

Investigation on the Chemical Reactivity of 2,4-Diamino-6-vinyl-*s*-triazine with Epoxide

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ABSTRACT: Simultaneously interpenetrating polymer network based on 2,4-diamino-6-vinyl-*s*-triazine (VT)/diglycidyl ether of bis-phenol A(DGEBA) was studied using differential thermal analysis and infrared spectroscopy. VT is a candidate of a monomer which increases the glass transition temperature and toughness of an epoxide resin simultaneously. The reactivity of amino groups of VT is considerably higher than 2,4-diamino-6-ethyl-*s*-triazine (ET) or melamine. Some of the amino groups of VT react with epoxide resin along with the polymerization of epoxide by imidazole. The polymerization of epoxide by imidazole is enhanced presumably by the catalyst effect of VT. The polymerization of double bonds is a fairly low unless peroxide is added at 150°C. Suitable molar ratio of peroxide and imidazole and the excess amounts of both compounds are required to complete both reactions simultaneously.

KEY WORDS 2,4-Diamino-6-vinyl-*s*-triazine / 2,4-Diamino-6-ethyl-*s*-triazine / Melamine / Epoxide Resin / Imidazole / Interpenetrating Polymer Network / DTA / IR / Gel Time /

The mechanical properties of polymers are modified by an interpenetrating polymer network (IPN). The synthesis, morphology, and physical properties of IPN have been described by many authors.¹⁻⁵ IPN is defined as a combination of two polymers in a network form, with the restriction that at least one of the polymers is synthesized and/or cross-linked in the immediate presence of the other.⁴ IPN is prepared by some methods such as sequential or simultaneous synthesis. In sequential synthesis, a performed cross-linked polymer is prepared with a monomer which is then polymerized to form another cross-linked polymer with in the original network.

On the other hand, monomers or linear pre-polymers are comined with their respectively cross-linking agents in simultaneous polymerization, followed by simultaneous polymerization and cross-linking of both phase. Kadota *et al.*⁶ studied simultaneous interpenetrating

polymer networks (SIN) prepared by the polymerization of methacrylic acid modified epoxide resin. They prepared SIN possessing some chemical bonds between each network to increase the compatibility. Epoxide and carbonyl groups of methacrylic acid were prepared, followed by the simultaneous homopolymerization of unreacted epoxides and double bonds of the modified epoxide resin using phthalic anhydride and dicumyl peroxide, respectively. In a previous paper,⁷ we reported the physical properties of a simultaneously cured compound of 2,4-diamino-6-vinyl-*s*-triazine (VT) and epoxide resin. The glass transition temperature (T_g) and the flexural strength of the simultaneously cured compound were superior to those of the cured epoxide resin polymerized with imidazole.

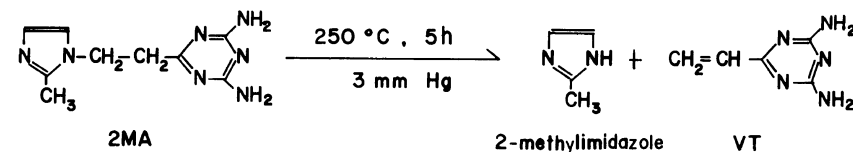
In this paper, we describe the chemical reactivity of VT as a possible monomer which increases T_g and enhances the toughness of ep-

oxide resin simultaneously by forming SIN in epoxide networks. The interesting point of VT is the reactivity of amino groups of *s*-triazine with epoxides. Therefore, VT may possess two functions as a monomer for a IPN and a curing agent for an epoxide resin simultaneously. Overberger *et al.* synthesized VT by the reaction of acryl chloride with biguanide sulfate for the first time in 1958.⁸ Some other ways of synthesis were reported later.⁹⁻¹² Recently, we established the new method of synthesis of VT, where VT is synthesized from 2,4-diamino-6-(2'-methylimidazolyl-(1'))-ethyl-*s*-triazine.¹³

EXPERIMENTAL

Materials

Synthesis of VT. The mixture of 2,4-diamino-6-(2'-methylimidazolyl-(1'))ethyl-*s*-triazine (2MA) and a quartz powder in the presence of sodium sulfide as polymerization inhibitor was heated at 250°C for 5 h under vacuum of 3 mm Hg. After being cooled, the sublimated product on the wall of the vessel was extracted with water, which gave a residue by filtration. The residue gave VT by recrystallization with water. The yield was close to 70% of the theoretical amount. The reaction can be written as follows;



VT obtained was examined using ¹H NMR, mass spectroscopy, and high performance liquid chromatography.

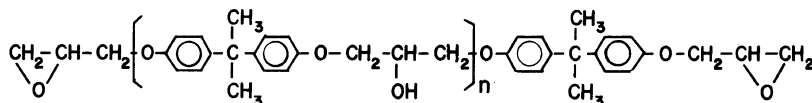
This compound had: ¹H NMR (DMSO-*d*₆): δ 6.76 (broad singlet, 4H), 6.35—6.45 (triplet, 2H), 5.59—5.72 ppm (quartet, 1H), IR (potassium bromide): ν 3338, 3180, 1653, 1640, 1537, 1456, 1424, 1363, 1263, 986, 835 cm⁻¹.

Anal. Found: C, 44.28%; H, 5.09%; N, 50.52%. Calcd for C₅H₇N₅: C, 43.80%; H, 5.11%; N, 51.09%.

Synthesis of ET. As the reference of VT, 2,4-

diamino-6-ethyl-*s*-triazine (ET) was synthesized by propionitrile and dicyandiamide.¹⁴ The product was obtained in 84% yield, mp 250°C. High performance liquid chromatography indicated 99.4% purity.

Melamine was used as pure grade reagent. Pure diglycidyl ether of bisphenol A (DGEBA) (mp 46°C) was kindly supplied from Yuka Shell Epoxy Co. and used for the experiments. The structural formula of DGEBA is as follows:



where the content of $n=0$ is 99.7%.

As initiators for VT, dicumyl peroxide (DCP) and *t*-butyl perbenzoate (BPB) were kindly supplied from Nippon Oil and Fats Co.

As the curing agent for DGEBA, 2MA was used. 2MA is a popular curing agent for

epoxide resin.¹⁵

Apparatus and Procedure

An infrared spectrophotometer (Hitachi 260-10) was used. A sample was placed between NaCl plates to form a liquid film and

spectra were obtained in the transmission mode. The NaCl plates with samples were kept in a conventional oven for a certain period of time, followed by the observation of the spectral change by infrared. Then, it was placed in the oven again for further heating. The quantitative study was carried out by calculating the band height in absorbance mode from transmission spectra of IR. The band assignment was carried out considering band assignment of melamine¹⁶ and some bands of VT by Oikawa and Kawahara¹⁷ as references. The amino groups show the vibration in the 3400—3000- cm^{-1} and 1770—1600 cm^{-1} regions. The spectral change in these regions is a good indicator to observe the extent of the reaction between NH groups and epoxides. Likewise, the CH wagging band of the olefine at 962 cm^{-1} was used to show the extent of the reaction of the double bonds. A Shimadzu thermal analyzer DT-20B was used for the differential thermal analysis (DTA). The chemical reaction between DGEBA and three compounds (VT, ET, and melamine) were studied using DTA. The sample was prepared by mixing 10.0 g of DGEBA and 2.0 g of each compound extensively. When one mol of amino group is considered to react with two mol of epoxide, 10.0 g of DGEBA and 2.0 g of VT is the stoichiometry. 20 mg of the mixture of DGEBA and each compound were measured as the samples. As a reference, 10 mg of Al_2O_3 were used. The heating speed was 5°C min^{-1} and 100 μV range was used for the experiment. The temperature was raised from room temperature to 300°C.

The gel time of the mixture of these three compounds and DGEBA were measured by the stroke curing method on a hot plate at 150°C following JIC C2104. The mixture was initially prepared by a slight heating of DGEBA to melt and 20 wt% of each compound was added. Then, they were mixture at room temperature and repeated mixing. A certain amount of 2MA was added and mixed well again.

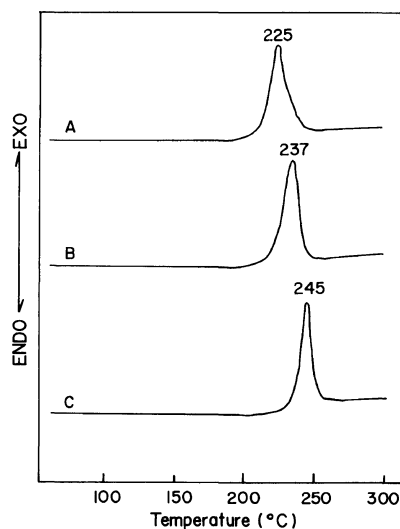


Figure 1. DTA spectra of the mixture of 10.0 g of DGEBA and 2.0 g of (A) VT, (B) ET, and (C) melamine. DGEBA, diglycidyl ether of bisphenol A; VT, 2,4-diamino-6-vinyl-*s*-triazine; ET, 2,4-diamino-6-ethyl-*s*-triazine.

RESULTS AND DISCUSSION

Chemical Reactivity of VT with Epoxide

The DTA spectra of the mixture of DGEBA and VT, ET, and melamine are shown as Figures 1A, 1B, and 1C, respectively. The mixture of DGEBA and VT (Figure 1A) showed an exothermic peak due to the chemical reaction between VT and DGEBA at 225°C. On the other hand, the mixture of DGEBA and ET and melamine showed exothermic peaks at 237 and 245°C, respectively, (Figure 1B and Figure 1C). These results indicate the differences in chemical reactivities of VT, ET, and melamine with DGEBA. The differences are probably due to the different π electron densities of the compounds. The electron donating property of the substituents increased in the order of $\text{CH}_2 = \text{CH} > \text{C}_2\text{H}_5 > \text{NH}_2$, which corresponds to the order of reaction temperature (peak position) of DGEBA and three compounds. The differences in reactivities among melamine, ET, and VT are possibly due to the differences in the reactivities of amino groups with ep-

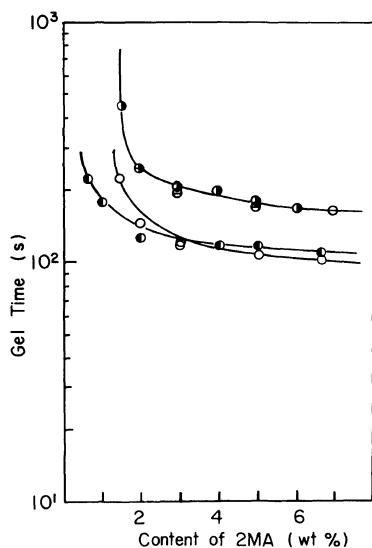


Figure 2. Relationship between gel time and amount of 2MA to the mixture of 100 g of DGEBA and 20 g of VT (●), ET (○), and melamine (⊖). (●) indicates the only 100 g of DGEBA as reference. 2MA, 2,4-diamino-6-(2'-methylimidazolyl-(1'))ethyl-*s*-triazine.

oxide resin. Higher π electron density of *s*-triazine provide higher chemical reactivity of amino groups with epoxide. The chemical reaction between melamine and epoxide resin has not been studied extensively because of the low chemical reactivity.

Additional Effects of Imidazole Compound

The chemical reaction between DGEBA and VT was further studied by observation of gel time and IR spectra. The relationship between gel time and the amount of 2MA added is shown in Figure 2. The gel time curve of DGEBA/melamine mixture did not show a major difference from the reference mixture of DGEBA and 2MA, indicating no acceleration of the gel time by melamine. On the other hand, DGEBA/VT and ET mixtures showed remarkable shortening of gel time by the addition of the 2MA compound to the reference mixture. The DGEBA/VT mixture especially indicates the rapid decrease in gel time by the addition of a slight amount of 2MA. The chemical reaction of the DGEBA/VT mixture

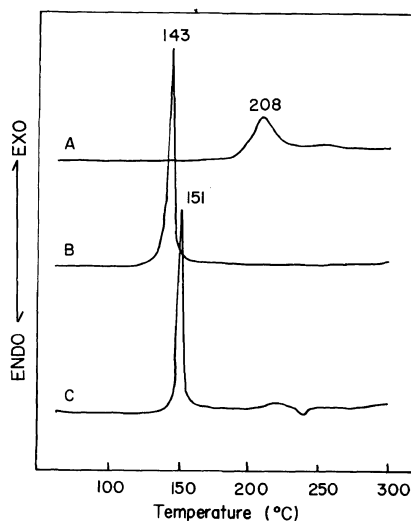


Figure 3. DTA spectra of the mixture of DGEBA/VT/2MA possessing the following composition (wt%): (A) 83.3/16.5/0.2; (B) 83.3/9.0/7.7; (C) 83.3/0/16.7.

by the addition of 2MA was further studied using DTA. Figures 3A, B, and C indicated DTA spectra of mixtures of DGEBA/VT/2MA with the composition of 83.3/16.5/0.2 wt%, 83.3/9.0/7.7, and 83.3/0/16.7, respectively. Figure 3A shows a relatively broad and small exothermic peak at 208°C with a shoulder, which is about 17°C lower than the mixture without 2MA (Figure 1A). The shifting of the peak to the low temperature is due to the catalytic effect of 2MA added. This effect is clearly seen in Figure 3B, where the peak position has shifted by 65°C to the lower temperature compared to Figure 3A. In addition, the peak position of Figure 3B is higher than Figure 3C by 8°C, which means the mixtures of 7.7 wt% of 2MA and 9.0 wt% of VT possess higher reactivity with epoxide resin than 16.7 wt% of 2MA. This indicates that VT was catalyzed by 2MA, resulting in the higher reactivity with epoxide than 2MA alone. From the infrared spectra of the cured compounds of VT and a commercial epoxide resin (Epikote #828) in the presence of 2MA at the peak of DTA thermograms,⁷ it was clear that the

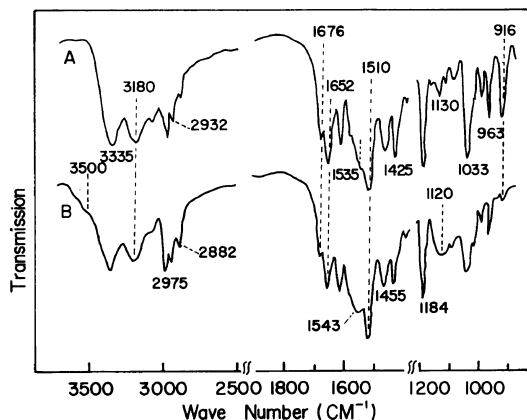


Figure 4. Infrared spectra of the mixture of DGEBA/VT/2MA (82.7/16.5/0.8 wt%): (A) initial; (B) after heating at 150°C for 2.2 h.

absorption of epoxide disappears almost on heating to 150°C, but the absorption of amino groups did not disappear on heating to 250°C.

The spectroscopic study of the chemical reaction of VT and DGEBA with a small amount of 2MA was carried out using IR spectroscopy. A good mixture of DGEBA/VT/2MA (82.7/16.5/0.8 wt%) was placed between NaCl plate to make a thin film. The spectral change was observed after heating for a certain period of time at 150°C. The initial spectrum of the mixture is shown as Figure 4A. The Figure 4B shows the spectrum heating at 150°C for 2.2 h several spectral changes due to the chemical reactions are observed. The intensity of NH₂ stretching bands at 3335 cm⁻¹ and 3180 cm⁻¹ and the bending at 1652 cm⁻¹ were reduced, indicating the chemical reaction between amino groups and epoxides. The broad band around 3500 cm⁻¹ in Figure 4B is due to both the polymerization of VT and OH groups produced by the chemical reaction between amino groups of VT and epoxide. The chemical reaction between amino groups and epoxides was enhanced by 2MA, because almost no reaction was observed without 2MA by heating at 150°C for this period of time. The new broad band at 1120 cm⁻¹ is due to the stretching band of O-C bond and C-N bond.

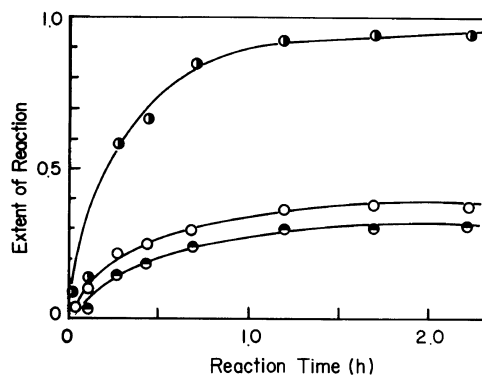


Figure 5. Relationship between reaction time and extent of reaction of epoxide (●), amino group (○), and double bond (◐) of the mixture of DGEBA/VT/2MA (82.7/16.5/0.8 wt%).

This is due to the anionic polymerization of epoxides by imidazole and its derivatives¹⁸⁻²² and the chemical reaction between epoxides and amines. The extent of the reaction of epoxides was observed by the band at 916 cm⁻¹. Most of the epoxides reacted by heating at 150°C for 2.2 h. However, the double bond at 963 cm⁻¹ still remained after heating.

The extent of reaction of amino groups, epoxides, and double bonds were plotted versus reaction time in Figure 5. The extent of reaction was obtained by calculating the absorbance from a transmission spectrum, followed by a comparison of the reduction in absorbance due to the reaction with the initial value. The deviation of the initial value from the curve is due to the method of experiment. It took about 2 min for the plate to become 150°C from temperature in the oven. Therefore, this insufficient heating resulted in the deviation from the curve in the region of the short time heating. The kinetic study of this reaction was not possible for this reason. However, the reaction curve of epoxide does not show the typical sigmoidal curve of Ricciardi²¹ and Kakiuchi²² due to imidazole curing, indicating that some other reactions take place at the same time. The reaction curves of both amino groups and double bonds showed similar trends to epoxides, even though the

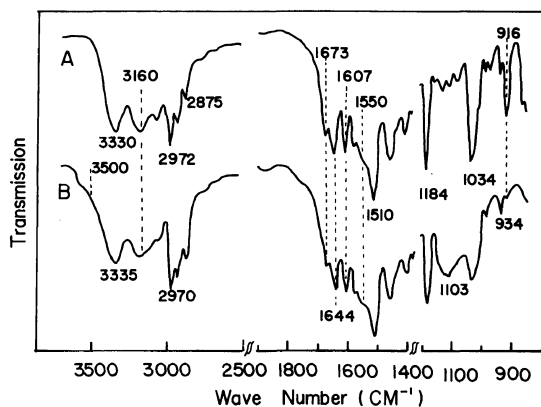


Figure 6. Infrared spectra of the mixture of DGEBA/VT/2MA (82.7/16.5/0.8 wt%): (A) initial; (B) after heating at 150°C for 8.3 h.

reactivities were lower than epoxides.²³ As the polymerization of epoxides progresses, other reaction speeds become low because of the lowered diffusion. The cleavage speed of double bonds is thus much lower than the reaction speed of epoxides. However, heating at higher temperature greatly enhances the reaction speeds of both double bonds and amino groups compared to that of epoxides.

The chemical reaction of DGEBA/ET/2MA (82.7/16.5/0.8 wt%) was studied in the same manner. The spectral changes due to the reactions are shown in Figure 6. The reactions of the amino groups at 1645 cm^{-1} and epoxide at 916 cm^{-1} were observed. However, the extent of reactions of amines was less than the VT mixture shown in Figure 4B. The relationship between the extent of reaction and reaction time of amines and epoxides is plotted in Figure 7, where the reaction speeds of epoxides are considerably low compared to Figure 5. The epoxides reacted gradually after 1.5 h, following the rapid initial reaction. About 20% of the amino groups reacted by heating for 1.5 h at 150°C. However, further reaction could not be observed after that.

The clear difference between VT and ET observed in Figure 2 was the different gel time, especially by the addition of less than 2.0 wt%

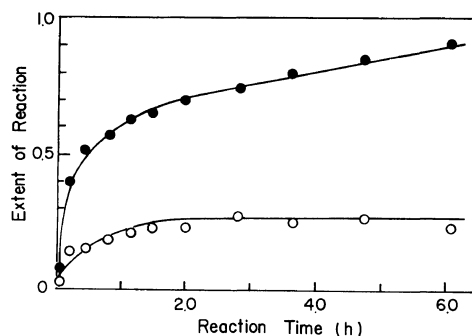


Figure 7. Relationship between reaction time and extent of reaction of epoxide (●) and amino group (○) of the mixture of DGEBA/ET/2MA (82.7/16.5/0.8 wt%).

of 2MA to the mixture. This was due to the difference in reactivities of amino groups of each compound with epoxide resin, and was attributed to the different π electron densities of the ring. The chemical reactions between amino groups and epoxides are catalyzed by imidazole. The degree of enhancement of the reactivity by the addition of 2MA also depends on the π electron density of the ring. VT with a higher electron density is catalyzed more than ET by a slight amount of 2MA addition. The initial reaction compound of the epoxides and each compound might give catalytic effects for the polymerization of epoxides. However, further study is required to confirm this.

Additional Effects of Peroxides

It was necessary to cleave double bonds to optimize the mechanical properties of the resin in IPN. However, considerable amounts of double bonds of VT were still observed after most of the epoxides reacted (Figure 4). Therefore, radical initiators such as dicumyl peroxide (DCP) or *t*-butyl peroxybenzoate (BPB) were added to the mixture of DGEBA/VT/2MA to complete the polymerization of double bonds. The infrared spectra of DGEBA/VT/2MA/DCP (82.6/16.5/0.2/0.7 wt%) mixture is shown in Figure 8A after heating at 150°C for 11.5 h. The spectrum shows the characteristic polymerization of VT

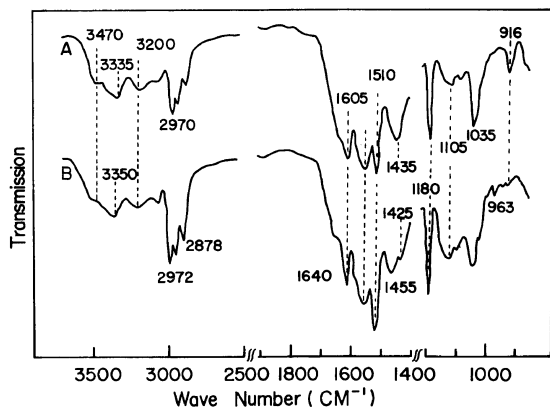


Figure 8. Infrared spectra of the mixture of DGEBA/VT/2MA/DCP of (A) 82.6/16.5/0.2/0.7 after heating for 11.5 h at 150°C and (B) 80.6/16.1/2.6/0.7 after heating for 3.3 h at 150°C. DCP, dicumyl peroxide.

at 3470, 3350, and 3200 cm^{-1} , as observed by the polymerization of VT by peroxides. In addition, the CH_2 wagging band of double bonds at 963 cm^{-1} disappeared almost completely. However, 40 wt% of the epoxides band at 916 cm^{-1} still remained after the heating. The mixture of DGEBA/2MA/DCP (80.6/16.1/2.6/0.7 wt%) containing more 2MA was studied to promote the reaction of epoxides. The infrared spectrum of the mixture after heating at 150°C for 3.2 h is shown in Figure 8B. The increased reaction of epoxide at 916 cm^{-1} was observed. Nevertheless, 23% of the double bonds still remained unreacted, which is much more than the mixture containing less 2MA (Figure 8A). This indicates that the increased addition of 2MA decreases the reaction of double bonds.

The extent of the reaction of the mixture containing different ratios of 2MA and peroxide are studied further in Figure 9. 100 g of DGEBA were mixed well with 20 g of VT. Then, a certain amount of 2MA and peroxide of different ratios were added to the mixture of DGEBA and VT. Finally, these compounds were again mixed well for spectroscopic study. The extent of the reactions of epoxides at 916 cm^{-1} and double bonds at 962 cm^{-1} were observed after 20 min and 1.3 h from the spec-

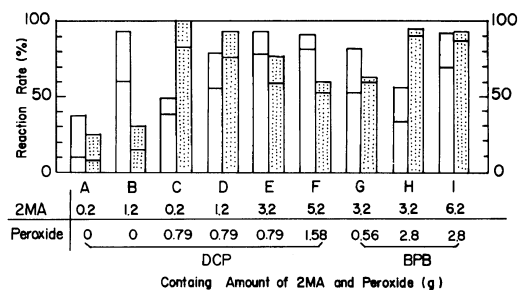


Figure 9. Extent of reaction of epoxide and a double bond at 150°C for 20 min and 1.3 h. Each compound contains 100 g of DGEBA and 20 g of VT and the mixture of 2MA/peroxide. □, epoxide; ▨, double bond; ■, after heating at 150°C for 20 min; ▩, after heating at 150°C for 1.3 h.

tral change. The mixture containing 0.2 g and 1.2 g of 2MA in the DGEBA and VT mixture are shown in Figure 9A and Figure 9B, respectively, and compared to the mixture containing both 0.2 g of 2MA and 0.79 g of DCP (Figure 9C). By the increase of 2MA, the reaction speed of peroxide obviously increased. However, the extent of the reaction of double bonds did not increase significantly (Figures 9A and 9B). By the addition of DCP the reaction speed of the double bonds increased very much (Figure 9C) compared to the one in Figure 9A.

Mixtures containing different ratios of 2MA/DCP in the presence of DGEBA and VT (1.2 g/0.79 g, and 5.2/1.58) are shown in Figures 9D, 9E, and 9F, respectively. It is interesting to compare Figures 9C, 9D, and 9E, because the amounts of DCP were constant, although the amount of 2MA varied. The extent of the reactions of epoxides increased by increasing 2MA. However, the extent of the reactions of double bonds decreased. The increased addition of both 2MA and DCP did not show remarkable increase in either reaction (Figure 9F).

The more reactive peroxide at considerably low temperature was used to improve the cleavage speed of double bonds (Figures 9G, 9H, and 9I). The decomposition temperature

of BPB is 128°C, which is 12°C lower than that of DCP. The extent of the reaction of the mixture containing different ratios of 2MA/BPB in the DGEBA and VT mixture (3.2/0.56 g, 3.2/2.8, and 6.2/2.8) is shown in Figures 9G, 9H, and 9I. 0.79 g of DCP and 0.56 g of BPB are equivalent moles. The different extents of reactions between DCP and BPB can be observed by comparing Figures 9E and 9G, where they contain the same amount of 2MA and the equivalent mole of another peroxide. The extent of the reaction of double bond in Figure 9G after heating for 20 min is slightly higher than Figure 9E, even though it did not increase by further heating. However, the extent of the reaction of epoxide by BPB in Figure 9G is lower than that by DCP in Figure 9E. This probably indicates the faster cleavage reactions of double bonds since BPB results in the depression of reactions of epoxides.

The extent of the reaction of the double bonds increased by increasing BPB (Figure 9H). However, the reaction of epoxide was depressed considerably. This is opposite to the phenomenon where depression of the cleavage of double bonds occurred by increasing 2MA. The extent of reactions of double bonds and epoxides depends on the ratios of peroxide and 2MA. Figure 9I shows the most extended reactions of epoxides and double bonds, which require fairly large amounts of 2MA and peroxides. The addition of 3.2 g of 2MA is enough to cure DGEBA and 0.56 g of BPB is also enough to polymerize VT separately. However, Figure 9I indicates that 6.2 g of 2MA and 2.8 g of BPB are necessary to complete both reactions simultaneously. These results above indicate the enhancement of reactivity of one group to cause a rapid drop of the diffusion of the system. Therefore, the other reactive groups can not obtain sufficient contacts for the reaction in a limited diffusion condition. Therefore, a suitable ratio of peroxide and 2MA and excess amount of these two compounds are required for the reactions in IPN to proceed.

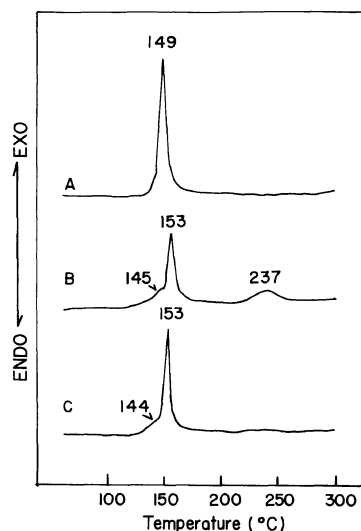


Figure 10. DTA spectra of DGEBA/VT/2MA/BPB mixture containing 100 g of DGEBA, 20 g of VT and 1MA/BPB of (A) 3.2 g/0.56 g, (B) 3.2/2.8, and (C) 6.2/2.8.

The DTA study of DGEBA/VT/2MA/BPB mixture was carried out as shown in Figure 10. The DTA spectra of Figures 10A, 10B, and 10C correspond to the same mixture of Figure 9G, 9H, and 9I, respectively. The molar ratio of 2MA/BPB of Figures 10A, 10B, and 10C are 3.2 g/0.56 g, 3.2/2.8, and 6.2/2.8, respectively. The extent of reactions of epoxide/double bonds of Figures 10A, 10B, and 10C after heating at 150°C for 1.3 h are 82%/63%, 55/95, and 92/93. Figure 10A shows the only one exothermic peak, which is probably due to the polymerization of epoxide by 2MA as well as the polymerization of double bonds by BPB. These two reactions probably occurred at the same temperature. Figures 10B and 10C show the small shoulder peak at 145°C besides the main peak at 153°C. This shoulder peak at 145°C is possibly due to the polymerization of VT and the peak at 153°C is due to the polymerization of epoxide. The shift of the main peak to higher temperature is probably due to the restricted reaction of epoxides caused by the initial polymerization of double bonds. The broad peak at 237°C in Figure 10B

is presumably due to the reaction of unreacted epoxide and poly VT, because most VT was polymerized initially as seen in Figure 9H. The chemical reaction between VT and DGEBA was observed at 225°C without 2MA in Figure 1A. Therefore, the same reaction possibly takes place between amino groups of poly VT and epoxide. In Figure 10C, the broad band at 237°C is not clearly observed, because of the progress of the polymerization of epoxide by the increased concentration of 2MA.

CONCLUSION

Melamine, ET, and VT showed different reactivities with DGEBA, because of the different π electron densities of s-triazine ring. An ET or VT mixture of DGEBA showed considerable decrease of gel time by the addition of 2MA. However, the melamine and DGEBA mixtures did not show this. This shortening of gel time is due to the catalyzed reactivity of the amino groups of ET and VT by 2MA. Amino groups of VT and ET react with epoxide along with the polymerization of epoxide by the addition of a slight amount of 2MA. The reaction curve of double bonds of VT was similar to those of the amino groups at 150°C. The reactivities of epoxide and amino groups of ET were lower than VT by the addition of 0.8 wt% of 2MA because of the lower π electron density of the ring. By the addition of DCP, the polymerization of double bonds increased. However, polymerization of epoxide was suppressed. On the other hand, the excess amount of 2MA caused depression of the polymerization of double bond. This is attributed to the rapid drop of diffusion caused by the progress of the reaction of one group. A suitable molar ratio of peroxide and 2MA and excess amount of these two compounds are necessary to complete two kinds of reactions simultaneously.

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