

Studies on the Effect of Epoxide Equivalent Weight of Epoxy Resins on Thermal, Mechanical, and Chemical Characteristics of Vinyl Ester Resins

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ABSTRACT: Three samples of vinyl ester resins (VERs) were synthesized using bisphenol-A-based epoxy resins of varying epoxide equivalent weights (EEW) and acrylic acid in presence of triphenylphosphine as a catalyst at $80 \pm 2^\circ\text{C}$. The cresyl glycidyl ether was used as reactive diluent during the synthesis of VERs. A suitable reaction mechanism was proposed and discussed for the reactions involving epoxide group and acid groups. This was further confirmed by infrared spectroscopic analysis. The maximum peak temperature from DSC were at 106.05°C , 114.20°C , and 128.86°C for benzoyl peroxide initiated VERs viz. samples V_1C_V , V_2C_V , and V_3C_V , respectively,

increased with the increase of EEW of the parent epoxy resin. It has also been found that the films of VER having highest EEW of bisphenol-A epoxy resin showed best chemical resistance amongst all other VERs in this study. The mechanical properties such as hardness and flexibility also showed a similar trend. The thermal stability was found to decrease with the increase of EEW of bisphenol-A epoxy resin in the VERs. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2406–2412, 2010

Key words: vinyl ester resins; chemical resistance; differential scanning calorimetry (DSC); hardness

INTRODUCTION

Vinyl ester resins (VERs) are produced usually by the reaction of epoxy resins based on bisphenol A¹ and novolac with ethylenically unsaturated acids (acrylic or methacrylic) in presence of basic catalysts.^{2–8} The epoxy resins⁹ are liquid, semisolid, or solid depending upon their epoxide equivalent weight (EEW). The EEW of the epoxy resins affects the crosslink density which finally influences the physical, chemical, and mechanical properties of VERs.^{2,10–12} The bisphenol A-based acrylate terminated VERs are preferred over methacrylate terminated VERs because of their greater reactivity resulting in rapid cured product having better chemical and mechanical properties.^{13–17} The cured VERs, with or without vinyl monomers, are brittle in nature and lacks in toughness¹⁸ because of high crosslink density of the cured VERs,^{19–21} whereas maleopimERIC epoxies- based methacrylate VERs show higher chemical and heat resistance than the acrylates.¹⁷ Triphenylphosphine was used as catalyst in the esterification reaction at elevated temperatures. This makes them a viable products for various industrial applications such as automotive parts, op-

tical fibers, metal foil laminates, fiber reinforced composites, radiation curable inks, and coatings (high solid/solvent less coatings).^{22–26} The high viscosity of neat VERs possesses problems in processing. The addition of reactive/nonreactive diluents reduces the viscosity of the VERs. The most commonly used reactive diluents are vinyl monomers, viz., styrene, α -methyl styrene, acrylates, and methacrylates.^{27–30} These diluents take part in the curing reactions and create a link between adjacent vinyl ester molecules.⁷ The vinyl group containing monoepoxy diluents reduces the viscosity at low concentrations and controls the crosslink density of the system, which provides a system of high flexural strength. The use of monoepoxy diluents during the synthesis of VERs is yet to be explored as limited work is reported in literature.³¹

EXPERIMENTAL

Materials

Bisphenol-A-based epoxy resins PG-100 (M/s Parikh Resins, Kanpur), ESC-200 and EPP- 984 (M/s SIP Resins, Chennai), cresyl glycidyl ether (CGE) (M/s Shell Chemical Co. USA), acrylic acid (AA), and triphenylphosphine (M/s Fluka A.G., Switzerland) were used for the preparation of VERs. Benzoyl peroxide (M/s S.D. Fine Chemicals, Mumbai) was used as curing agent for VERs. Hydrochloric acid (M/s

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Qualigen Fine Chemicals, Mumbai), sulphuric acid, nitric acid, (M/s Sarabhai M. Chemical, Vadodara), sodium hydroxide, potassium hydroxide (M/s Ranbaxy Laboratories, Punjab), acetone, methyl ethyl ketone (MEK) (M/s Central Drug House, Delhi), and mineral turpentine oil (MTO) obtained from the local market were used to study the effect of various chemicals and solvents on the cured films of VERs.

Synthesis of VERs

VERs were synthesized by the method similar to that reported in our earlier publication.³² A reaction mixture consisting of 1 : 0.9 mole ratio of bisphenol-A epoxy resins of varied EEWs and AA with CGE (40% g of the resin) by weight of epoxy resin) was charged into a three-necked flask (500 mL) equipped with a mechanical stirrer, nitrogen inlet tube, and thermometer. The reaction was carried out in an oil bath at $80 \pm 2^\circ\text{C}$ with the addition of triphenylphosphine as catalyst (1% by weight of the resin) in the reaction mixture. The reaction was carried out for 5, 6, and 7.5 h till the acid value mg KOH /g reached to less than 10. The using epoxy resins of EEW 185 (V_1C_V), 408 (V_2C_V), and 881 (V_3C_V) eq/g, respectively, were used in this study.

Fourier transform infrared (FTIR) spectroscopic analysis

The structure of synthesized resins were analyzed by Perkin Elmer Paragon 1000 FTIR Spectrophotometer. KBr pellets (0.3 mm) of VERs (~1% sample) were formed under pressure and scanned from wave number 200–4000 cm^{-1} . The IR spectra were examined for characteristic bands/peaks of VER to check and to confirm the identity of the synthesized resins. The peaks related to synthesized VERs were matched with the available spectra for similar VERs in the Henkel Corporation Series Library, Germany.³³

Cure schedule

The cure schedule of the VERs was determined using DSC of TA instruments, USA (Model 2910) in dynamic and isothermal mode to identify the cure temperature and the cure time for the completion of the curing reactions. Benzoyl peroxide (2%) was used as initiator during the curing of VERs.

Thermal stability

Thermal Analyst 2000 (TA Instruments) equipped with 2950 thermal gravimetric analyzer was used to study the decomposition behavior of cured VERs. TG analysis was performed under nitrogen atmos-

phere from 50–700°C at the heating rate of $10^\circ\text{C min}^{-1}$.

Chemical resistance

Preparation of panels

The panels were prepared by applying the VERs samples on sand blasted steel sheet panels of size 150 mm \times 100 mm \times 1.25 mm using Bird Film applicator (M/s Sheen Instruments, UK). These panels were further sealed from four sides by using molten paraffin wax. The dry film thickness of about 150 microns was maintained on all the panels. These films were then cured as per the cure schedule determined by DSC.

Exposure of panels to different chemicals

The panels were examined for a visible change in the conditions of the film samples at regular intervals, when exposed in different chemicals like acids, alkalis, and solvents at ambient temperature for a period of 3 months.

Mechanical properties

The coated films of VERs on the mild steel panels were tested for its scratch hardness using H, 2H, and 4H pencils. The flexibility of cured VER samples was checked by bending the panel to 180° around 1/4 inches mandrel (M/s Sheen Instruments, UK).

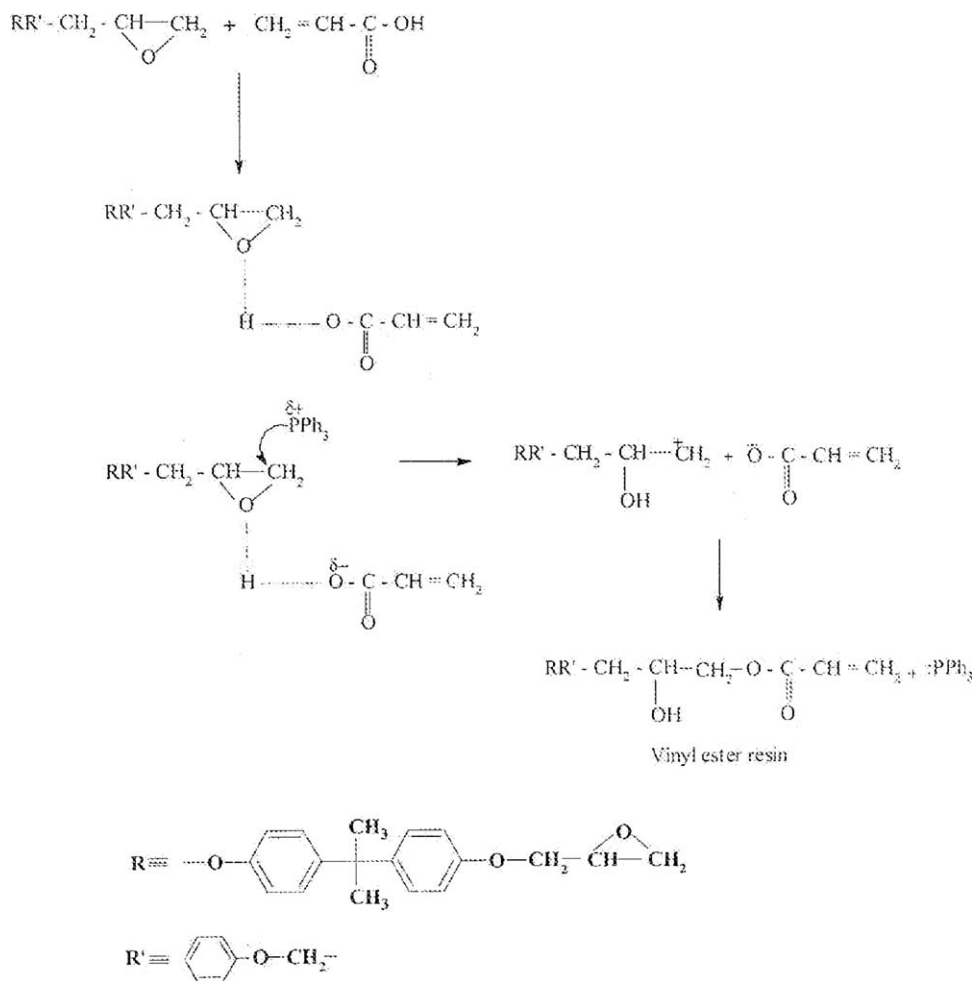
RESULTS AND DISCUSSION

Synthesis of VERs

The esterification reaction of bisphenol-A epoxy resin and CGE with AA, in presence of triphenylphosphine (PPh₃), proceeded with the formation of a hydrogen bond between oxirane oxygen of epoxy resin and acid group from AA as shown in Scheme 1. The catalyst PPh₃ attacked on electron deficient center, i.e., the terminal carbon of the epoxy ring. This might be due to inductive effect (-I) of group attached to the epoxy ring. This formed a bond between terminal carbon and the acrylate anion, and the catalyst was regenerated after the esterification reaction. A proposed mechanism showed the reactions involved during the synthesis of VERs.

FTIR analysis of VERs

Figure 1 showed the FTIR spectra of V_1C_V , V_2C_V , and V_3C_V . It is clear from Figure 1 that the peak at 910 cm^{-1} due to oxirane group of epoxy resin³⁴ disappeared and new peaks at 1724 cm^{-1} , 1730 cm^{-1} , and 1755 cm^{-1} were observed in the spectra of



Scheme 1 Reaction mechanism for the synthesis of vinyl ester resin.

V_1C_V , V_2C_V , and V_3C_V , respectively. These peaks might correspond to the stretching vibrations of the aromatic carbonyl group of the ester formed.³⁵ The band appeared near 1603, 1622, and 1630 cm^{-1} ,

respectively, in the spectra of V_1C_V , V_2C_V , and V_3C_V (Fig. 1) might be attributed to the formation of acryloyl double bond. These spectra were also matched with the standard IR spectra of epoxy acrylate given

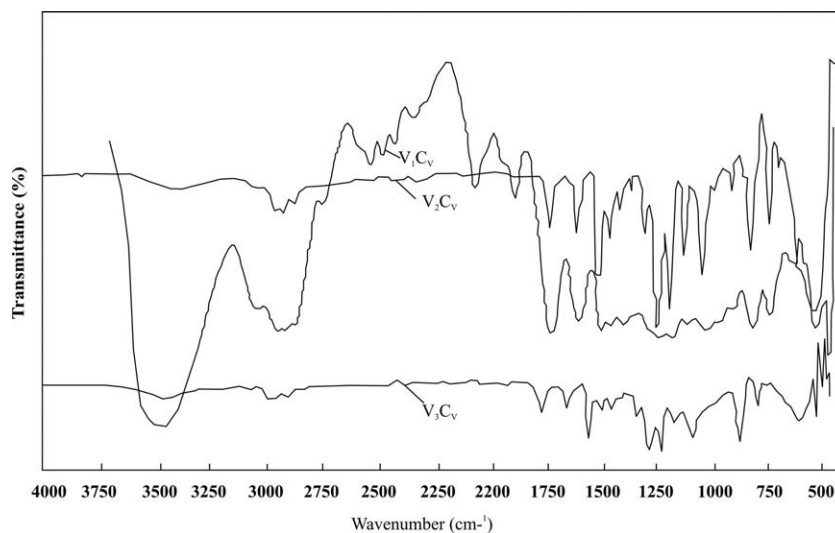


Figure 1 FTIR spectrum of synthesized V_1C_V , V_2C_V , and V_3C_V .

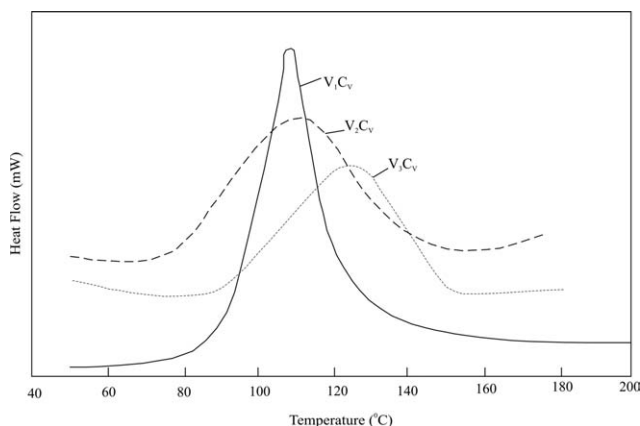


Figure 2 Dynamic DSC scans for the curing of vinyl ester resins (V_1C_V , V_2C_V , and V_3C_V) mixed with 2% Benzoyl Peroxide by weight at $10^\circ\text{C min}^{-1}$.

in the literature³⁴ and found to be in close agreement, upto 94%, which confirmed the formation of VERs.

Cure schedule

Typical dynamic DSC scans for the curing of V_1C_V , V_2C_V , and V_3C_V resins mixed with 2% benzoyl peroxide as initiator at $10^\circ\text{C min}^{-1}$ have been shown in Figure 2. The figure showed that the exothermic curves were found to be in the range $70\text{--}50^\circ\text{C}$, and the related data for all the samples have been presented in Table I. The thermograms showed that the rate of curing reaction was sluggish in the early stages of the reaction, whereas it was comparatively faster in the later stages. The onset temperature of (T_o) of curing, peak exothermic temperature (T_m), and the final temperature (T_f) of curing were obtained, which increased with the increase in the value of EEW of the base epoxy resin used for the

TABLE I
Curing Behavior of the Blend of Vinyl Ester Resins Mixed with 2% Benzoyl Peroxide at a Heating Rate 10°C/min

Sample code	^a T_o ($^\circ\text{C}$)	^b T_m ($^\circ\text{C}$)	^c T_f ($^\circ\text{C}$)	^d ΔH (J/g)
V_1C_V	81.0	106.05	126.06	197.6
V_2C_V	85.1	114.20	145.53	121.1
V_3C_V	89.8	128.86	147.80	73.09

^a Onset temperature by extrapolation.

^b Temperature of cure maximum.

^c Temperature at the end of cure.

^d From area of the dynamic DSC scans.

synthesis of VERs. The cure time data also increased with the increase of EEW at fixed temperature, that is, 120°C . The overall heat of curing (ΔH) value of V_3C_V was found to be lower than the sample V_1C_V and V_2C_V . This might be attributed to the higher crosslink density produced in the cured product of V_1C_V , as it has been synthesized using epoxy resin of low EEW in comparison to V_2C_V and V_3C_V .^{36,37} A similar trend was observed by Agrawal et al.² in their studies on VERs for epoxy resin having (EEW 190 eq/g) using different catalyst systems.

Thermal stability

Thermal behavior of cured resins was evaluated by TGA in a nitrogen atmosphere. The TGA/DTGA traces of sample V_1C_V , V_2C_V , and V_3C_V are shown in Figure 3. The results of TGA are summarized in Table II. Also, the temperatures for 1 and 5% weight loss in TGA curves for cured VER samples have been presented in Table III. The data clearly indicated the higher thermal stability of sample V_1C_V than the sample V_2C_V and V_3C_V , if 5% weight loss is considered as an indicative of initial degradation

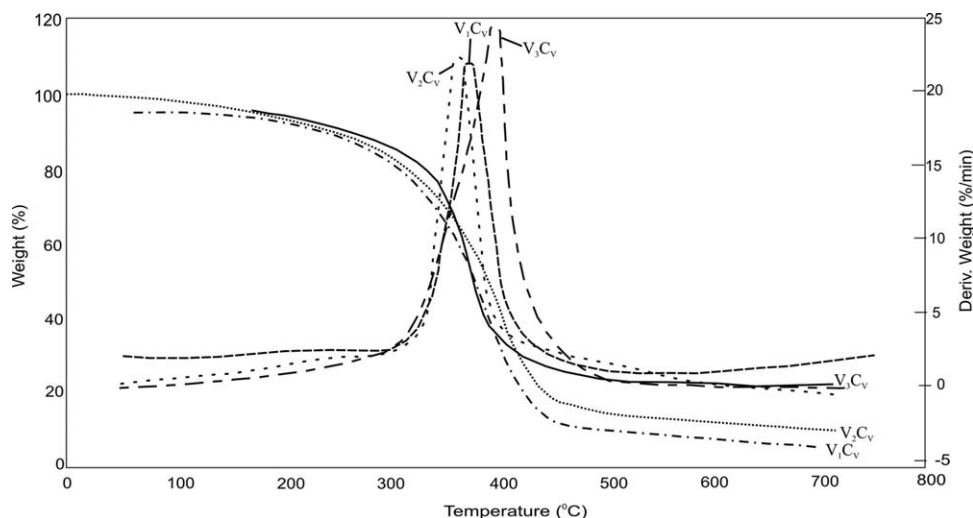


Figure 3 Dynamic TG and DTG scans of vinyl ester resins (V_1C_V , V_2C_V and V_3C_V).

TABLE II
Thermal Behavior of Vinyl Ester Resins at 10°C/min

Sample code	T_i (°C)	T_m (°C)	T_f (°C)	Char Yield at 700°C (%)
V ₁ C _V	342.85	372.32	417.24	23.95
V ₂ C _V	314.81	368.74	396.65	20.05
V ₃ C _V	292.95	390.40	429.05	12.25

T_i Initial Temperature of decomposition.

T_m Peak Temperature of decomposition.

T_f Final Temperature of decomposition.

temperature.³⁸ All VERs showed single-step decomposition behavior with only one sharp maxima at 372.32, 368.74, and 390.40 for the cured samples V₁C_V, V₂C_V, and V₃C_V, respectively. The temperature of maximum rate of weight loss was higher for the sample V₃C_V with lower initial decomposition temperature. The char yield (Table II) was found to be maximum in V₁C_V, that is, 24%, whereas it was 20% and 12% for samples V₂C_V and V₃C_V, respectively (refer Fig. 3). This indicated the higher crosslink density of sample V₁C_V. The higher crosslink density also increased T_o and T_m values as obtained from DSC analysis (refer Table I). These experimental results indicated that V₃C_V was thermally less stable than V₁C_V and V₂C_V.

Chemical resistance of VERs

Effect of concentrations of acids on the cured film of VERs

The effect of concentrations of acids on the films of samples V₁C_V, V₂C_V, and V₃C_V when exposed to different acids such as sulphuric acid, hydrochloric acid, and nitric acid as concentrations ranging between 5 and 20% with an interval of 5% has been shown in Table IV. These results were based on the visible changes on the surface of the films noted in the interval of 2 days upto a period of 3 months. It is clear from the observations that the cured films of samples V₂C_V and V₃C_V were found to be com-

TABLE III
Temperature of 1 and 5% Weight Loss in Thermogravimetric Analysis of Cured Samples

Weight loss (%)	Temperature (K)		
	V ₁ C _V	V ₂ C _V	V ₃ C _V
1	438	408	390
5	513	495	483

pletely unaffected by different concentrations of nitric acid up to 3 months, whereas the films of V₁C_V showed some blistering with change in color and gloss. The films completely left the surface of the panel after 3 months of immersion in 20% nitric acid. A similar type of observations were seen when cured films of VER samples were exposed to sulphuric acid and hydrochloric acid (Table IV). From these results, it could be inferred that the increase in concentration of any acid adversely affected the acid resistance of the films. The VER based on higher molecular weight epoxies showed better acid resistance than VER produced with low molecular weight epoxy. This might be due to higher crosslink density of V₁C_V.

Effect of concentrations of alkalis on the cured films of VERs

The effect of concentrations of alkalis on the cured films of V₁C_V, V₂C_V, and V₃C_V have been shown in Table IV. The results of exposure of cured ester films in KOH and NaOH (concentration varied from 5 to 20%) indicated that increase in concentration of the alkalis had adversely affected the film surface. The V₃C_V were observed to be resistant for a month in both the alkalis of all concentration. The cured films were found to be resistant up to 2 months by 20% NaOH solution. The ester based on higher molecular weight epoxies showed better acid resistance than the ester prepared with low molecular weight epoxies. It is also inferred from the results of Table IV that the surface of the cured films of VER resins

TABLE IV
Comparative Acid, Alkali, and Solvent Resistance of the Films of Vinyl Ester Resins Showing the Period after Which the First Effect Was Detected When Immersed for Months at Ambient Temperature

	V ₁ C _V				V ₂ C _V				V ₃ C _V			
	5%	10%	15%	20%	5%	10%	15%	20%	5%	10%	15%	20%
H ₂ SO ₄	>3 m	2 m	30 d	20 d	>3 m	>3 m	>3 m	30 d	>3 m	>3 m	>3 m	>3 m
HCl	>3 m	30 d	20 d	5 d	>3 m	>3 m	>3 m	2 m	>3 m	>3 m	>3 m	>3 m
HNO ₃	>3 m	30 d	10 d	5 d	>3 m	>3 m	>3 m	2 m	>3 m	>3 m	>3 m	>2 m
NaOH	>3 m	30 d	10 d	2 d	>3 m	>3 m	>3 m	20 d	>3 m	>3 m	>3 m	30 d
KOH	>3 m	2 m	10 d	5 d	>3 m	>3 m	>3 m	30 d	>3 m	>3 m	>3 m	30 d
Acetone		5 d				10 d				30 d		
MEK		10 d				20 d				30 d		
MTO		30 d				2 m				>3 m		

d, Days; m, Months.

was strongly affected by sodium hydroxide as compared to potassium hydroxide of same concentration. The film surfaces were found to be more resistant in acids than the alkalis. This might be primarily due to the formation of ester linkages. However, the number of ester linkages might be quite less but are sufficient for the hydrolysis of vinyl ester. The carbon-to-carbon double bonds, located at the end of polymer chains of VERs, usually reacted completely during polymerization resulting in enhanced chemical resistance, particularly toward acids.³⁹

Effect on the films of VER samples of solvents

The results of the exposure of the cured films of esters V_1C_V , V_2C_V , and V_3C_V , in acetone, methyl ethyl ketone (MEK), and mineral turpentine oil (MTO) are given in Table IV. It is apparent from the observed data that only the surface of cured film prepared from V_3C_V was able to with stand for a month in acetone, whereas the films of V_1C_V and V_2C_V and have been blistered and softened with in this time. The exposure of the films in various solvents for 3 months clearly indicated the order of the resistance of the esters as $V_3C_V > V_2C_V > V_1C_V$. The behavior of the films when exposed to methyl ethyl ketone (Table IV) indicated the similar pattern as was observed with acetone. It could also be concluded that the acetone showed comparatively more damaging effect on the surface of the films as compared to MEK, which could ultimately deteriorated the properties of the films. Also, the cured film of V_3C_V was totally unaffected by MTO in 3 months duration, whereas the films of V_2C_V and V_1C_V have shown minor changes in color, gloss, and blistering in the same time period.

Mechanical properties

Hardness and flexibility of the films

The results of scratch hardness of cured films of VER samples using pencils of different hardness ranging between H to 4H. The film of sample V_3C_V showed better hardness as compared to the films of V_1C_V and V_2C_V . Also, the film surface coated on steel panel bent up to 180° in the case of samples V_2C_V and V_3C_V , whereas the film of V_1C_V failed in mandrel test. This showed the better flexible nature of films of V_2C_V and V_3C_V . The higher hardness and flexibility of film surfaces of V_3C_V might be due to lower crosslink density of the VER.⁴⁰⁻⁴² The hardness may not solely depend on the crosslink density. However, the hardness may be influenced by the microgel structure of the VER.⁹ A similar conclusion

was discussed with the thermal stability data in the preceding section.

CONCLUSIONS

The esterification of bisphenol-A epoxy resin of EEW 185 (V_1C_V), 408 (V_2C_V), and 881 (V_3C_V) with AA in presence of CGE and triphenylphosphine at 80°C well suited the synthesis of VER as evidenced by FTIR spectra of VERs, which is also cleared from the mechanism proposed for the esterification reaction. It is concluded from the results that V_3C_V , VER prepared with higher EEW epoxy, took higher cure time and temperature than the V_1C_V and V_2C_V , VER prepared with lower EEW epoxy. The V_1C_V was found to be most thermally stable than the V_2C_V and V_3C_V . This resulted in inferior chemical and mechanical properties. These results might be attributed to the variation in the crosslink density of the cured resin.

References

1. Soule, E. R.; Fine, T.; Borrigo, J.; Willials, R. J. J.; Pascault, J. P. *J Appl Polym Sci* 2006, 100, 1742.
2. Agrawal, S.; Singhal, R.; Rai, J. S. P. *J Macromol Sci Pure Appl Chem* 1999, 36, 741.
3. Srivastava, A.; Pal, N.; Agrawal, S.; Rai, J. S. P. *Adv Polym Tech* 2005, 25, 1.
4. Burchill, P. J.; Pearce, P. J. *Polymeric Materials Encyclopedia*; Salomone, J. C., Ed.; CRC: Boca Raton, FL, 1996; p 3.
5. Gawdzik, B.; Matynia, T. *J Appl Polym Sci* 2001, 81, 2062.
6. Cook, W. D.; Simon, G. P.; Burchill, P. J. *J Appl Polym Sci* 1997, 64, 769.
7. Abadi, M. J. M.; Meknissi, K.; Burchill, P. J. *J Appl Polym Sci* 2002, 84, 1146.
8. Groszek, G.; Maziopa, J. *Polimery (warsaw)* 2004, 49, 280.
9. Kocsis, J. K.; Gryshchuk, O.; Schmitt, S. *J Mater Sci* 2003, 38, 413.
10. Agarwal, N.; Verma, I. K.; Choudhary, V. *J Appl Polym Sci* 2005, 99, 2414.
11. Hsia, H. C.; Ma, C. C. M.; Li, M. S.; Li, Y. S.; Chen, D. S. *J Appl Polym Sci* 1994, 52, 1137.
12. Brill, R. P.; Palmese, G. R. *J Appl Polym Sci* 2000, 76, 1572.
13. Ziace, S.; Palmese, G. R. *J Appl Polym Sci* 1999, 37, 725.
14. Gaur, B.; Rai, J. S. P. *Polym J* 1993, 29, 1149.
15. Dhulipala, R.; Kreig, G.; Hawley, M. C. *Polym Mater Sci Eng* 1993, 68, 175.
16. Li, P.; Yang, X.; Yu, Y.; Yu, D. *J Appl Polym Sci* 2004, 92, 1124.
17. Atta, A. M.; Elsaheed, S. M.; Farag, R. K. *React Funct Polym* 2006, 66, 1596.
18. Karger, K. J.; Gryshchuk, O.; Jost, N. *J Appl Polym Sci* 2003, 88, 2124.
19. Henne, M.; Breyer, C.; Niedermeier, M.; Ermanni, P. *Polym compos* 2004, 25, 255.
20. Dinakaran, K.; Alagar, M. *Int J Polym Mater* 2003, 52, 957.
21. Silva, A. L. N. D.; Teixeira, S. C. S.; Widal, A. C. C.; Coutinho, F. M. B. *Polym Test* 2001, 20, 895.
22. Tasic, S.; Bozic, B.; Dunjic, B. *Prog Org Coat* 2004, 51, 320.
23. Vallo, C. I.; Hu, L.; Frontine, P. M.; Williame, R. J. J. *J Mater Sci* 1994, 29, 2481.

24. Mosiewicki, M.; Borrajo, J.; Aranguren, M. L. *Polym Int* 2005, 54, 829.
25. Lowe, A.; Kwon, O. H.; Mai, Y. W. *Polymer* 1996, 37, 565.
26. Boyard, N.; Vayer, M.; Sinturel, C.; Erre, R.; Levitz, P. *Polymer* 2005, 46, 661.
27. Cuadrado, T. R.; Borrajo, J.; William, R. J. J.; Slare, F. M. *J Appl Polym Sci* 2003, 28, 485.
28. Siva, P.; Varma, I. K.; Patel, D. M.; Sinha, T. J. M. *Bull Mater Sci* 1994, 17, 1095.
29. Kant, K.; Mishra, A.; Rai, J. S. P. *Polym Int* 1992, 28, 189.
30. Takao, I.; Masao, T.; Akio, S.; Hiroshi, K. *Eur Polym J* 1991, 27, 851.
31. Pal, N.; Srivastava, A.; Rai, J. S. P. *Mat Manuf Proc* 2005, 20, 317.
32. Pal, N.; Srivastava, A.; Rai, J. S. P. *Int J Chem Kinet* 2004, 36, 280.
33. Henkel Corporation Series Library, Vol. 1; Germany. p 363 B.
34. Lee, H.; Neville, K. *Characterization of Uncured Epoxy Resins. Handbook of Epoxy Resin*; Mc Graw Hill Book Co: New York, 1967.
35. Pal, N.; Srivastava, A.; Rai, J. S. P. *Polym Plast Tech Engg* 2003, 42, 105.
36. Malik, M.; Choudhary, V.; Varma, I. K. *J Appl Polym Sci* 2001, 82, 416.
37. Hearn, O.; Paul, T. *Eur. Pat.* 33,542, (1981).
38. Choudhary, M. S.; Varma, I. K. *Angew Makromol Chem* 1993, 209, 33.
39. Pachha, R. R.; Thakkar, J. R.; Patel, R. D.; Patel, R. G.; Patel, V. S. *Die Angew Makromol Chem* 1994, 214, 221.
40. Agrawal, D.; Maithani, A. *Paintindia* 2004, 52, 43.
41. Maithani, A.; Srivastava, D.; Agrawal, D. *Paintindia* 2006, 56, 97.
42. Glu, G. B.; Kahraman, M. V.; Apohah, N. K.; Gungor, A. *Polym Adv Tech* 2007, 18, 173.