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Epoxy resin cured with poly(4-vinyl pyridine)

FANLIANG MENG, WEIAN ZHANG, SIXUN ZHENG*
Department of Polymer Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China
E-mail: szheng@sjtu.edu.cn

Poly(4-vinylpyridine) (P4VP) was used as the macromolecular curing agent to prepare epoxy networks. The crosslinking structures were investigated by means of Fourier transform infrared spectroscopy (FTIR). It is identified that depending on the ratios of DGEBA to P4VP, different reactions dominated the formation of the crosslinking networks, which were involved the formation of pyridone (or cyclic amide) resulting from epoxide groups of DGEBA and pyridine rings of P4VP, the Diels-Alder reaction of *in situ* formed conjugated 3,5-diene in a 6-member ring and the homopolymerization of DGEBA initiated by pyridine moiety of P4VP. Differential scanning calorimetry (DSC) showed that all the DGEBA-P4VP co-crosslinked thermosets displayed single glass transition temperature (T_g), suggesting that the crosslinked networks are homogenous. In addition, it is noted that the T_g's of the DGEBA-rich network are greatly dependent on the molecular weight of P4VP used. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

The concept of thermoplastics-modified thermosets has been widely accepted in order to establish the balance between toughness and thermal stability associated with the rubber toughening of thermosets. Generally, thermoplastics-modified thermosets are prepared starting from the homogeneous solutions of thermoplastic polymer and thermoset precursors and the heterogeneous morphology is generally generated *via* phase separation induced by polymerization [1, 2].

Epoxy resins are a class of important thermosetting materials, which have widely been used as structural adhesive, matrices of composites and electronic encapsulating materials. The modification of epoxy resin by thermoplastics has been extensively investigated during the last decades [1, 2]. However, completely homogeneous thermosets involved with epoxy resin and thermoplastics resulting from either physical miscibility or chemical reaction are not very common [3–9]. Nonetheless, the utilization of reactive thermoplastic modifiers to obtain the homogeneity of epoxy resin was also paid the considerable attentions during the past years. Of them, epoxy-polycarbonate (PC) blends were extensively investigated [10–15]. It has been proven that the homogeneity was attributed to the transesterification reactions between epoxy and PC. More recently, Huang and Woo *et al.* reported the homogeneity in the thermosetting blends of epoxy resin and poly(4-vinyl phenol) [16]. It was identified that diglycidyl ether of bisphenol A (DGEBA) can significantly react with poly(4-vinly phenol) at the elevated temperature and thus the homogenous networks were formed. In addition, polyamides are also frequently used as the macromolecular curing agent [17–22].

Poly(4-vinylpyridine) (P4VP) is an important functional polymer and its pyridine ring bearing tertiary nitrogen atom endows this polymer with distinct features. The crosslinked P4VP has been used as electrode and chromatographic packing materials (*viz.* stationary phase) [23–27]. When P4VP is mixed with DGEBA, it was assumed that pyridine rings of P4VP could initiate the homopolymerization of epoxy resins [28] and thus the semi-interpenetrating polymer networks (semi-IPN) between crosslinked epoxy and P4VP would be formed. Nonetheless, Xue *et al.* [29] argued that the reaction between pyridine and epoxide groups did not result in the homopolymerization of epoxy groups and the pyridone (or cyclic amide) structures were formed during the reaction.

The goal of this work is to investigate structure and properties of epoxy resin when poly(4-vinylpyridine) (P4VP) is used as a macromolecular curing agent. To the best of our knowledge, the structure and thermal properties of epoxy resin cured with P4VP have not been well investigated as a function of composition although there have been the reports on the chemical reaction between pyridine and epoxide compounds [29, 30]. In the present work, the structure of the cured products with various content of P4VP will be examined by means of Fourier transform infrared spectroscopy (FTIR). The thermal properties of the cured products

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*Author to whom all correspondence should be addressed.

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are investigated on the basis of differential scanning calorimetry (DSC).

2. Experimental

2.1. Material and preparation of samples

The epoxy monomer, diglycidyl ether of bisphenol A (DGEBA) with epoxide equivalent weight 185–210 was obtained from Shanghai Resin Co., China. Both 4-methylpyridine (4MP) was purchased from Sigma-Aldrich Co.. Poly(4-vinylpyridine) (P4VP) was synthesized in this lab with two molecular weights: $M_n = 7{,}000$ and $M_n = 70{,}000$, respectively, which were measured using gel permeation chromatography (GPC) relative to polystyrene standard.

The P4VP of the lower molecular weight was synthesized by a reversible addition-fragmentation transfer (RAFT) polymerization of 4-vinyl pyridine (4VP) in the presence of azoisobutylacrylonitrile (AIBN) with benzyl dithiobenzoate (BDB) as the chain transfer agent (CTA). The bulk polymerization of 4VP was carried out in an ampoule. 4VP (8.100 g), the chain transfer agent (0.150 g) and AIBN (0.026 g) were mixed and charged into the ampoule. The solution was degassed by three freeze pump- thaw cycles and placed in an oil bath of 70°C prior to the polymerization. At the end of the reaction, the reaction mixture was diluted with THF, and precipitated in large amount of petroleum ether. The product was dried at room temperature *in vacuo* to constant weight (4.34 g). The P4VP of the higher molecular weight was synthesized *via* AIBN-initiated free radical polymerization. Typically, 4-vinyl pyridine (10.0 g), AIBN (0.05 g) and THF (10 ml) were mixed and charged into 100 ml flask. Then the flask was purged with dry N_2 and immersed in an oil bath with continuously stirring at 60°C for 6 h. After the reaction was completed, the product was dissolved in THF and then precipitated in petroleum ether. Prior to use, the P4VP samples were dried in a vacuum oven at 60°C for 48 h in order to remove the moisture.

The mixtures of DGEBA with P4VP were prepared by casting from methanol solution (5 wt%) at room temperature. The most of solvent was evaporated at room temperature and the residual solvent was removed by drying in a vacuum oven at 60°C for 48 h. The dried films were further cured at 150°C in nitrogen atmosphere to obtain the thermosetting materials.

2.2. Techniques and measurements

2.2.1. Differential scanning calorimetry (DSC)

Thermal analysis was performed on a Perkin Elmer Pyris-1 differential scanning calorimeter in dry nitrogen atmosphere. The instrument was calibrated with a standard Indium. In order to measure glass transition temperatures, all the cured samples (about 10 mg in weight) were heated up to 150°C and held at this temperature for 5 min to eliminate thermal history, followed by quenching to −70°C. A heating rate of 20°C/min was used in all cases. Glass transition temperature (T_g) was taken as the midpoint of the heat capacity change.

2.2.2. Fourier transform infrared spectroscopy (FTIR)

The FTIR measurements were performed on a Perkin-Elmer Paragon 1000 Fourier transform infrared spectrometer. The thermosetting samples were granulated and the powder was mixed with KBr and then pressed into small flakes for FTIR measurement. All the specimens used in the study were sufficiently thin to be within a range where the Beer-Lambert law is obeyed. The spectra were obtained at the resolution of 2 cm^{-1} and were averages of 64 scans.

3. Results and discussion

3.1. Reaction of DGEBA and P4VP

The mixtures of DGEBA and P4VP were prepared *via* casting from the methanol solutions. As the solvent was evaporated at room temperature, the solutions gradually became green and the colority of the films increased with increasing the content of P4VP. The change in color for the binary mixtures suggests that there could be the strong intermolecular specific interactions between DGEBA and P4VP or the chemical reactions between both components occurred [31]. All the films were homogenous and transparent, indicating that the two components are miscible. The films of DGEBA-P4VP mixtures were cured at elevated temperature and the dark blue solids were obtained. It is noted that the cured products were no longer soluble in the common solvents such as tetrahydrofuran (THF), chloroform and *N*, *N*′-dimethylformamide (DMF), indicating that the crosslinked networks were formed between DGBEA and P4VP.

The thermosetting materials were subject to Fourier transform infrared spectroscopic (FTIR) measurement. Fig. 1 shows the FTIR spectra of DGEBA, P4VP and the crosslinked copolymer containing 30 wt% of P4VP in the range of 4000–750 cm^{-1}. Pure P4VP is characterized by the stretching vibration band of pyridine ring at 1553 cm^{-1}. Upon mixing with DGEBA at 60°C, the intensity of the band was significantly reduced and a new band simultaneously appeared at 1640 cm^{-1}, which is ascribed to unconjugated carbon double bonds (C=C) [29, 30]. In addition, it is noted that the intensity of the initial weak hydroxyl band at 3513 cm^{-1} for pure DGEBA is dramatically increased and is found to shift to the lower frequency at 3335 cm^{-1}. After the samples were cured at 150°C, the intensity of the band at 1640 cm^{-1} was further increased whereas the stretching vibration band of pyridine rings at 1553 completely disappeared. The depletion of the band at 1553 cm^{-1} suggests that the structure of pyridine ring was destroyed due to its reaction with epoxide groups of DGEBA and the new structure associate with the stretching band at 1640 cm^{-1} could be simultaneously formed.

In terms of the above observations, the following possible reactions involved in the crosslinking of P4VP with DGEBA are proposed as depicted in Scheme 1. The reaction was initiated by the nucleophilic attack of the tertiary nitrogen atom of P4VP on the epoxide groups of DGEBA, forming a salt. In the second step, the oxygen ion immediately attacks the α-position of

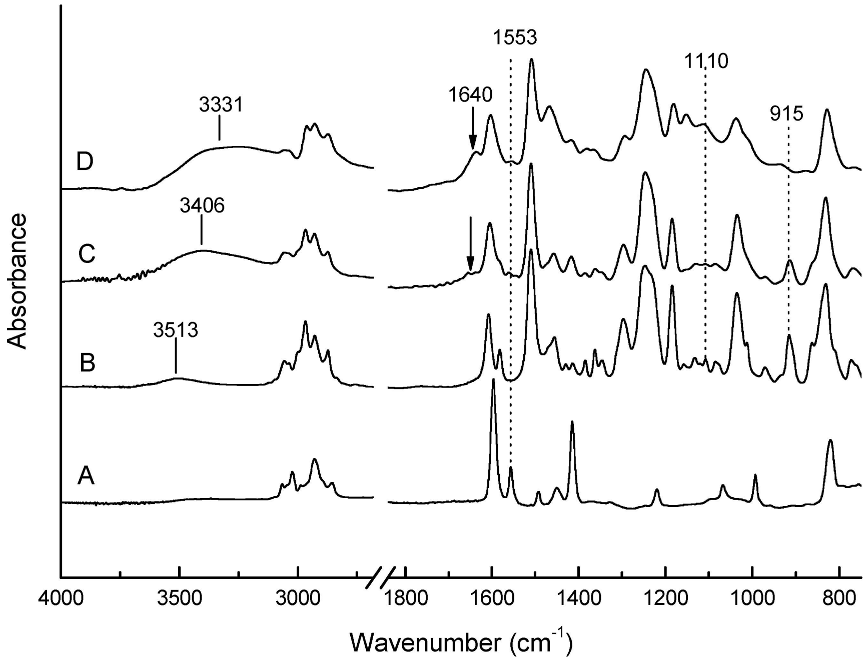
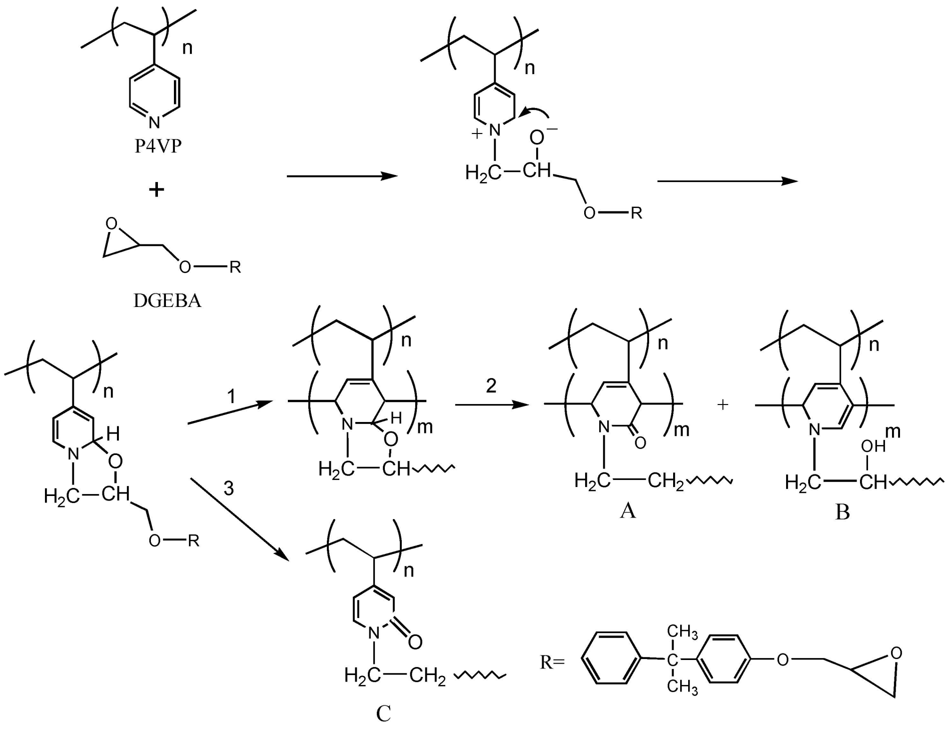


Figure 1 The FTIR spectra in the range of 4000–750 cm^{-1} for P4VP (A), DGEBA (B), the crosslinked copolymer containing 30 wt% of P4VP (C) at 60°C for 24 h and the crosslinked copolymer containing 30 wt% of P4VP (D) cured at 150°C for 2 h.



Scheme 1 Crosslinking reactions between DGEBA and P4VP.

pyridine ring and the aromatic structure of pyridine ring is destroyed, forming a conjugated 3,5-diene in the 6-membered ring. The conjugated 3,5-diene could undergo Diels-Alder reaction (2) at elevated temperature and then rearrangement could take place to form a cyclic amide (pyridone) structure (A) or a hydroxyl-containing product (B). Alternatively, the conjugated 3,5-diene can directly rearrange into another carbonyl-containing product (C) as schemed by reaction (3). It should be pointed out that the mechanisms proposed in this work are different from those previously reported by Xue *et al.* [29, 30], especially in the interpretation of hydroxyl bands.

In order to verify the occurrence of the Diels-Alder reaction of 3,5-diene, 4-methyl pyridine (4MP) that was used as the model compound of P4VP was employed to react with diglycidyl ether of bisphenol A (DGEBA). The reaction afforded a dark blue solid, which is insoluble in the common solvents such as THF, chloroform and DMF. The formation of the crosslinked products could be ascribed to the occurrence of Diels-Alder reaction of 3,5-diene and the homopolymerization of DGEBA. The FTIR spectrum of the products of reaction between equimolar 4-methyl pyridine and DGEBA is presented in Fig. 2. It is seen that the bands of pyridine at 1600, 1553, 1418 and 822 cm^{-1} were

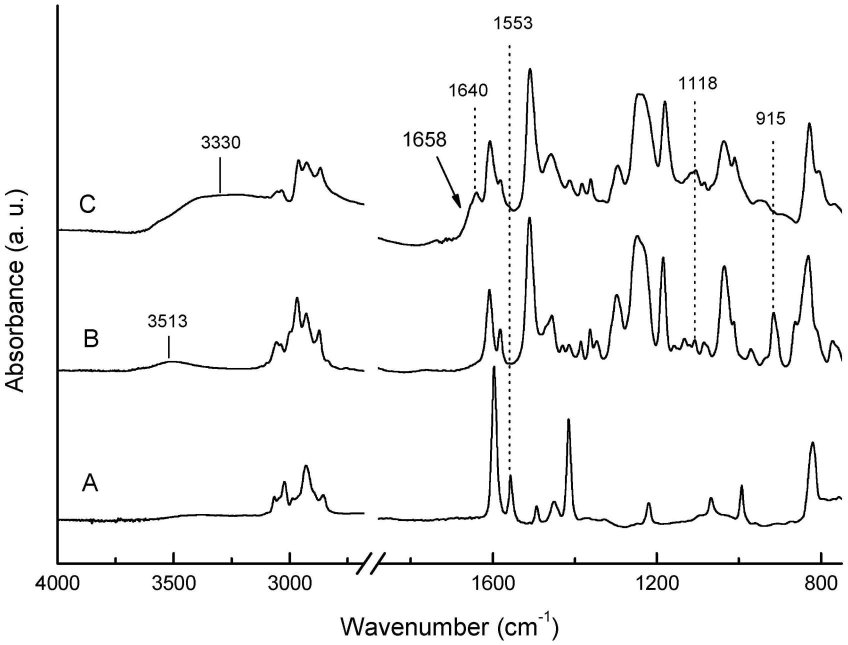


Figure 2 The FTIR spectra of 4-methyl pyridine (4-MP) (**A**), DGEBA (B), their equimolar mixture cured at 150°C for 2 h (C).

virtually depleted, suggesting that the pyridine rings were destroyed upon reacting with DGEBA. At the same time, there appear the new strong bands at 1658 and 1640 cm^{-1}, which could be ascribed to the carbonyls of pyridone and the unconjugated carbon double bonds. It should be pointed out that the appearance of the stretching vibration bands for the unconjugated carbon-carbon double bonds indicates the occurrence of the Diels-Alder reaction of 6-membered 3,5-diene. In addition, the quite strong hydroxyl stretching vibration band at 3428 cm^{-1} suggested the reaction of rearrangement proposed above. Apart from the Diels-Alder reaction, the homopolymerization of DGEBA could be involved with the crosslinking reactions, which is evidenced by the increase in intensity for aliphatic ether band at 1110 cm^{-1}. Nonetheless, it is proposed that the homopolymerization of DGEBA could be initiated by the intermediate zwitterions (i.e., cyclic amide or pyridone) [32, 33] other than pyridine ring of 4MP since the FTIR spectroscopy shows that the pyridine ring was easily destroyed by epoxide groups (See Curve C in Fig. 1).

From Figs 1 and 2, it is seen that the stretching vibration band of epoxide groups at 915 cm^{-1} also completely disappeared with the occurrence of the crosslinking reaction. The epoxide groups of DGEBA could be involved in the two reactions during the curing. Firstly, the epoxide groups reacted with the pyridine rings of P4VP, which resulted in the destruction of pyridine rings. In addition, the epoxide groups could undergo the homopolymerization, which results in the formation of aliphatic ether structure. The homopolymerization of epoxide groups can be evidenced by the observation that that the intensity of stretching vibration band for aliphatic ether (C–O–C) at 1110 cm^{-1} was increased with the occurrence of curing reactions (see Fig. 2). It is proposed that the homopolymerization of epoxide groups could be initiated by the nitrogen atoms of pyridine rings or the tertiary amine in pyridones (cyclic amides) *in situ* formed *via* the reaction of pyridine rings and epoxide groups. It should be pointed out that under the identical curing condition the homopolymerization of DGEBA is a quite slow process in the absence of P4VP.

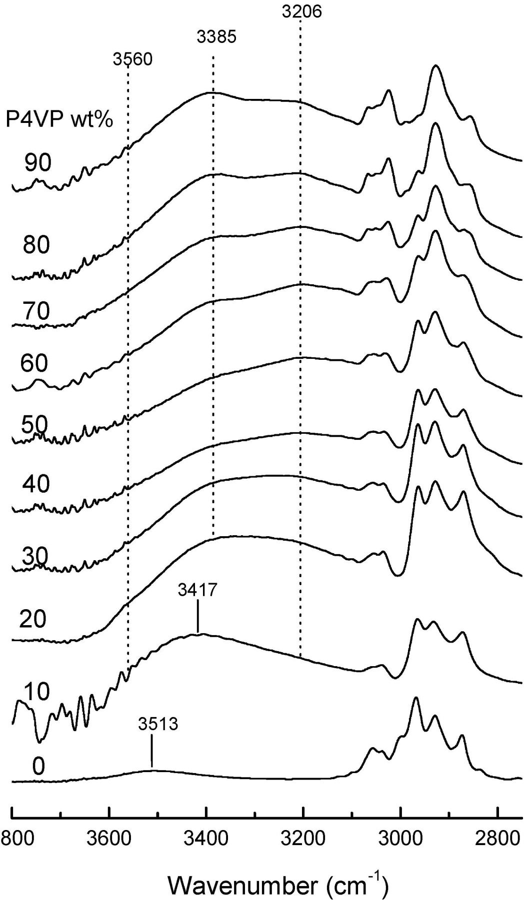


Figure 3 The FTIR spectra of DGEBA and its co-crosslinked products with P4VP in the range of 2750 to 3800 cm^{-1}.

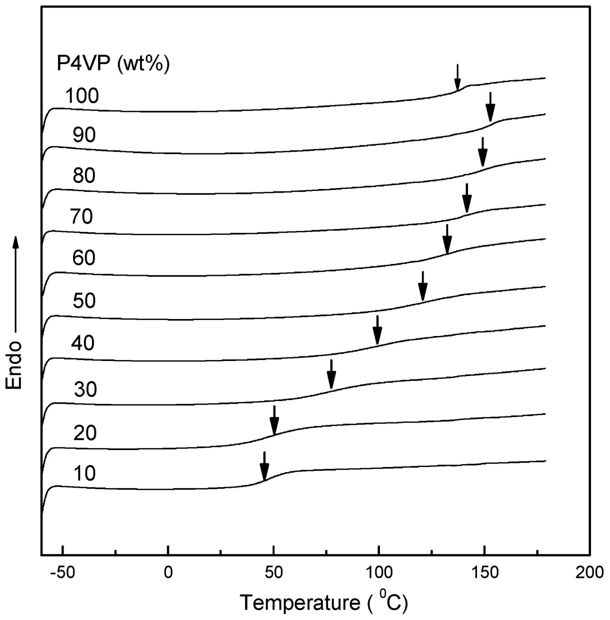


Figure 4 The DSC curves of P4VP-cured epoxy networks (M_n of P4VP: 70,000).

3.2. Intermolecular specific interactions

It has been shown that both pyridone (or cyclic amide) structure and hydroxyl groups were formed in the occurrence of crosslinking reactions. Therefore, there could be the intermolecular hydrogen bonding interactions between the carbonyl and hydroxyl groups, which are readily detected by means of Fourier transform infrared spectroscopy (FTIR). Shown in Fig. 3 are the FTIR spectra of DGEBA and its co-crosslinked products with P4VP in the range of 2750 to 3800 cm^{-1}. The spectroscopic bands are ascribed to hydroxyl stretching vibration. The broad bands reflect the wide distribution of hydrogen-bonded hydroxyl stretching frequencies. The shoulder bands centered at 3560 cm^{-1} are ascribed to the free hydroxyls. For pure DGEBA, the weak absorptive band is observed to be at c.a. 3513 cm^{-1}. It is proposed that the hydroxyls of DGEBA mainly existed in the sample in the free (or unassociated) form since the concentration of hydroxyls in the DGEBA used is very low. Upon mixing with 10 wt% of P4VP and curing under in standard condition, the intensity of hydroxyls was dramatically increased and the bands of hydroxyl groups were found to shift to the lower frequency at 3417 cm^{-1}. With increasing the concentration of P4VP, the bands of hydroxyl stretching vibration further shifted to the lower frequencies (c.a., 3385 cm^{-1}) and the new component simultaneously appeared at 3206 cm^{-1}. These observations indicate that the formation of the intermolecular hydrogen bonding interactions of the hydroxyls with pyridone (or cyclic amide) and pyridine. The interchain specific interactions just resemble the cases in the miscible blends of poly(hydroxyether of bisphenol A) with poly(N-vinyl pyrolidone) [33, 34] and Poly(4-vinylpyridine) [35]. The frequency difference ($\Delta\nu$) between free and H-bonded hydroxyl groups is a measure of the average strength of the intermolecular hydrogen bonding interactions [36, 37]. For DGEBA, the $\Delta\nu$ value is 143 cm^{-1}, whereas the value of $\Delta\nu$ is found to be175 cm^{-1} for the thermosetting materials with P4VP feed exceeding 10 wt%. For the lower-frequency component of the hydroxyl bands the $\Delta\nu$ value is found to be 354 cm^{-1}. The increased $\Delta\nu$ values suggest that the interchain hydrogen bonding interactions between hydroxyl groups and pyrodine (and/or pyridine) groups are much stronger than that of the self-association of hydroxyl groups.

3.3. Glass transition behavior

The DGEBA-P4VP thermosets were subject to differential scanning calorimetry (DSC) measurement and the DSC thermograms were presented in Fig. 4. In the experimental temperature range from –50–200°C,

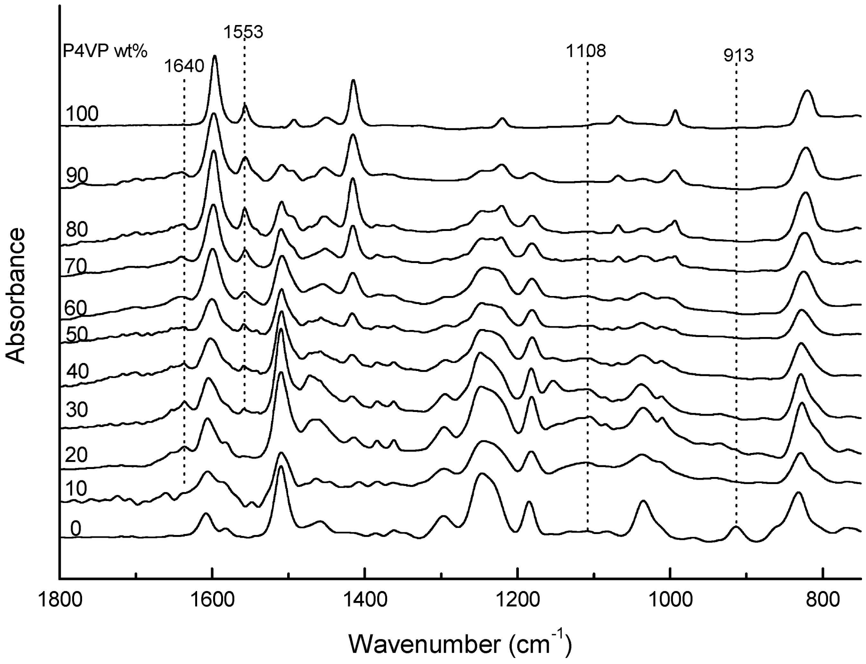


Figure 5 The FTIR spectra of the cured products in the range of 1800–750 cm^{-1}.

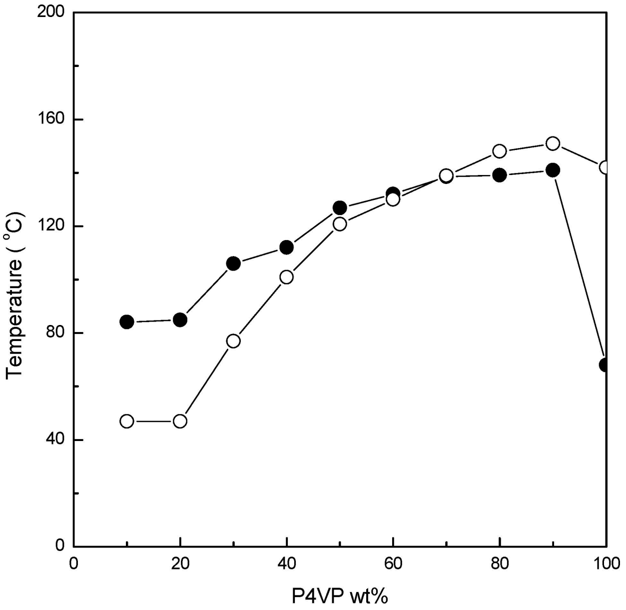


Figure 6 Plots of T_g's as functions of P4VP concentration for P4VP-cured epoxy networks. (●): The networks cured with P4VP with the molecular weight of $M_n = 7{,}000$; (○): The networks cured with the P4VP with the molecular weight of $M_n = 70{,}000$.

all the thermosetting materials displayed single glass transition temperature (T_g's) in the entire composition, which varied with the blend composition. The behavior of single glass transition temperatures indicates that the networks are homogenous, i.e., no phase separation occurred at the scale exceeding the wavelength of visible light, which is in marked contrast to other thermoplastics-modified epoxy resins.

It is propose that in the present case there are at least three types of crosslinking structures, which contributed to the overall glass transition temperatures (T_g's) of the DGEBA-P4VP thermosets. As shown in Scheme 1, Structure A resulted from the reaction between pyridine ring of P4VP and epoxide groups of DGEBA. Accompanying with this reaction, the conjugated 3,5-diene in the 6-membered ring was simultaneously produced, which could undergo Diels-Alder reaction at elevated temperature, i.e., Structure B was formed. In addition to the crosslinking structures resulting from the above inter-component reactions, DGEBA could undergo the self-crosslinking, which was initiated by pyridine moiety (Structure C). It is proposed that the content of the individual crosslinking structure is greatly dependent on the ratio of DGEBA to P4VP. For the DGEBA-rich thermosets, Structure C is dominant and the T_g's of the materials mainly rely on the self-crosslinking density of DGEBA. With increasing the concentration of P4VP, the content of Structures A and B increased while the content of self-polymerized DGEBA decreased. Therefore, the increased T_g's are mainly contributed by Structures A and B. When DGEBA is the minor component, the contents of Structure B and C are lower and the crosslinked networks cab be taken as DGEBA-cured P4VP. It is noted that the thermosetting materials displayed the higher T_g's when the concentrations of P4VP ranges from 50 to 90 wt% as shown in Fig. 4.

As the macromolecular curing agent of epoxy, the molecular weights of P4VP will significantly affect the T_g's of thermosets, especially for DGEBA-rich samples. In the present work, the P4VP of two different molecular weights ($M_n = 7{,}000$ and $M_n = 70{,}000$) were used to cure DGEBA, respectively. The DSC measurements showed that the thermosets cured with P4VP of low molecular weight displayed the much higher T_g's than those with the counterpart of higher molecular weight although the T_g (*c.a.* 67°C) of P4VP with $M_n = 7000$ is much lower than that ($T_g = 84°C$) of the P4VP of high molecular weight. It is noted that with increasing the concentration of P4VP the difference in T_g between the two systems became small and while the content of P4VP is up to 30 wt%.

4. Conclusions

Poly(4-vinylpyridine) (P4VP) was used as the macromolecular curing agent to prepare the epoxy networks. The structure of the crosslinked networks was investigated by means of Fourier transform infrared spectroscopy (FTIR). It is identified that depending on the ratio of DGEBA to P4VP the networks possesses various crosslinking structures, which result from the reaction of epoxide groups of DGEBA and pyridine rings of P4VP, Diels-Alder reaction of *in situ* formed conjugated 3,5-diene in a 6-member ring and the homopolymerization of DGEBA initiated by pyridine moiety of P4VP. Differential scanning calorimetry (DSC) showed that all the DGEBA-P4VP networks are homogenous. The glass transition temperatures (T_g's) of the networks varied with the composition. In addition, it is noted that the T_g's of the DGEBA-rich network are greatly dependent on the molecular weight of P4VP used.

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