensile strength. If the amine hardener (compared with the epoxy resin) is based on PEG, the resulting network will have superior tensile strength. Moreover, the neat epoxy films could be significantly elongated prior to break, and their elongation at break was found to be about 25%. On the other hand, the presence of silica nanoparticles causes an appreciable increase in both the tensile strength (~0.5 MPa) and the elongation at break (~8%). As stated, simultaneous enhancements in tensile strength and elongation at break indicates an enhancement in the toughness of the specimen under study. Hence, the silica-loaded film D has greater toughness than its neat counterpart (film A). Table 3 presents the results of ultimate tensile strength and elongation at break for films of the three neat networks (films A, B, and C) as well as one of the epoxy/silica films obtained from the combinational manner (film D).

### 3.5. Loss factors and storage moduli

The resulting PEG-based epoxy and epoxy/silica networks were examined by DMA technique. Fig. 7 illustrates Tan δ (loss factor)-temperature profiles of the neat epoxy networks (A, B, and C) and the

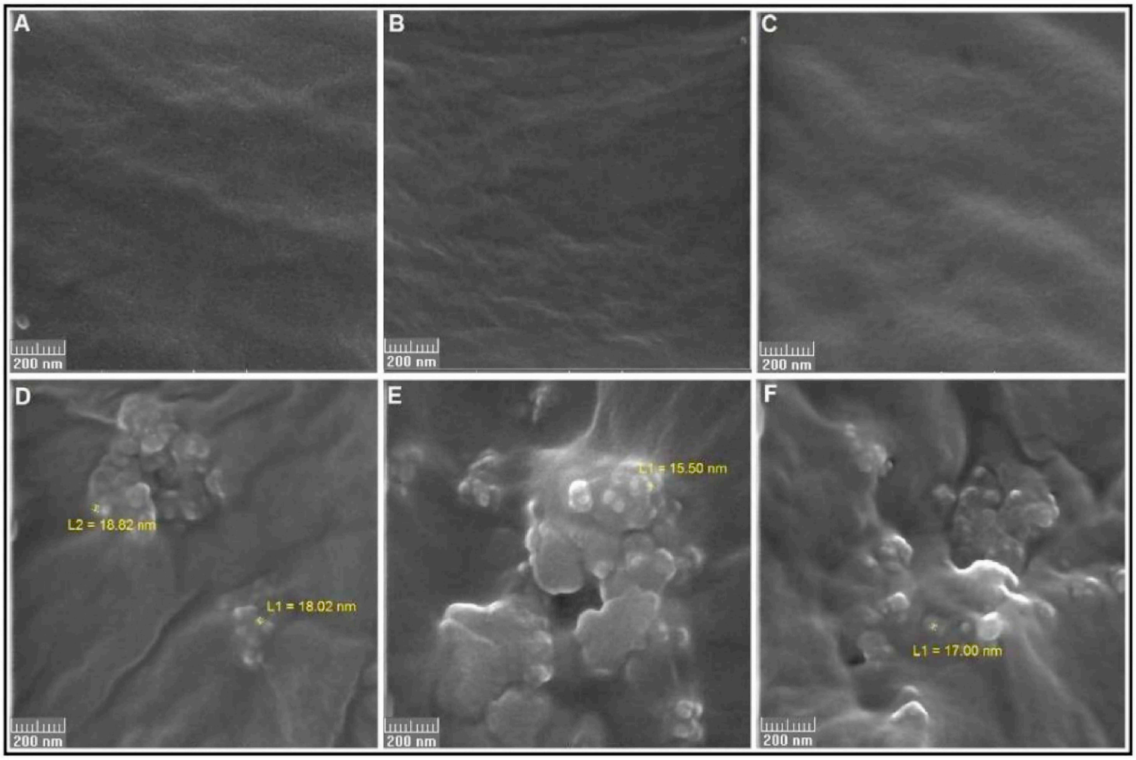


**Fig. 4.** FE-SEM images taken from the surfaces of neat and silica-loaded epoxy films.

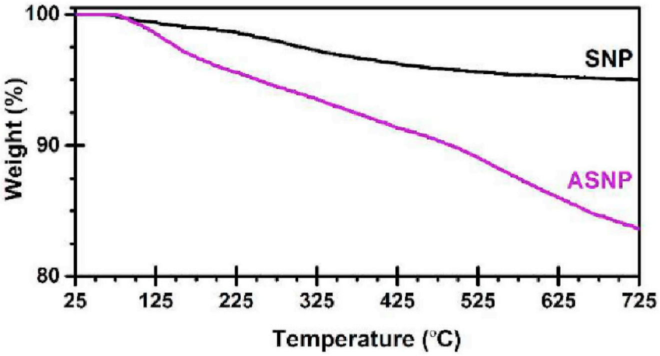


**Fig. 5.** TG thermograms of the silica nanoparticles used before and after surface modification.

epoxy/silica nanocomposites (D, E, and F). The peaks associated with their α-relaxations ($T_g$ values) appeared in the thermal range of (−)27 - (+)20 °C. This is quite reasonable since polyoxyethylene segments of PEG strongly increase chain mobilities, leading to significant decreases in the $T_g$ values. Hence, all of these thermosetting materials are found to be rubber-like at room temperature. On the other hand, among the six networks prepared, the silica-containing networks had greater $T_g$ values than their neat counterparts. As Table 4 shows, this enhancement in $T_g$ value was found to be more than 20 °C for network E. The amine-functionalized silica nanoparticles can restrict the macromolecular motions due to their strong interactions with the epoxy matrix. Amine-functionalization of the inorganic nanoparticles allowed them to be covalently linked to the organic polymer during the curing process. Consequently, homogeneous dispersion of the nanoparticles into the PEG-based epoxy network can occur in this condition. In addition, the nanoparticles caused a decrease in the height and an increase in the width of the peaks which appeared (E and F in comparison with B and C, respectively), which is in agreement with those reported in the literature [34]. In general, incorporation of inorganic nanoparticles into polymer matrices expands the thermal range associated with α-relaxations. Another important result obtained from the Tan δ-temperature profiles is that if the epoxy resin (not amine hardener) is based on PEG, a greater decrease in the $T_g$ value will occur. This seems to be reasonable because in the curing process 1 mol of hardener reacts with 2 mol of resin. As a result, network C with the formula of DGEBA/APEG has the higher $T_g$ value in comparison to the other two neat networks (A and B).

DMA measurements also gave us some important information regarding the storage moduli (E′ values) of the epoxy networks vs. temperature. The storage modulus of a polymer is a measure of its elastic response, and is related to the stored energy. Fig. 8 shows the E′ values of the neat epoxy networks compared with those of epoxy/silica nanocomposites. Although, at temperatures below −35 °C, the neat networks A and B had storage moduli greater than the corresponding epoxy/silica networks (D and E), at higher temperatures from −35 °C to the $T_g$ (glassy region) and at the temperatures above $T_g$ (rubbery region), the silica-containing epoxy networks showed better behavior. Among the neat networks, network A exhibited the highest values of storage moduli from −50 °C to about −30 °C. This means that if polyoxyethylene units are used alongside the rigid structures of DGEBA and IPDA in the formulas of both resin and hardener, the resulting epoxy networks will have higher modulus values. This indicates that the use of a combinational model in the utilization of resin and hardener is a superior choice from a storage moduli point of view. Furthermore, when the E′ values of the neat network C are compared with those of epoxy/silica F, the reinforcing role of silica nanoparticles can be realized more clearly. This silica-loaded network behaved obviously better than the neat network C throughout the temperatures investigated.

## 4. Conclusions

The most popular polyoxyalkylene namely PEG was used for preparing both epoxy resin and amine hardener. The PEG-derived epoxy resin (DGEPEG) was then cured by the PEG-derived amine hardener

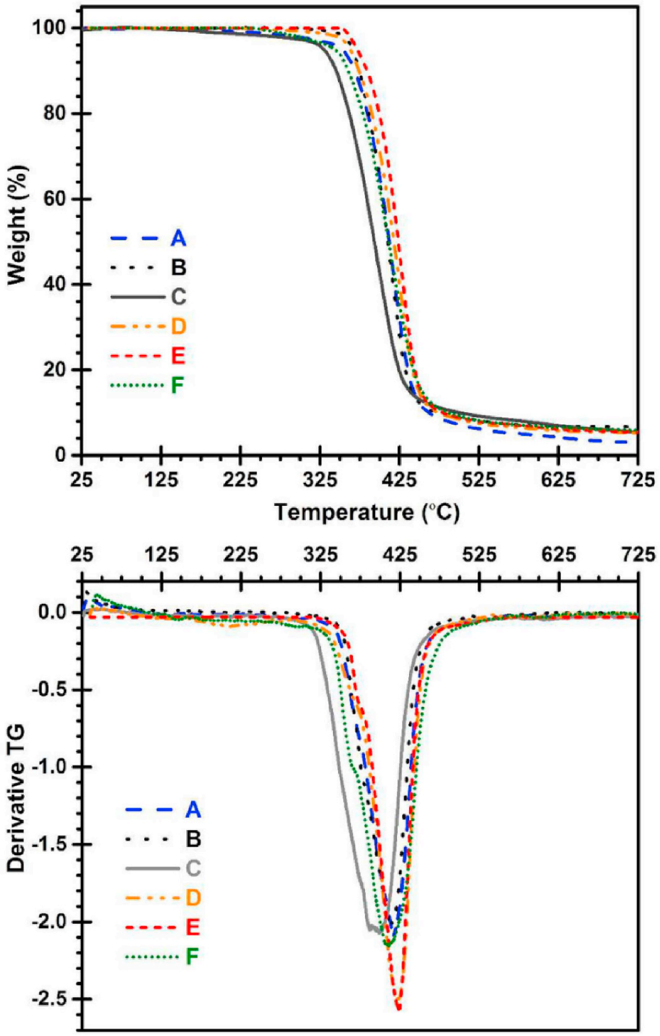


**Fig. 6.** TG/DTG thermograms of the resulting PEG-based epoxy networks.

**Table 2**
Some thermal data obtained from the TG/DTG thermograms.

| Cods | [a] $T_{d\ 5\%}$ (°C) | [b] $T_{d\ 10\%}$ (°C) | [c] $T_{d\ max}$ (°C) | [d] CY (%) |
|---|---|---|---|---|
| A | 352 | 369 | 416 | 2.92 |
| B | 366 | 375 | 413 | 6.56 |
| C | 330 | 345 | 405 | 5.45 |
| D | 362 | 374 | 426 | 5.20 |
| E | 371 | 384 | 424 | 5.90 |
| F | 344 | 361 | 414 | 5.45 |

[a] Temperature with 5% weight loss from TG thermograms.
[b] Temperature with 10% weight loss from TG thermograms.
[c] Temperature with maximum weight loss from DTG thermograms.
[d] Char Yield at 725°C.

**Table 3**
Tensile strength and elongation at break for films A, B, C, and D.

| Cods | Formula | Tensile strength (MPa) | Elongation at break (%) |
|---|---|---|---|
| A | DGEPEG:DGEBA/APEG:IPDA | 0.69 | 21 |
| B | DGEPEG/IPDA | 0.60 | 23 |
| C | DGEBA/APEG | 0.65 | 23 |
| D | DGEPEG:DGEBA/APEG:IPDA/5.0 wt% $SiO_2$ | 1.11 | 29 |

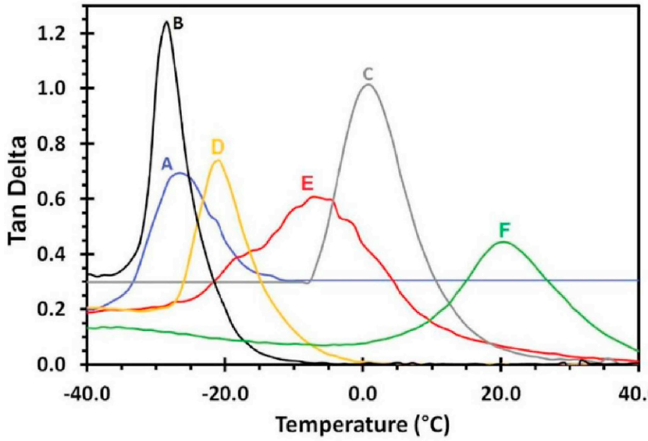


**Fig. 7.** Tan δ-temperature profiles of the neat epoxy networks (A, B, and C) and the epoxy/silica nanocomposites (D, E, and F).

**Table 4**
$T_g$ values of the neat epoxy networks (A, B, and C) and the epoxy/silica nanocomposites (D, E, and F) obtained from Tan δ-temperature profiles.

| Cods | Formula | $T_g$ (°C) |
|---|---|---|
| A | DGEPEG:DGEBA/APEG:IPDA | −26 |
| B | DGEPEG/IPDA | −27 |
| C | DGEBA/APEG | +2 |
| D | DGEPEG:DGEBA/APEG:IPDA/5.0 wt% $SiO_2$ | −20 |
| E | DGEPEG/IPDA/5.0 wt% $SiO_2$ | −6 |
| F | DGEBA/APEG/5.0 wt% $SiO_2$ | +20 |

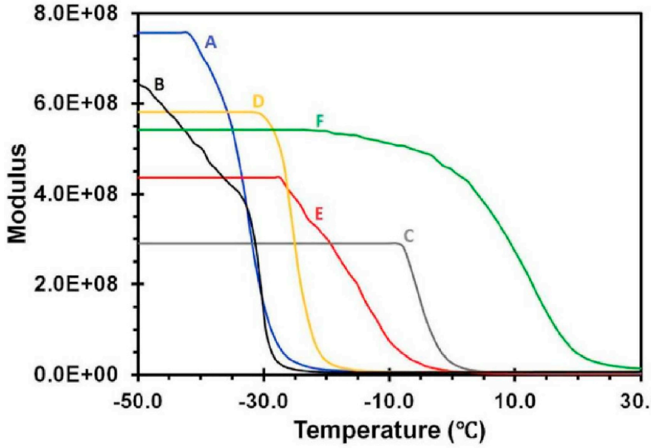


**Fig. 8.** Storage moduli of the neat epoxy networks (A, B, and C) and the epoxy/silica nanocomposites (D, E, and F).

(APEG). In order to achieve better thermal, mechanical, and thermomechanical properties, two rigid structures, i.e. DGEBA resin and IPDA hardener, were also used. Two combinational and non-combinational manners with/without amine-functionalized silica nanoparticles were performed in the curing processes. The presence of nano-sized silica particles was verified by FE-SEM micrographs. Among the neat networks obtained, the network cured by IPDA hardener showed the most thermal stability. It was found that the nanoparticles improved the heat-stability of the epoxy thermosetting materials. The network obtained from combinational manner, i.e., network A, showed the most ultimate tensile strength and elongation at break. Both of these mechanical properties increased by increasing the amine-functionalized silica nanoparticles. As a result, the toughness of the epoxy networks was reinforced by adding ASNP filler. In addition, the loaded nanoparticles affected the storage and loss moduli, and consequently the loss factors (Tan δ). The $T_g$ values could significantly increase by adding the nanoparticles. To summarize, it seems that among all of the epoxy networks prepared, network D which resulted from the combinational manner and possessing amine-functionalized silica nanopowder, showed the best behavior especially from a mechanical point of view.

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