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Physical miscibility and chemical reactions between diglycidylether of bisphenol-A epoxy and poly(4-vinyl phenol)

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Abstract

Physical miscibility at ambient and chemical interactions at elevated temperatures between a difunctional epoxy of diglycidylether of bisphenol-A (DGEBA) and a linear phenylhydroxyl-containing polymer, poly(4-vinyl phenol) (PVPh), were investigated by differential scanning calorimetry, Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy, and solid-state ^{13}C nuclear magnetic resonance (NMR). The DGEBA/PVPh mixture was proven to be homogeneous and miscible. At elevated temperatures, the epoxy/PVPh mixture developed a network-like homogeneous solid, which was a result of reactions between the epoxide of DGEBA epoxy and phenylhydroxyl of the linear PVPh polymer. By using FT-IR and solid-state ^{13}C NMR techniques, mechanisms of reactions leading to a homogeneous network between the DGEBA epoxy resin and PVPh polymer have been probed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Diglycidylether bisphenol-A epoxy; Poly(4-vinyl phenol); Miscibility

1. Introduction

Mixtures of linear polymers with uncured liquid epoxy resins might form homogeneous blends/mixtures before curing. But most often these homogeneous blends would turn into networks of phase separations after they undergo cross-linking cure reactions [1–4]. Complete network homogeneity, either due to physical miscibility, chemical bonding, or copolymerization, in cured polymer/epoxy networks is quite rare. The hydrogen bonding interaction between the ether group of poly(ethylene oxide) (PEO) and the hydroxyl group of diglycidylether of bisphenol-A (DGEBA) epoxy was observed before and after cure, and the hydrogen bonding interaction was considered to be one of the main factors for the physical miscibility in the cross-linked network of thermoplastic–thermosetting system of PEO/DGEBA cured with a common curing agent of 4,4′-diamino diphenylsulfone (DDS) [5–8]. In addition, cured epoxy/bisphenol-A polycarbonate (PC) network is homogeneous, which has been proven to be resulting from the chemical links between these components [9]. Further, we have reported the effects of polymeric additives, PC, polyetherimide (PEI) and poly(hydroxyl ether of bisphenol-A) (phenoxy), in epoxy systems on the epoxide reactives. In our recent studies, it was also found that a homogeneously miscible cross-linked network was demonstrated in DGEBA/poly(4-vinyl phenol) (PVPh) with a curing agent, DDS. Therefore, it is of great academic interests to probe the mechanisms of phase homogeneity in the cross-linked networks comprised of networking DGEBA/DDS and linear polymer.

For DGEBA, it has been known that the cure reactions can be promoted with catalysis effects of –OH group [10]. In addition, some suggested that a catalysis effect in observing that the side-branching in epoxide resins [11,12] may be a result of epoxide groups reacting directly with the phenylhydroxyl groups. Other studies [13] have also pointed out that isomerization of tetraglycidyl-4,4′-diaminodiphenylmethylene (TGDDM) can proceed at high temperatures and produce various low-M_w species with —OH or aldehyde C=O groups.

By using Fourier-transform infrared spectroscopy (FT-IR) studies, Coleman et al. [14,15] found interesting shift trends in the infrared bands attributed to varying intermolecular bonding interactions between, e.g. PVPh hydroxyl and the carbonyl-containing polymers (e.g.

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poly(ε-caprolacton) or poly(vinyl pyrrolidone), or the ether-containing polymers such as PEO, poly(vinyl methyl ether), poly(vinyl ethyl ether), or poly(vinyl isobutyl ether). Zhang et al. [16–18] have utilized the solid-state ^{13}C NMR technique to investigate on interactions or reactions between PVPh and the ether-containing polymers (e.g. PEO) or carbonyl-containing polymers such as PMA and PMMA. Qin et al. [19] have also shown that the phenol groups in neat PVPh can be either hydrogen bonded (self-associated) or non-hydrogen bonded, based on FTIR and ^{13}C NMR results. Owing to the insolubility of cured thermosetting resins, solid-state NMR is indeed a powerful technique that has been utilized in analyzing the reactions of epoxy resins or novolac resins cured with hardeners (hexamethylenetetramine) [20–22].

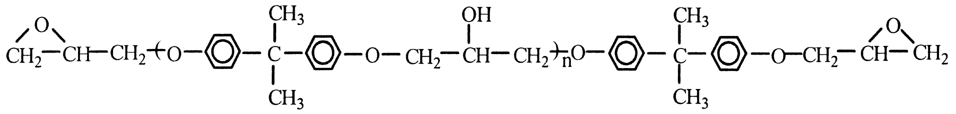
What promoted this study was an observation that, during melt-blending of PVPh with the epoxy resin, the viscosity of the DGEBA/PVPh increased rapidly and unexpectedly at the mixing temperature of ca. 150 °C, before the introduction of the curing agent, DDS. The fact suggests that the briefly heated PVPh/epoxy mixtures apparently became gelled, in absence of DDS. This apparently was due to either physical gelling or a chemical-bonding formation. Thus, this study aimed at two objectives. One involved clarification of physical gelling vs. chemical reactions between the DGEBA monomers and PVPh upon mixing temperatures of 150 °C or above. The other objective was to investigate mechanism of homogeneous network comprised of linear polymer and cross-linking epoxy. To avoid unnecessary complexity introduced by a third component, no curing agents were added in the binary DGEBA/PVPh mixture. Mechanisms of any chemical reactions, if present, leading to networking molecular structures in DGEBA/PVPh were proposed.

2. Experimental

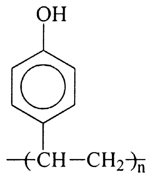
2.1. Materials and sample preparation

DGEBA was obtained from Fluka Co. (USA) with an epoxide equivalent weight of 178 g (or a degree of polymerization, $n \approx 0.04$). PVPh was obtained from a specialty polymers supplier (Polysciences, Inc., USA) with $M_v = 2.2 \times 10^4$ g/mol and $T_g = 153$ °C. The chemical structures of DGEBA and PVPh are as follows:

DGEBA:



PVPh:



DGEBA/PVPh mixtures were prepared by solution-blending and casting using tetrahydrofuran (THF) at room temperature. The sample casting condition of DGEBA/PVPh mixtures was performed under a hood at controlled temperature, 45 °C for 12 h. The solvent in the cast-film was then removed in a vacuum at 80 °C for 96 h to insure complete drying. The cast and dried mixtures were then subjected to designated isothermal temperatures for various times for sample preparations.

2.2. Apparatus

The glass transition temperatures and other thermal transitions of the blend samples were measured with a differential scanning calorimeter (Perkin–Elmer DSC-7) equipped with a mechanical intra-cooler (down to −60 °C) and a computer for data acquisition/analysis. Unless otherwise specified, all T_g measurements were made at a scan rate of 20 °C/min on second scanning and taken as the onset temperature of the transition. The morphology of the gelled/solidified DGEBA/PVPh blends after prescribed thermal treatments at elevated temperatures was examined using a scanning electron microscope (SEM; JEOL JXA-84). The fracture surfaces of the samples were coated with gold by vapor deposition using a vacuum sputter.

Two spectroscopic techniques were used. Fourier-transform infrared spectroscopy (FT-IR Nicolet Magna-560) was used for investigating molecular interactions between the constituents. Spectra were obtained at 4 cm^{-1} resolution and average were obtained from at least 64 scans in the standard wavenumber range of 400–4000 cm^{-1}. Thin films for FT-IR studies were obtained by casting DGEBA/PVPh solutions onto potassium bromide (KBr) disks at 45 °C and then removed in vacuum at 80 °C. When the samples were dried completely, IR characterization was performed as soon as possible to avoid moisture effect on the KBr pellets. For evaluation of chemical reactions at high temperature, samples were heated at designated thermal treatments (isothermal 177, 187, or 197 °C for 1 h). The samples cast

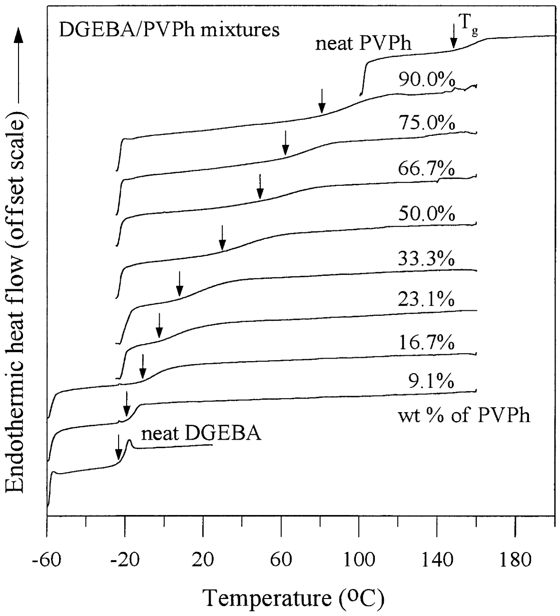


Fig. 1. DSC thermograms of unheated DGEBA/PVPh blends of various compositions.

on KBr pellets were first heated, cooled to ambient, and then examined using FT-IR.

To determine the solid-state network structure, solid-state ^{13}C cross-polarization (CP)/magic angle spinning (MAS) NMR was performed on a Bruker AVANCE-400 spectrometer, equipped with a Bruker double-tuned 7 mm probe, with resonance frequencies of 100.62 MHz for ^{13}C nuclei and 400.13 MHz for ^{1}H nuclei. The Hartmann–Hahn condition for $^{1}H \rightarrow {}^{13}C$ CP experiments was determined using adamantane. The ^{13}C chemical shifts were externally referenced to tetramethylsilane.

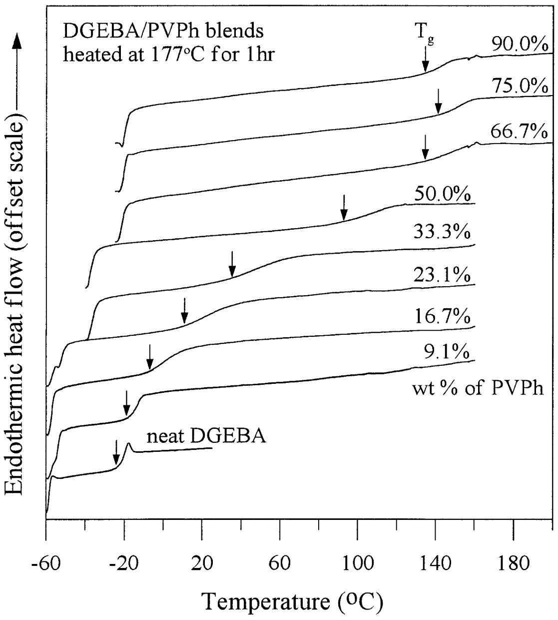


Fig. 2. DSC thermograms of heated DGEBA/PVPh blends (heating for 1 h at 177 °C) of various compositions.

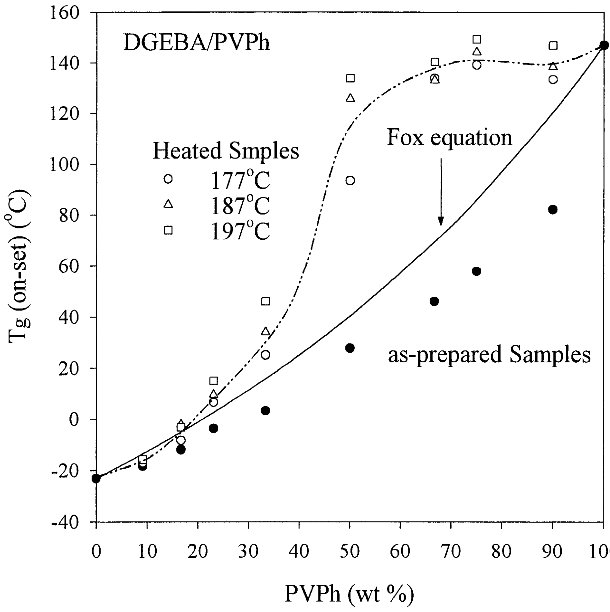


Fig. 3. Comparisons of T_g for DGEBA/PVPh blends before and after isothermally heating at 177, 187, and 197 °C, respectively, for 1 h.

3. Results and discussion

Fig. 1 shows that the DSC thermograms exhibit a single glass transition temperature for all the as-prepared DGEBA/PVPh blend samples prior to being exposed to 177 °C or any other high temperatures. Miscibility of the as-prepared blends in the whole composition range could be concluded from the appearance of single and relatively sharp T_g in the DSC thermograms for the blends. Furthermore, the DGEBA/PVPh blends were subsequently heated at several isothermal temperatures (177, 187, and 197 °C) for 1 h.

DSC characterization was performed on these post-heated blends to determine the glass transition temperatures. Fig. 2 shows the thermograms of the heated DGEBA/PVPh blends of various compositions. All blends were subjected to heating at 177 °C for 1 h prior to DSC characterization. Similar results were obtained for the samples heated at the other two higher temperatures (187 and 197 °C), and thus, their DSC results are not shown here for brevity. All the heated blends showed a single T_g, whose temperature, however, is elevated in comparison to that of the unheated blend. The single T_g again indicated a homogeneous phase in the heated blends. All the T_gs of the heat-treated DGEBA/PVPh blends are now significantly higher in comparison to the unheated one, but the extent of T_g increases seemed to be dependent on the blend compositions. Furthermore, the T_g transition breadth for the heated DGEBA/PVPh blends (especially the intermediate compositions) are more broadened in comparison to the unheated ones, suggesting that the molecular state of inter-chain mixing between DGEBA and PVPh might have changed in the micro-heterogeneity scale.

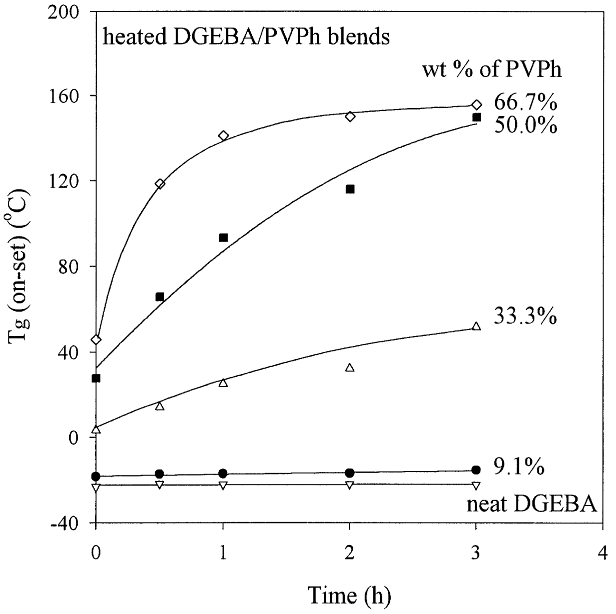


Fig. 4. T_g of heated DGEBA/PVPh blends (compositions as indicated) as a function of time at 177 °C.

Heat-treatments of the blends at the other two temperatures (187 and 197 °C) resulted in similar and the DSC traces are not repeatedly shown here for brevity.

To show the quantitative composition dependence of the transition behavior of all DGEBA/PVPh blends prior to and after the heating treatments, their T_gs were plotted as a function of blend composition. Fig. 3 summarizes the T_g measured as a function of composition for the as-cast blends (filled circles), in comparison to those for the blend samples heated for 1 h at the three isothermal temperatures of 177, 187, and 197 °C, respectively (open circles, triangles, and cubes). The commonly used model of the Fox equation ($1/T_g = w_1/T_{g1} + w_2/T_{g2}$) for describing the T_g behavior of copolymers was plotted as a solid curve for comparison with the experimental data. The T_g behavior of as-prepared blends of DGEBA/PVPh is distinctly miscible; however, its T_g-composition relationship exhibits a slight negative deviation from the Fox equation ($1/T_g = w_1/T_{g1} + w_2/T_{g2}$). This result suggested that the mixing state between DGEBA and PVPh in the as-prepared (unheated) blends were probably less than ideal. It is yet to be understood whether or not some types of specific interactions might exist between the polar groups of these two components. On the other hand, the blend mixtures of DGEBA/PVPh of various compositions after heating exhibited a distinct elevation of T_g. Interestingly, the T_g increase after heating was found to be especially significant for the heated DGEBA/PVPh blends of the PVPh-rich compositions (PVPh wt% between 50 and 100), as shown by the asymmetrical and notably large positive deviation from the Fox model. Furthermore, the positive deviation from the Fox equation of the experimental T_g data for the heated DGEBA/PVPh blend indicated that the interactions between these two components after heating might no longer be interpreted by a simple physical state of mixing. Nor can this be interpreted by specific interactions, such as hydrogen bonding.

The blends after heating apparently gelled and solidified, thus, the interactions responsible for the T_g increase in the heated DGEBA/PVPh blends are likely stronger than regularly physical/polar/H-bonding forces. These results indicated that chemical reactions between DGEBA and PVPh might have occurred after the heating at elevated temperatures. In addition, the increase of the T_g of the heated blends was more significant for those of higher PVPh weight fractions. Owing to the limiting reagent, it was observed that the reacted equivalence of PVPh was more than that of DGEBA. The extents of chemical reactions between DGEBA and PVPh were affected not only by the temperature but also by the PVPh contents in the blends.

To explicitly show the increase of T_g as a function of time of heating imposed on the blends as well as dependence of compositions, determination was made on T_g of the DGEBA/PVPh blends for various compositions subjected to various times (0–4 h) of heating at 177 °C. Fig. 4 is a plot of T_g for the various compositions as a function of heating time at 177 °C. It shows that the T_gs of the neat DGEBA and the blends of lower contents of PVPh (9.1 wt%) in the DGEBA/PVPh mixtures remain almost same as the unheated samples, and their T_gs were virtually independent of the heating time at 177 °C for blends of low PVPh contents. However, for the blends of higher contents of PVPh in the DGEBA/PVPh mixtures, T_gs of the blends after heating at 177 °C increased quite significantly with the time of the heat-treatment, and the T_g elevation is the most significant for the some middle compositions (PVPh = 50.0–66.7 wt%).

Attempts to determine the molecular structures of the blends before and after heating were made with FTIR analysis. Results for the as-prepared blend samples were discussed first. Fig. 5 shows the FT-IR spectrums for the epoxide group of DGEBA and the phenylhydroxyl group of PVPh before heating, respectively. The hydrogen bonding is apparent in neat PVPh. Spectrum-V of neat PVPh (in Fig. 5A) shows an absorbance shoulder band at 3525 cm^{-1} attributed to free or non-hydrogen bonded phenylhydroxyl and a broad band at 3346 cm^{-1}, which is assigned to a wide distribution of hydrogen bonded phenylhydroxyl groups (self-association in the same molecules). When the PVPh content in the DGEBA/PVPh blends decreased, the band of the free phenylhydroxyls still remained at the same frequency (3525 cm^{-1}), but the band of the hydrogen bonded phenylhydroxyls with the decreasing PVPh content shifted from 3346 cm^{-1} (neat PVPh) to high frequency (3386 cm^{-1}) for the blends. The frequency difference between the free phenylhydroxyl absorbance and those of the hydrogen bonded species ($\Delta\nu$) [23] is a measure of the average strength of the intermolecular interactions. The above result implied that the average strength of the hydrogen bonding in neat PVPh (a shift of

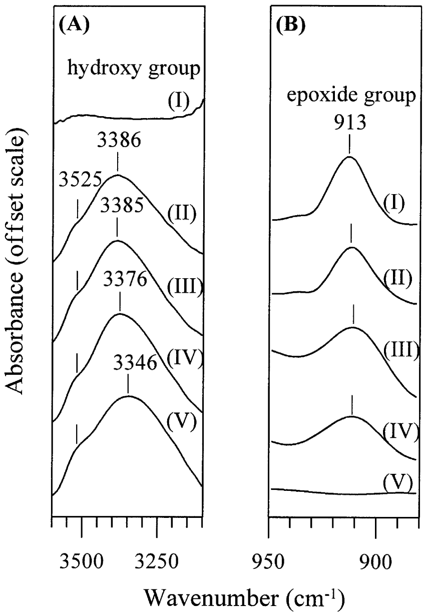


Fig. 5. FT-IR spectra of as-prepared DGEBA/PVPh blends: (A) phenylhydroxyl group and (B) epoxide group, with various contents of PVPh from (I) 0 wt% (neat DGEBA), (II) 33.3 wt%, (III) 50 wt%, (IV) 66.7 wt% to (V) 100 wt% (neat PVPh), respectively.

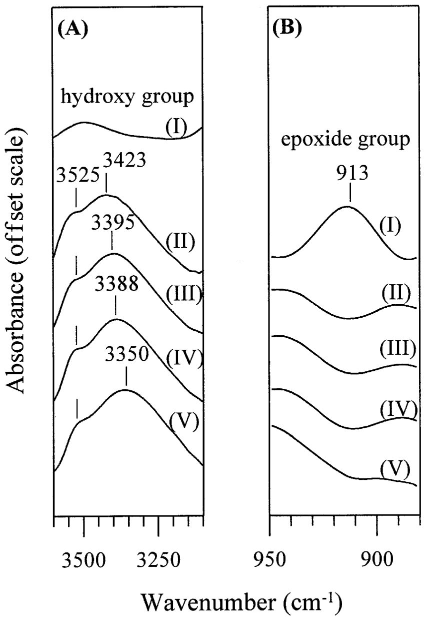


Fig. 6. FT-IR spectra of DGEBA/PVPh blends upon heating for 1 h at 177 °C: (A) phenylhydroxyl group and (B) the epoxide group, with various contents of PVPh from (I) 0 wt% (neat DGEBA), (II) 33.3 wt%, (III) 50 wt%, (IV) 66.7 wt% to (V) 100 wt% (neat PVPh), respectively.

$\Delta\nu = 179\ \mathrm{cm}^{-1}$) was more than that in the DGEBA/PVPh ($\Delta\nu = 139\ \mathrm{cm}^{-1}$). This implies that self-association of phenylhydroxyl group in neat PVPh may be stronger than the interaction between the DGEBA and PVPh molecules in the blends. Apparently, the hydrogen bonding (intramolecular) interaction in neat PVPh resulted from the self-association of the PVPh phenylhydroxyl group and is independent of the structure of DGEBA monomers. Fig. 5B shows that the epoxide group of DGEBA exhibited an absorbance peak at 913 cm^{-1}. The intensity of the epoxide group decreased with the DGEBA content in the DGEBA/PVPh blends. Besides, the epoxide peak remained at the same frequency and was independent of the compositions of the blends, which implies that DGEBA monomer remains non-reactive and that the hydrogen bonding interactions mainly originate from the phenylhydroxyl group of PVPh.

For comparisons, IR vibration modes in the heated DGEBA/PVPh blends of various compositions were examined. Fig. 6 shows the FT-IR spectrum of the DGEBA/PVPh blends after heating for 1 h at 177 °C. For the neat DGEBA heated for 1 h at 177 °C, FT-IR spectrum shows that the shoulder peak of the hydrogen group occurred at 3525 cm^{-1} that might resulted from the trace moisture absorbed in the epoxy resin but the intensity of the epoxide peak almost remained at 913 cm^{-1} and its intensity was not nearly affected. Therefore, the reaction extent between the neat DGEBA at high temperature was slight and could be ignored. In comparison with the result in Fig. 5 shown earlier, the broad band of hydrogen bonding phenylhydroxyl group for the same composition of the DGEBA/PVPh blends shifted to higher frequency after heating (Fig. 6A). Nevertheless, the self-association of neat PVPh remained at the same frequency and was unaffected by the thermal treatment.

In other words, the frequency difference between the free phenylhydroxyl absorbance and those of the hydrogen bonded species ($\Delta\nu$) became less after heating the blends for 1 h at 177 °C. The result is summarized in Table 1. Hydrogen bonding in the heated DGEBA/PVPh blends becomes less in comparison with that in the unheated counterparts. In addition, the peak of the epoxide group of DGEBA disappeared after the isothermal heat treatment. Therefore, the addition of PVPh into DGEBA favored opening of the epoxide group of DGEBA. It suggests that the epoxide group of DGEBA participated in chemical-bonding links with the phenylhydroxyl group of PVPh. Consequently, in heated blends, the formation of networking structure could impose a further steric-hindrance and reduced the extent of physical hydrogen bonding interactions. Instead, a chemical bonding can become increasingly more prominent in the heated DGEBA/PVPh blends that start to develop a networking structure.

Table 1
The frequency difference between the free phenylhydroxyl absorbance and those of the hydrogen bonded species ($\Delta\nu$) for the various PVPh contents in the DGEBA/PVPh blends before and after heated for 1 h at 177 °C

PVPh content	$\Delta\nu$ of the as-prepared blends (cm^{-1})	$\Delta\nu$ of the heated blends (cm^{-1})
33.3 wt%	139	102
50 wt%	140	130
66.7 wt%	149	137
Neat PVPh	179	175

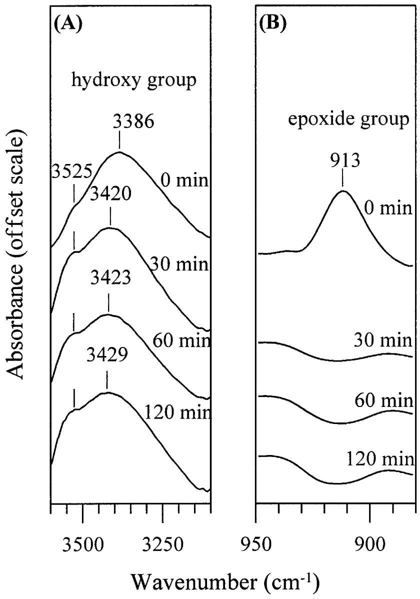


Fig. 7. FT-IR spectra of DGEBA/PVPh blends with 33.3 wt% of PVPh upon heating at 177 °C for times from 0 to 120 min: (A) phenylhydroxyl group and (B) epoxide group.

Effects of heating time on the intermolecular state of the mixtures were examined on the blend sample of a fixed composition (PVPh = 33.3 wt%). Fig. 7A and B shows the FT-IR spectra for the phenylhydroxyl group of PVPh and the epoxide group of DGEBA in a heated DGEBA/PVPh blend sample (PVPh = 33.3 wt%, heated at 177 °C for various times). The epoxide IR peak intensity (at 913 cm^{-1}) in Fig. 7B apparently decreased with the heating time, which implies that the epoxide groups were opened upon heating. Consequently, from Fig. 7A, the broad band of hydrogen bonding phenylhydroxyl group of PVPh in the blend (PVPh = 33.3 wt%) shifted from 3386 cm^{-1} (as-prepared unheated samples) to a higher wavenumber (3429 cm^{-1}) after heating. Therefore, the values of $\Delta\nu$ decreased from 139 to 96 cm^{-1}, which suggested that the hydrogen bonding interactions in the heated blends decreased with the time of thermal treatment. In addition, the extent of the reactions between DGEBA and PVPh heated for various times could influence the hydrogen bonding interactions. The above result confirmed that the DGEBA/PVPh blend after heating at 177 °C led to reactions between the epoxide group of DGEBA and the phenylhydroxyl group of PVPh, which in turn led to a networking structure in the heated blends.

3.1. Network structure analysis

For the detailed mechanisms of the reactions between DGEBA and PVPh molecules, we further used the solid-state ^{13}C NMR for analysis. A zirconium oxide rotor with a diameter of 4 mm and Kel-F cap was used to acquire ^{13}C CP/MAS NMR spectra with a CP contact time of 1 ms, a repetition time of 4 s. However, a 13 kHz spinning speed was chosen for neat PVPh but that for neat DGEBA was zero due to the limit of its relatively high viscosity at ambient temperature. In general, the resolution of the various polymer carbon signals is quite good. Fig. 8 shows the ^{13}C CP/MAS NMR spectra of neat PVPh and neat DGEBA. The corresponding resonance peaks are assigned to specified carbons as indicated in the inset chemical structures. The assignment of the resonance peaks is summarized in Table 2. The spectrum of neat PVPh (Spectrum-A) consists of the phenol carbon (Ar-OH) at 153 ppm and five resonances in the range of 110–150 ppm, which arises from the carbon sites in the aromatic ring and the resonances in the range of 307–60 ppm due to the methyl groups. For the neat DGEBA (Spectrum-B), the resonances at 158, 146, 129 and 116 ppm are assigned to protonated and non-protonated aromatic carbons, respectively. The resonances at 71 ppm are ascribed to the linear carbons linking with the oxygen molecule (CH–O and $\mathrm{CH_2}$–O), and the resonances at 52 and 45 ppm are owing to the epoxide rings. Additionally, the resonance at 43 ppm is the signal of the quaternary carbons in the main chain and the resonance at 32 ppm is assigned to methyl groups.

For comparisons with the spectra for the neat components shown in the previous figure, Fig. 9 shows the solid-state ^{13}C NMR spectra for the heated DGEBA/PVPh blend (50/50, w/w, heating at 177 °C for various times). To prevent the spinning sidebands, a spinning rate (13 kHz) was chosen to record the solid-state ^{13}C NMR spectra for the DGEBA/PVPh blends. It is observed that the phenol carbon (C–OH) of PVPh in DGEBA/PVPh slightly shifted to downfield (156 ppm) in comparison with that for neat PVPh (shown earlier in Fig. 8A). It implies that PVPh might have reacted with DGEBA monomer even at the casting/drying condition of 80 °C for 96 h. Furthermore, by comparing Spectrum-A and Spectrum-B, the intensity of the epoxide group (ca. 52 and 45 ppm) apparently decreased after the thermal treatment and the relative intensity of the linear carbon links with the oxygen (ca. 70 ppm) immediately increased. In addition, the signal of the phenol carbons (156 ppm) shifted downfield (158 ppm) that belonged to the phenol–ether carbons. Furthermore, for the heated DGEBA/PVPh mixtures (heated at 177 °C for a long time of 4 h), Spectrum-C shows that the signals of the epoxide group (52 and 45 ppm) disappeared through the thermal treatment while the intensity of the linear ether carbons (the resonance at 70 ppm) became stronger. Therefore, the result suggests that the epoxide group of DGEBA indeed were opened and reacted with the phenylhydroxyl group of PVPh at high temperatures.

Direct comparisons of solid-state ^{13}C NMR spectra were made for the blends heated at various temperatures. Fig. 10 shows the solid-state ^{13}C NMR spectra for the DGEBA/PVPh (50/50, w/w) samples in situ heated at various temperatures. To acquire spectra at higher operating temperatures, a spinning rate was chosen at 5.5 kHz that generated the spinning sidebands but did not overlap with

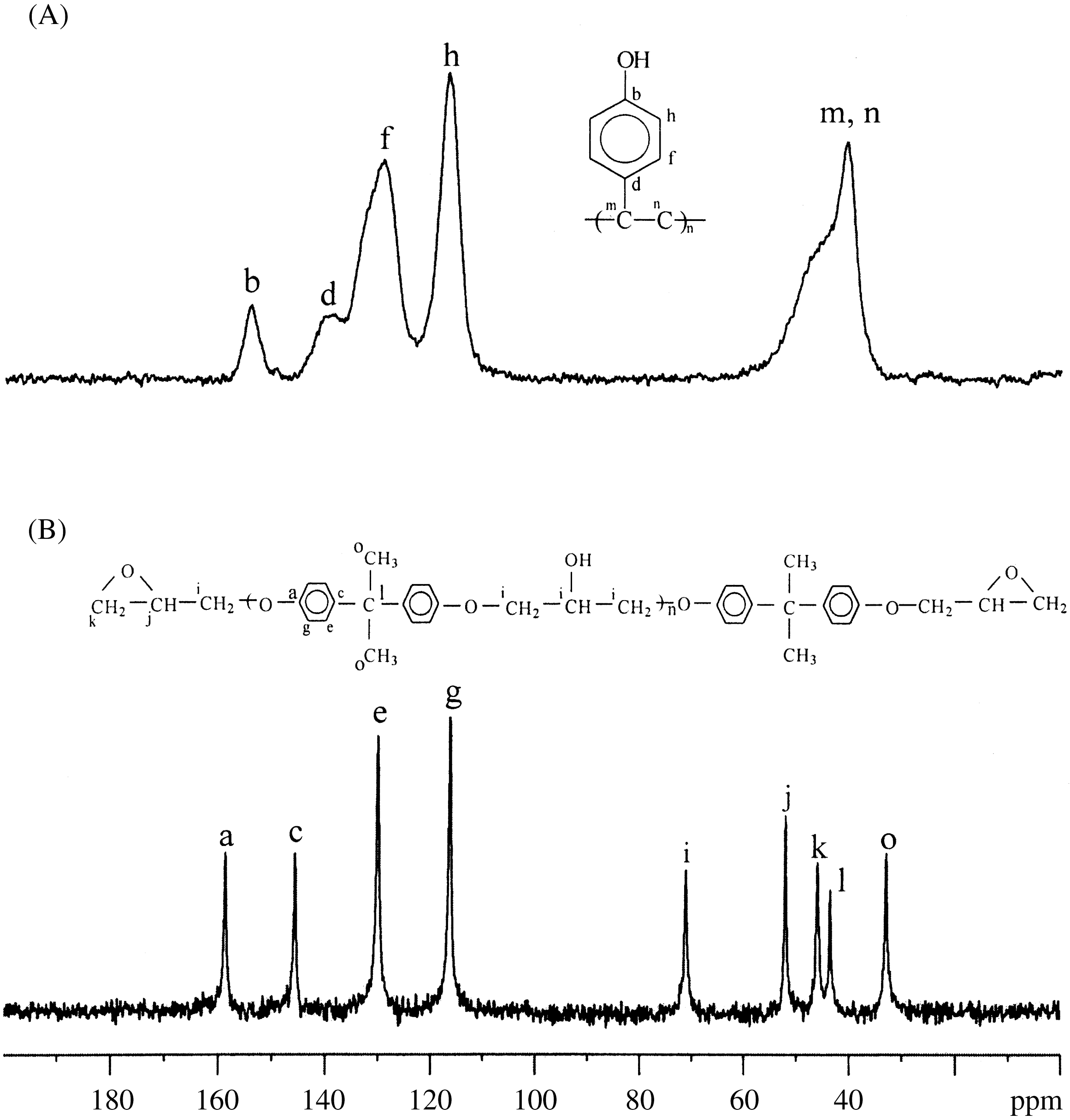


Fig. 8. ^{13}C CP/MAS NMR spectra of (A) neat PVPh and (B) neat DGEBA, all examined at room temperature and spinning speed of 13 and 0 kHz, respectively.

Table 2
Assignments of the ^{13}C chemical shifts for neat PVPh and DGEBA

Peak label	Chemical shift (ppm)	Type of carbon
a	158	C–O (aromatic, DGEBA)
b	153	C–OH (aromatic, PVPh)
c	145	Quaternary carbon (aromatic, DGEBA)
d	138	Quaternary carbon (aromatic, PVPh)
e, f	128	Aromatic CH (DGEBA and PVPh, respectively)
g, h	116	Aromatic CH (DGEBA and PVPh, respectively)
i	71	C–O (main chain, DGEBA)
j	52	Epoxide methylidyne CH (DGEBA)
k	45	Epoxide methylene CH_2 (DGEBA)
l	43	Quaternary carbon (backbone, DGEBA)
m, n	40	Methylene and methylidyne groups (PVPh)
o	32	Methyl group CH_3 (DGEBA)

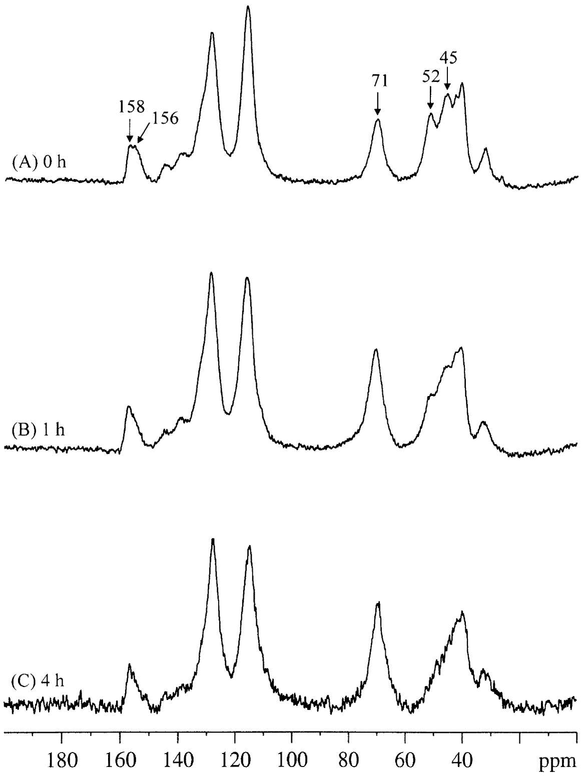


Fig. 9. ^{13}C CP/MAS NMR spectra of DGEBA/PVPh = 50/50 (w/w) previously heated at 177 °C for different times: (A) 0 h, (B) 1 h and (C) 4 h, all examined at room temperature and spinning speed of 13 kHz, respectively.

the resonances from the assigned carbons. Although the NMR signals of the spectra were weaker when the apparatus were operated at in situ high temperatures, it was still good enough to assign the specified carbons for the chemical structures of DGEBA and PVPh, respectively. Spectrum-A is the result for the as-prepared (unheated) DGEBA/PVPh at 27 °C, indicating resonances of the unreacted epoxide ring at 52 and 45 ppm. As the temperature of acquiring the solid-state NMR spectra was raised from 27 to 167 °C (Spectrum-C), the intensity of the unreacted epoxide ring became weaker gradually. Finally, as the operating temperature for the solid-state NMR spectrum reached to 177 °C,

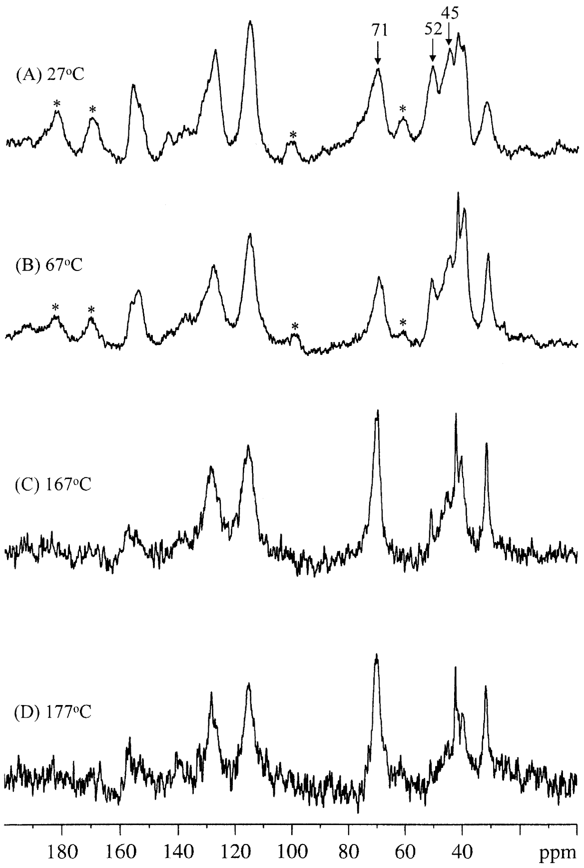
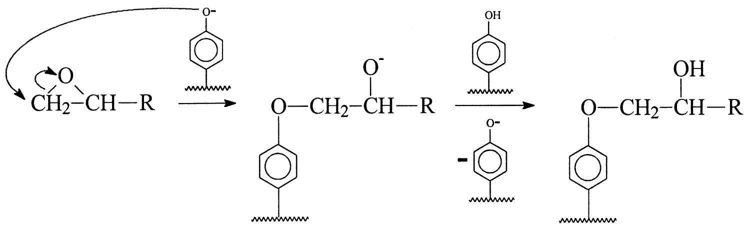


Fig. 10. ^{13}C CP/MAS NMR spectra of as-prepared DGEBA/PVPh = 50/50 (w/w), examined at a spinning speed of 5.5 kHz and at various temperatures: (A) 27 °C, (B) 67 °C, (C) 167 °C and (D) 177 °C, respectively.

reactions with the phenylhydroxyl groups of PVPh at high temperatures. Therefore, the result from the solid-state ^{13}C NMR indeed showed a good agreement with that of the FT-IR, in showing that in the heated blend, the chemical reactions occurred between the epoxide group of DGEBA and the phenylhydroxyl group of PVPh.

From the FT-IR data and solid-state ^{13}C NMR results, the mechanism for reactions in the heated DGEBA/PVPh blend is proposed as follows:



(1)

Spectrum-D shows that the resonance of the epoxide ring almost disappeared, but the intensity of the ether carbon became stronger. It is proposed that the epoxide ring of DGEBA was opened after heating, owing to the addition of PVPh, and the epoxide ring of DGEBA underwent chemical

Because the alkyl group at the 4-position of the aromatic ring in the structure of PVPh is an electron-donating group (EDG), it may induce the phenol group ionized to the phenoxide. This structural consideration makes ionized-PVPh very active to attack the epoxide rings. A similar

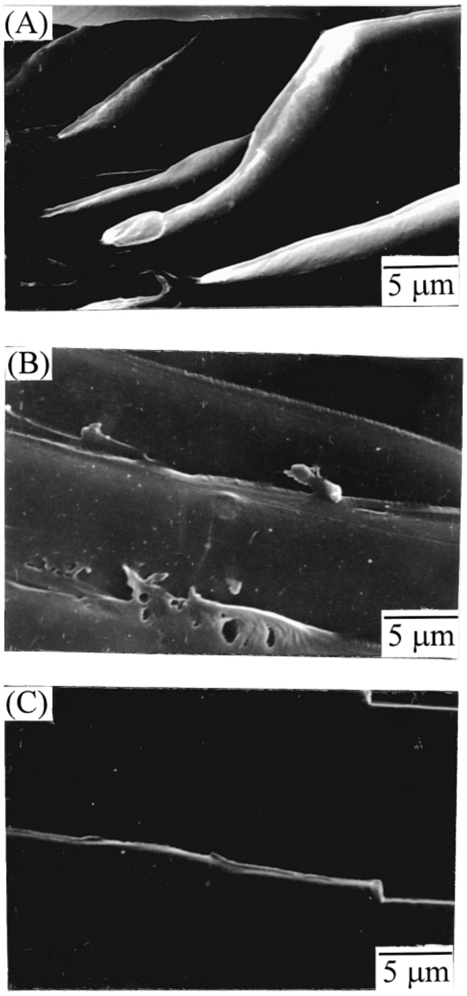


Fig. 11. SEM micrographs for fracture surface DGEBA/PVPh (PVPh = 33.3 wt%) blends upon heating at 177 °C for various times: (A) 30 min, (B) 60 min, (C) 120 min, all as fractured without THF solvent-etching.

reaction mechanism has been earlier proposed by Boyd and Marle [24] to show base-catalyzed reaction of phenol with ethylene oxide in 1914. The mechanisms between the epoxide groups and the hydroxyl groups were also discussed by Shechter and Wynstra [25]. Therefore, DGEBA monomers would mainly react with PVPh molecules according to the mechanism described in Eq. (1). It must be noted that not all hydroxyl-containing polymers would have similar interactions with epoxy resins. For examples, mixtures of DGEBA and bisphenol-A phenoxy (with –OH on the aliphatic carbon) do not undergo similar reactions upon heating at the same temperature [5]. The –OH group in phenoxy polymer might acts as catalysis to enhance the curing rates in DGEBA/DDS system, and does not participate in reactions with DGEBA as observed in this present case of DGEBA/PVPh.

3.2. Morphology characterization of networks

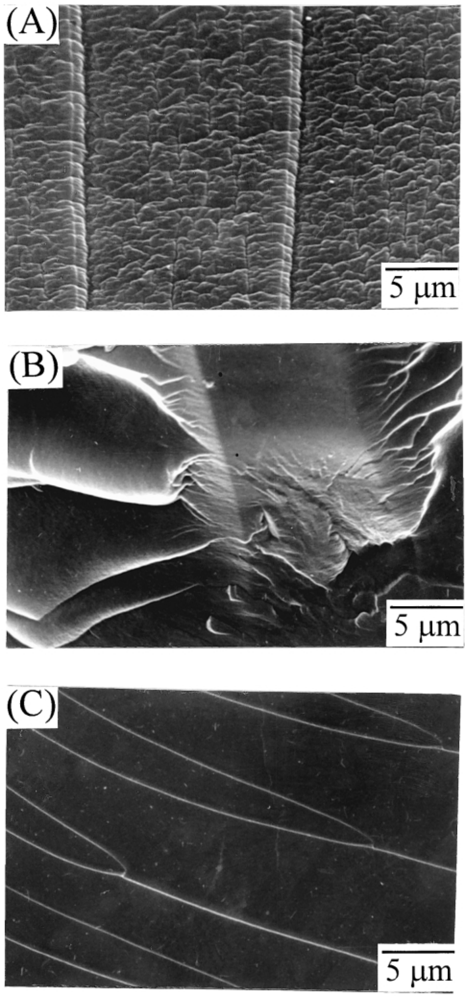


Fig. 12. SEM micrographs for fracture surface DGEBA/PVPh (PVPh = 33.3 wt%) blends upon heating at 177 °C for various times: (A) 30 min, (B) 60 min, (C) 120 min. All samples etched by THF.

To further probe the structure in the heated DGEBA/PVPh blends as a result of chemical interactions between DGEBA and PVPh, the morphology of the heated blends were examined by using SEM. Fig. 11 shows the SEM graphs of DGEBA/PVPh (33.3 wt% of PVPh) blend samples (heated for 30, 60 and 120 min, respectively, all at 177 °C). Graphs A, B, and C show the fracture surface of the heated DGEBA/PVPh samples at 177 °C for 30, 60 and 120 min, respectively. The morphology was quite homogeneous and free of any discernible domains, which agreed with the single-T_g result of the heated blend.

Furthermore, the fracture surface of the heat blends was etched using the solvent THF, which was used to dissolve and extract the unreacted reagents from the gelled networks. A different morphology was observed. Fig. 12 (Graphs A, B and C) shows the fracture surfaces of the heated blends (samples heated at 177 °C for 30, 60 and 120 min, respectively). All SEM samples prior to sputter-coating and microscopy characterization were etched using THF. For the DGEBA/PVPh blends heated for 30 min at 177 °C, the extent of the reactions between these components was likely not complete. Therefore, significant amounts of unreacted reagents were dissolved by THF and an incomplete networking structure was observed. As the heating time was increased, the heated blend sample became gradually unaffected by the solvent etching. At greater extents of reactions between DGEBA and PVPh, the amount of unreacted and dissolvable reagents became less and a networking structure was now more apparent. Completely homogeneous network morphology was found in the heated DGEBA/PVPh blends at sufficient reaction extents. When the reaction between DGEBA and PVPh was advanced to a certain degree, the fracture surfaces of the heated blends remained smooth and homogeneous, even after etching by THF. More extensive chemical links between DGEBA and PVPh occurred and a networking structure consequently resulted.

4. Conclusion

A single, composition-dependent T_g was found for the as-blended DGEBA/PVPh mixtures in the whole composition range. In addition, upon heating the DGEBA/PVPh mixture readily transformed into a solidified network, suggesting a certain chemical reaction occurred between the linear PVPh polymer and the epoxy. T_g of the heated blends increased with the temperature or duration of isothermal heating. T_g of the unheated blends, as well as the heated DGEBA/PVPh mixtures, was found to be a function of the composition, which suggests that the uncured mixture and final cross-linked network both exhibit a homogeneous single phase.

The single phase in the unheated mixture of DGEBA/PVPh was a result of physical miscibility, while the heated mixture was proven that the phenyl-OH of PVPh reacted with the epoxide group in epoxy and led to a gelled state. The thermal behavior as demonstrated in the T_g-composition relationship for the heated blend also suggested that there were certain chemical reactions between DGEBA and PVPh molecules, and that PVPh in the blends was the limiting agent for the reaction to proceed. The result of FT-IR also proved that although the stereo-hindrance of the network structure resulted in a decrease in the physical hydrogen bonding, a chemical reaction between DGEBA and PVPh developed to ensure a homogeneous and cross-linked network in the heated DGEBA/PVPh blend. The *para*-alkyl group in the aromatic of PVPh is an EDG, thus it induces the phenylhydroxyl to form phenoxide ions at high temperatures. In addition, the negative phenoxide ions of PVPh can attack the epoxide group of DGEBA monomer.

According to the solid-state NMR ^{13}C NMR spectra, the assigned peak for the phenol carbon (Ar-OH) of PVPh in the DGEBA/PVPh blend shifted downfield after heating at 177 °C. Furthermore, for the heated blends, the peaks of the epoxide carbons disappeared and the relative intensity of the linear ether carbons of DGEBA immediately increased. Therefore, from the detailed studies of the solid-state ^{13}C NMR, it is further evidenced that the stated chemical reactions occurred between the epoxide group of DGEBA and phenylhydroxyl group of PVPh. As a result of heating at relatively low temperatures of casting or blending (80 °C) and above this temperature the reactions of DGEBA and PVPh occurred more readily.

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