

Synthesis and curing behavior of novel multifunctional hybrid oligomers

Jianhua Qian,^{1,2} Zuozhen Liu,^{1,2} Jianhui Chen,¹ Rui Huang,² Chao Shi,² Weihong Guo^{1,3}

¹Polymer Processing Laboratory, Key Laboratory for Preparation and Application of Ultrafine Materials of Ministry of Education, School of Material Science and Engineering, East China University of Science and Technology, Shanghai 200237, People's Republic of China

²Shanghai Engineering Research Center of New Anticorrosion Material, Sino Polymer Co., Ltd., Shanghai 200237, China

³Anhui Collaborative Innovation Center for Petrochemical New Materials, Anhui, People's Republic of China

Correspondence to: W. H. Guo (E-mail: guoweihong@ecust.edu.cn)

ABSTRACT: Novel multifunctional hybrid vinylized epoxide oligomers (MVEOs) containing two different reactive groups were synthesized through the esterification of tetraglycidyl 4,4'-diaminodiphenylmethane (TGDDM) with acrylic acid (AA) at various molar ratios. The changes of vinyl ester and epoxy groups in MVEOs were studied by Fourier Transform Infrared Spectroscopy, Nuclear Magnetic Resonance, and Gel permeation chromatograph. It was found that more amount of AA in the reactant would increase the contents of vinyl ester and molecular weight. The curing behavior of MVEOs has been studied by scanning differential scanning calorimetry (DSC). Two distinct exothermic peaks were observed in the MVEOs which can be attributed to the radical polymerization of vinyl ester/styrene and condensation polymerization of epoxy/MeTHPA, respectively. Two different kinds of curing programs have influenced each other which makes the exothermic peaks overlapped. The DSC scan of MVEO-2 indicated that the radical initiated curing reaction of vinyl ester won't notably affect the curing of epoxy without MeTHPA. However, the thermal curing of vinyl ester in MVEO-2 without MEKP/Co would be occurred with the temperature rising. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42276.

KEYWORDS: addition polymerization; differential scanning calorimetry (DSC); monomers; oligomers and telechelics; radical polymerization; synthesis and processing

Received 8 November 2014; accepted 29 March 2015

DOI: 10.1002/app.42276

INTRODUCTION

Tetraglycidyl 4,4'-diaminodiphenylmethane (TGDDM) has been widely used in various applications ranging from advanced composites to electronic insulation and structural adhesives owing to its excellent thermal and mechanical properties, excellent adhesion to carbon fibers and low shrinkage.^{1–3} However, the high cross-link density results in brittleness of epoxies which limits their application. Rubber, thermoplastic, nanoparticles and core-shell particles have been used as toughening agents of TGDDM.^{4–7} But the incorporation of modifiers will increase the viscosity and decrease the processability of the resin systems.

Vinyl ester resin (VER) is a blending cross-linking monomer such as styrene with the esterification product of epoxy resin with an acrylic or methacrylic acid. VERs combine the mechanical and thermal properties of epoxy resins with the rapid cure of unsaturated polyester resins. VERs are important thermosetting materials widely used in advanced composite manufacturing processes such as hand lay-up, pultrusion, compression, and resin infusion moulding because of their high mechanical prop-

erties, low viscosity, and ease of processing and outstanding corrosion resistance.^{8,9}

In this article, novel multifunctional hybrid vinylized epoxide oligomers (MVEOs) were developed through the esterification of AA and TGDDM. The vinyl ester groups of MVEOs can be copolymerized with vinyl monomers by free radical initiators while the epoxy groups of MVEOs can be cured with anhydride by condensation polymerization. An insoluble and infusible three dimensional network structure was formed from the curing of two kinds of reactive groups in MVEOs simultaneously. These different kinds of molecular chains penetrated each other and get the interpenetrating polymer network structure, which leading to the superior performance than TGDDM for toughening and no losing of original inherent characteristics.^{10–16} Thermal stability of cured MVEOs remain high because functionality and cross-linking density of the oligomers are unchanged. Processing properties of MVEOs were improved greatly because the viscosity, gel time, and curing performance can be easily controlled not only by curing agent and

temperature^{17–19} but also by the changes of vinyl ester and epoxy groups in MVEOs. The processing properties of novel MVEOs are easier to meet requirements of different composites molding.

The structures and properties of MVEOs were investigated. The vinyl ester and epoxy groups of MVEOs and MVER were analyzed by Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance (NMR), and Gel permeation chromatograph (GPC), results were compared with those of TGDDM. The curing behavior of MVEOs and MVER with different contents of vinyl ester and epoxy groups was investigated compared with TGDDM. The interactions between the curing of vinyl ester groups and the curing of epoxy groups in MVEO-2 were also investigated by using differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

TGDDM (trade name Adbest AG-80) with an epoxy equivalent weight (EEW) of 118 was supplied by Shanghai Huayi resin. Acrylic acid (AA) was purchased from Shanghai Huayi AA. Methyl ethyl ketone peroxide (MEKP, trade name Butanox M-50) supplied by Akzo-nobel Functional Chemical. Cobalt octoate (trade name NL-49P, 1% Co solution in aliphatic ester) supplied by Akzo-nobel Functional Chemical. Styrene was purchased from Shanghai SECCO Petrochemical. Methyl Tetrahydrophthalic Anhydride (MeTHPA) Supplied by Zhejiang Alpharm Chemical Technology. Benzyltrimethylammonium Chloride (TMBAC) supplied by Sino Polymer. Mono-tertiary-butylhydroquinone (MTBHQ) supplied by Sino Polymer. All other chemicals used in this study were standard laboratory reagents obtained from various manufacturers. The related molecular formulas are shown in Scheme 1.

Synthesis of MVEOs

MVEOs and multifunctional vinyl ester resin (MVER) were prepared by using different molar ratios of AA and TGDDM. The specific molar ratios of AA/TGDDM were 1 : 1, 2 : 1, 3 : 1, 4 : 1 respectively.

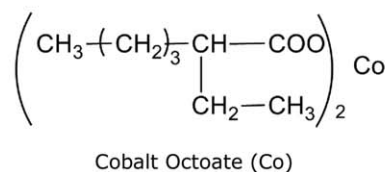
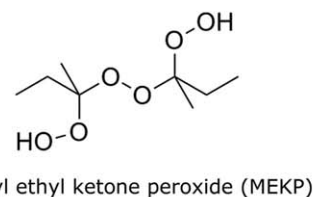
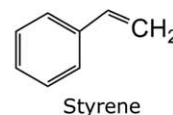
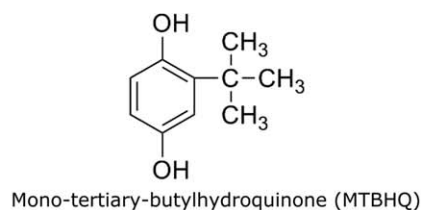
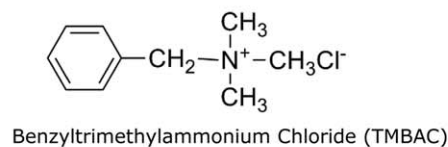
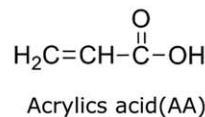
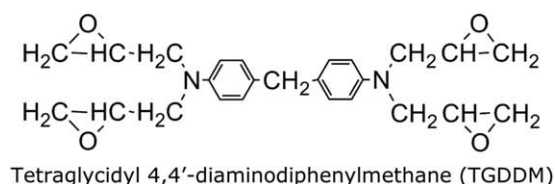
The esterification was carried out in the presence of 3 wt % BTMAC and 3 wt % MTBHQ at 75°C. 1.1 times (molar) AA of styrene was added into the vessels. The reaction was monitored by determining the acid value and EEW intermittently. The reaction was continued until the acid number became zero for MVEOs. The terminal acid number was below 10 mg KOH/g for MVER.

Curing of MVEOs, MVER, and TGDDM

MEKP was used as initiators at a concentration of 2 wt % of the MVEOs and MVER. In some studies, cobalt octoate (Co) was used as an accelerator for MEKP at a level of 1% based on the MVEOs and MVER. The MVEOs and TGDDM were cured with a stoichiometric amount of MeTHPA.

Measurements

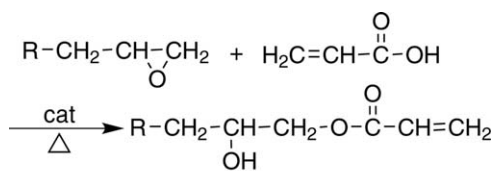
Acid Value. Approximately 0.4 g of resin mixture was dissolved in 20 mL mixture of toluene and ethanol absolute. Three drops of 10 g/L phenolphthalein were added to the mixture to deter-



Scheme 1. Related molecular formulas.

mine the neutralization point. The solution was then titrated with 0.2 N potassium hydroxide until the solution remained slightly red in color for 30 s.

Epoxy Equivalent Weight. To determine the EEW of resins containing epoxy-vinyl ester multifunctional oligomers, epoxy



Esterification mechanism

Scheme 2. Esterification mechanism.

titration was performed as Hydrochloric acid-acetone method. The epoxy resin was dissolved in 20 mL Hydrochloric acid-acetone solution (the Hydrochloric acid-acetone solution should prepare currently) and was kept at about 20°C for 2–3 h. Three drops of methyl red were added to the mixture to determine the neutralization point. The sample was titrated with 0.25*N* sodium hydroxide until the solution remained yellow in color for 30 s.

FTIR Analysis. Fourier Transform Infrared Spectroscopy (FTIR) was used to measure the concentration of unreacted epoxides and the generated ester bond, double bond (attached acrylate groups). A Thermo Nicolet IS5 FTIR was used in absorbance mode, taking 16 scans per spectrum with a resolution of 4 cm⁻¹. The FTIR spectra of VER with four groups show that the peaks representing epoxy groups were disappeared after reaction. This result indicates that the epoxy groups were exhausted by reacting with AA.

¹HNMR Spectroscopy. ¹HNMR analysis of MVEOs was recorded on Bruker 400 MHz FT-NMR spectrophotometer in the temperature range of -90°C to 80°C. About 20 mg of the sample, in 10 mm diameter sample tube, was dissolved in about 5 mL of chloroform-d₁ (CDCl₃), which was used as a solvent, along with tetramethylsilane (TMS) as internal standard. Finally, the spectra were recorded on computer.

Gel Permeation Chromatograph. GPC was recorded with GPC (waters 1515) to determine the number-average molecular weight of the synthesized resins. The column used for GPC calibration was of cross-linked polystyrene. THF was used as both

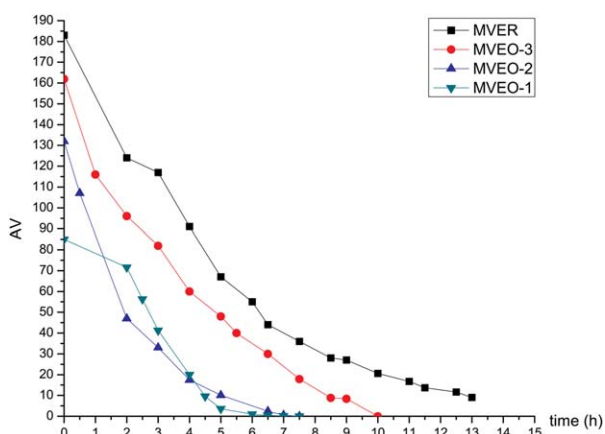


Figure 1. Acid value versus reaction time for MVEOs and MVER. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

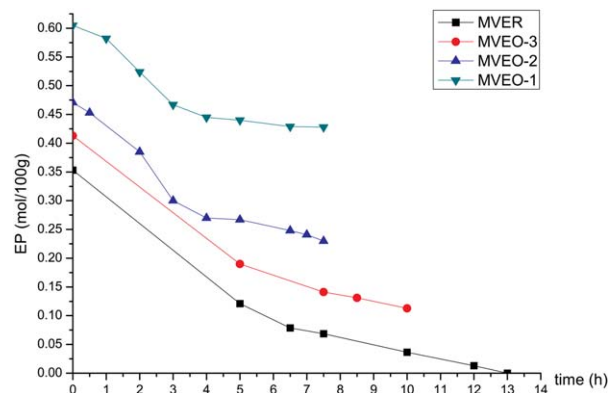


Figure 2. Epoxy value versus reaction time for MVEOs and MVER. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mobile and stationary phase for the experiment. Polystyrene standard at molecular weight were used for calibration.

Differential Scanning Calorimetric. All DSC studies of the curing behavior were performed with the TA Q20 differential scanning calorimeter under a nitrogen atmosphere. High purity indium was used to calibrate the calorimeter. All samples were contained within sealed aluminium DSC pans. Approximately 6–15 mg resins were sealed in aluminium pans and scanned from 30 to 300°C. The heat rate for all scanning runs was 5°C/min. All exothermic energies are reported as Joules per gram of total resin.

RESULTS AND DISCUSSION

Analysis and Characterization of MVEOs

Reaction Mechanism. The epoxy groups of TGDDM could react with AA, as following the esterification mechanism in Scheme 2.

One vinyl ester group was introduced at the end of TGDDM oligomer by the esterification of one epoxy group with AA. Novel hybrid oligomers with different contents of vinyl ester and epoxy groups were obtained as TGDDM have four epoxy groups theoretically. Oligomers with three vinyl ester groups and one epoxy group (MVEO-1), two vinyl ester groups and two epoxy groups (MVEO-2), one vinyl ester group and three epoxy groups (MVEO-3) were synthesized while the ratio of AA/TGDDM were 1 : 1, 2 : 1, 3 : 1 respectively. Oligomer with four vinyl ester groups (MVER) was gained if the molar ratio of AA/TGDDM was 4 : 1.

The average degree of functionality of TGDDM is 3.6 as EEW of TGDDM by titration is 118 and its molecular weight is 422. All these means TGDDM is a mixture including tetra-functional oligomer and other multifunctional oligomers. So MVEOs obtained from TGDDM and AA are mixtures with various oligomers, most of which with a theoretical structure.

Synthesis of MVEOs and MVER

Figures 1 and 2 show the esterification of TGDDM with different ratios of AA in the presence of TMBAC and MTBHQ. It is obvious that the acid value and epoxy value decreased with the

Table I. Analysis of Epoxy Groups in MVEOs

Signal	Molar ratio (AA/TGDDM)	Epoxy value by titration, Eq./100 g	Theoretical epoxy value, Eq./100 g
TGDDM	0 : 1	0.85	0.85
MVEO-1	1 : 1	0.43	0.45
MVEO-2	2 : 1	0.24	0.24
MVEO-3	3 : 1	0.10	0.10
MVER	4 : 1	0	0

reaction time. The curve was not linear in the initial stage of the reaction because of the high concentration of the reactive sites and the greater reaction rates of acid and epoxy groups.²⁰ The terminal acid value of MVEOs dropped to zero indicating the free carboxylic acid in the reactant exhausted. The terminal acid value of MVER was 9.0 mg KOH/g.

The terminal epoxy values of MVEOs by titration and theoretical calculated are listed in Table I. The theoretical epoxy value is based on that all AA in the reactants reacted with TGDDM to form vinyl ester groups, without any other byproducts. It was apparent from Table I that the terminal epoxy value of MVEOs titrated conform with theoretical calculated, indicating all AA in the reactant reacted the epoxy groups of TGDDM. Table I shows the contents of epoxy groups in MVEOs decreased with more amount of AA in the reactant. The epoxy value of MVER was zero indicated that all the epoxy groups of TGDDM participate in the esterification.

FTIR Spectrometer

The FTIR spectrum of MVEOs, MVER, and TGDDM are shown in Figure 3. The absorption peaks for epoxide ring of TGDDM and MVEOs appears at 910 cm^{-1} . Absorption peaks at 1723 cm^{-1} are attributed to carbonyl groups in MVEOs and MVER. The 1634 cm^{-1} absorption peaks correspond to the stretching vibration of C=C in MVEOs and MVER. The bands at 910 cm^{-1} decrease while the bands at 1723 and 1634 cm^{-1} are enhanced gradually from TGDDM to MVER. No peaks at 910 cm^{-1} are observed in MVER while the peaks

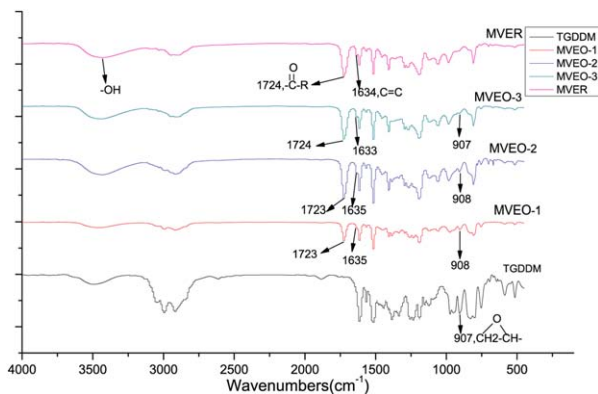


Figure 3. FTIR spectrum of MVEOs, MVER, and TGDDM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Absorption Peak Height Ratios of Ester Groups, Epoxy Groups to Benzene Ring in MVEOs

Signal	Molar ratio (AA/TGDDM)	Peak height ratio of ester/benzene ring	Peak height ratio of epoxy/benzene ring
TGDDM	0 : 1	0	0.44
MVEO-1	1 : 1	1.06	0.21
MVEO-2	2 : 1	1.38	0.16
MVEO-3	3 : 1	1.90	0.06
MVER	4 : 1	1.97	0.05

at 1723 and 1634 cm^{-1} reach maximum, which indicates that all the epoxy groups of TGDDM are involved in the esterification. The band at 3473 cm^{-1} belongs to the characteristics absorption peak of R-OH. The peak is observed in spectra of all the oligomers. These findings are consistent with the previous work.^{16,20}

The absorption peak height ratios of ester groups and epoxy groups to benzene ring in MVEOs are given in Table II using the height of benzene ring as standard. From Table II, the contents of vinyl ester groups in MVEOs increases with more amount of AA in the reactant, meanwhile the contents of epoxy groups decreases. The results of Table II agree well with Table I.

¹HNMR Spectrum of MVEOs

¹HNMR spectrum of MVEOs, MVER, and TGDDM are shown in Figure 4. Multiplets because of double bond protons of vinyl ester are observed at 5.78–6.13 ppm^{8,20} in MVEOs and MVER. No peak at 5.78–6.13 ppm is observed in NMR spectrum of TGDDM. The peaks increase from MVEO-1 to MVER, which indicate the content of vinyl ester increased gradually. The strength of MVER reached maximum indicating the contents of vinyl ester groups in MVER are maximum.

The peaks displayed around the region 2.53–2.79 ppm were attributed to methylene protons of ethoxylated groups.^{21,22} The extent of esterification reaction was determined by measuring

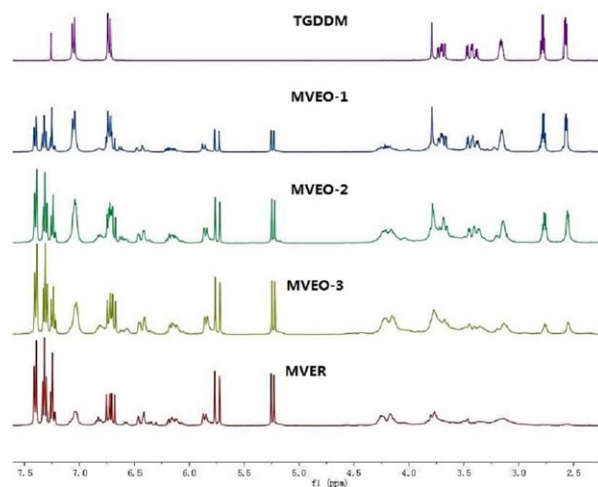
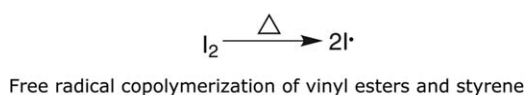


Figure 4. ¹HNMR of MVEOs, MVER, and TGDDM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

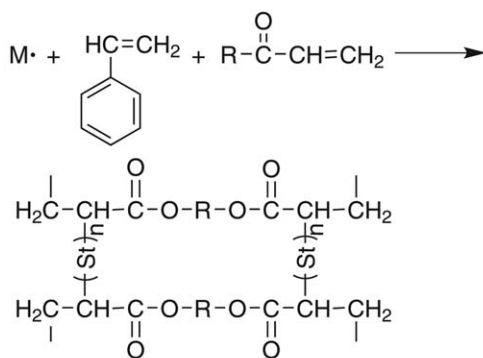
Table III. Molecular Weight and Molecular Weight Distribution of MVEOs, MVER, and TGDDM

Signal	Mn (g/mol)	Mw (g/mol)	Polydispersity
TGDDM	526	566	1.08
MVEO-1	613	872	1.42
MVEO-2	718	1282	1.79
MVEO-3	787	1110	1.41
MVER	846	1128	1.33

the height of the peaks in the region from 2.53 to 2.79 ppm. The epoxy peaks decreased gradually from TGDDM to MVER. The epoxide peak were nearly invisible in MVER indicating



(M represents styrene or vinyl group)

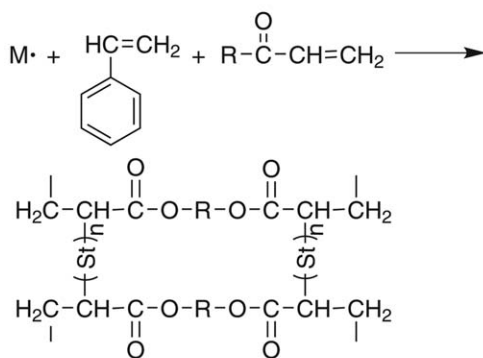


Free radical polymerization

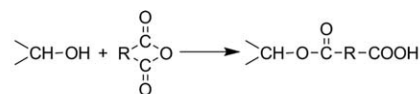


(M represents styrene or vinyl group)

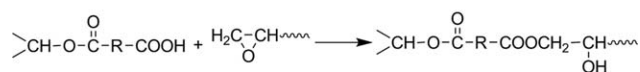
Thermal curing polymerization



Thermal curing polymerization

Scheme 3. Free radical copolymerization of vinyl esters and styrene.

Curing reaction of epoxy with acid anhydride



Reaction of epoxy group and carboxyl

Scheme 4. Condensation polymerization of epoxy groups/anhydride.

epoxy conversions greater than 99%, verifying the FTIR results.²²

The Molecular Weights and Molecular Weights Distribution of MVEOs

The molecular weights and molecular weights distribution of MVEOs, MVER, and TGDDM are shown in Table III. The number-average molecular of MVEOs increased gradually with more amount of AA in the reactant compared with TGDDM, which showed that TGDDM reacted with AA to form higher molecular weight oligomers. The number-average molecular of MVER reached maximum because all the epoxy groups reacted with AA. The results verified the results of FTIR and ¹HNMR.

The GPC curves show the MVEOs are not unimodal, but made of a number of peaks with wider distribution. Even TGDDM has certain molecular weight distribution, rather than a single compound. TGDDM is actually a hybrid system including mainly tetrafunctional and various multifunctional oligomers. The molecular weight distributions of MVEOs were wider compared with TGDDM, indicating the esterification of TGDDM with AA broaden the molecular distribution. The polydispersity of MVEO-2 was widest in MVEOs.

Curing Behavior of MVEOs

Curing Mechanism. Vinyl ester/styrene can be cured by free-radical initiated polymerization in the presence of MEKP, the reaction is accelerated by Co due to the redox reaction between MEKP and Co. Thermal curing polymerization of vinyl ester/styrene is occurred at higher temperature. A schematic of the general radical polymerization and thermal curing of vinyl esters is illustrated in Scheme 3.

Condensation polymerization mechanism of epoxy groups/anhydride is illustrated in Scheme 4. The reaction was accelerated in the presence of TMBAC which used in the esterification.²³

Curing Behavior of MVEOs

MEKP-Initiated Vinyl Esters and MeTHPA Cured Epoxy Groups Simultaneously. The scanning DSC of MEKP-initiated vinyl esters and MeTHPA-cured epoxy groups of MVEOs, MEKP-initiated MVER and MeTHPA cured TGDDM are shown in Figure 5. The DSC curves of MVER/MEKP resin and TGDDM/MeTHPA each exhibit single exothermic peaks whereas the MVEOs exhibit two distinct exotherms. Based on the close correspondence of peak temperature in the MVEOs, MVER and TGDDM, the lower and higher exotherms observed in the

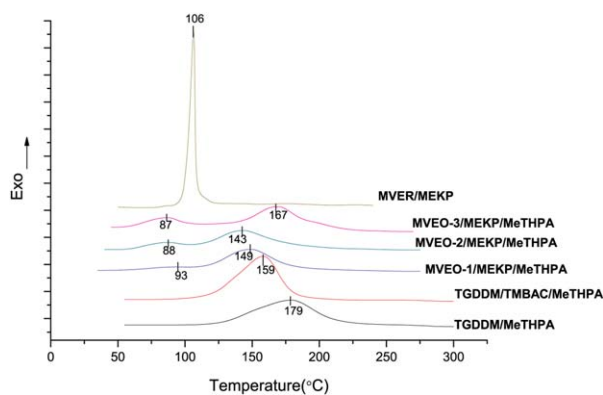


Figure 5. DSC scanning of MVEOs/MEKP/MeTHPA, MVER/MEKP and TGDDM/MeTHPA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

MVEOs can be attributed to the cure of vinyl ester and epoxy, respectively.

The peak of vinyl ester in MVEOs shifts from 106°C to approximately 90°C for the vinyl ester cured by MEKP. According to Dean's²⁴ report, a strong redox interaction between the peroxide and amine curing agent would result in enhanced radical production. The peak height of MEKP-initiated vinyl ester increases from MVEO-1 to MVER. The peak of TGDDM/MeTHPA/TMBAC shifts to 159°C compared with 179°C for TGDDM/MeTHPA because of the acceleration of residual catalyst TMBAC used in the esterification. The peaks of epoxy shift from 159°C to 149°C, 143°C for MVEO-1 and MVEO-2, respectively, whereas the peak of epoxy shifts from 159°C to 167°C for MVEO-3. The reaction rate epoxy/MeTHPA is improved for MVEO-1 and MVEO-2 may be attributed to the exotherm released by vinyl ester curing and the H-bonding between OH groups and epoxide groups of MVEOs.²⁴ However, the reaction rate of one component might be reduced because of the effects by the other components.^{24–27} Jin *et al.*²⁹ suggested the change in viscosity of the IPN (Interpenetrating Polymer Network) because of the reaction of one component may affect the curing behavior of the second component. Lin and Chang^{30–32} proposed a “network interlock effect” in which mutual entanglements between the

two polymer networks produces a sterically hindered environment resulting in reduction in the rate of the component systems. Since the amounts of vinyl ester groups is enhanced in MVEO-3, the viscosity and network interlock effect increase dramatically resulting in reduction reaction rate for MVEO-3. Similar results have been observed by HUA *et al.*³³ that the epoxy network formation for SIN (Simultaneous Interpenetrating Networks) consisting of less amount of epoxy (epoxy/urethane acrylate resin=20/80) was suppressed even more seriously than those containing more epoxy (epoxy/UAR \geq 50/50).

The polymerization enthalpy and peak temperature for MVEOs, MVER, and TGDDM are listed in Table IV. The total polymerization enthalpies for MVEO-1, MVEO-2 and MVEO-3 are 312, 325, and 335 J/g, which are lower than the averages enthalpies calculated from corresponding ratios of TGDDM and MVER (409, 387, and 364, J/g respectively), suggesting that MVEOs were not fully cured. MVEOs are not be fully cured because of the cross-linking of vinyl ester/St, which restrict the curing degree of epoxy/MeTHPA.^{33–35}

The conversion of vinyl ester and epoxy groups in MEVOs cured with MEKP and MeTHPA is listed in Table IV. The overall conversion of MVEO-3 is higher than MVEO-1&2 may be because of the increase amounts of vinyl ester and the faster reaction of vinyl ester. Conversion of epoxy groups for MVEO-3 exceed 100%, accounting for the exothermic peak of epoxy contains heat of vinyl ester, the two peaks of epoxy and vinyl ester are influenced and superimposed each other.

MEKP/Co Initiated Vinyl Esters and MeTHPA Cured Epoxy Groups. The scanning DSC of MEKP/Co initiated vinyl esters and MeTHPA cured epoxy groups of MVEOs are shown in Figure 6. The data analyses of these curing systems are also given in Table V.

When cobalt octoate is included in the MVER, the narrow peak at 106°C is shifted to 64°C, confirming that the production of radicals from MEKP has been enhanced by redox reaction of cobalt and MEKP.²⁴ The MVEO-1 shows one broad exotherm peak whereas MVEO-2 and MVEO-3 exhibit two exotherm peaks. These two peaks may attribute to the cure of vinyl ester and epoxy groups, respectively. The vinyl ester exotherm peak of MVEO-1 is

Table IV. Scanning DSC Results and Conversion of Vinyl Ester and Epoxy in MEVOs Cured with MEKP and MeTHPA

Signal	Exothermic peak temperature (°C)	Polymerization heat (J/g)	Calculated heat (J/g)	Conversion of vinyl and epoxy (%)
TGDDM	179	431	-	-
TGDDM/TMBAC	159	411	-	-
MVEO-1	93	76	86	88.9
	149	236	323	73.1
MVEO-2	88	157	171	91.8
	143	168	216	77.8
MVEO-3	87	204	256	79.4
	167	131	108	121.3
MVER	106	342	-	-

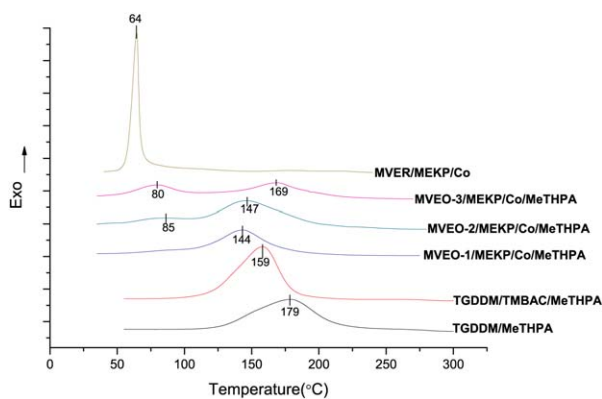


Figure 6. DSC scanning of MVEOs/MEKP/Co/MeTHPA, MVER/MEKP/Co, and TGDDM/MeTHPA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

negligible for the overlapping of epoxy peak. The peak of vinyl ester groups becomes clearer from MVEO-1 to MVER.

As shown in Table V, the total polymerization enthalpies for MVEO-1, MVEO-2 and MVEO-3 are 332, 357, and 319 J/g, which are less than the averages enthalpies calculated from corresponding ratios of TGDDM and MVER (410, 389, and 368 J/g respectively). As the cross-linking network of vinyl ester/st restricted the degree of cure of epoxy/MeTHPA, MVEOs was not cured completely.

The conversion of vinyl ester and epoxy groups in MEVOs cured with MEKP/Co and MeTHPA is listed in Table V. The overall conversion of MVEO-2 is higher than MVEO-1 and MVEO-3.

The Interactions Between the Curing of Vinyl Ester and Epoxy Groups. The curing process of MVEOs is complicated since MVEOs contains two different reactive groups—vinyl ester and epoxy. Vinyl ester groups and epoxy groups are quite different types of reactive functional groups, and can be cured according to different polymerization mechanisms. The interactions between the curing of these two groups have been studied, taking an example of MVEO-2. Three different curing programs were designed in this article for MVEO-2.

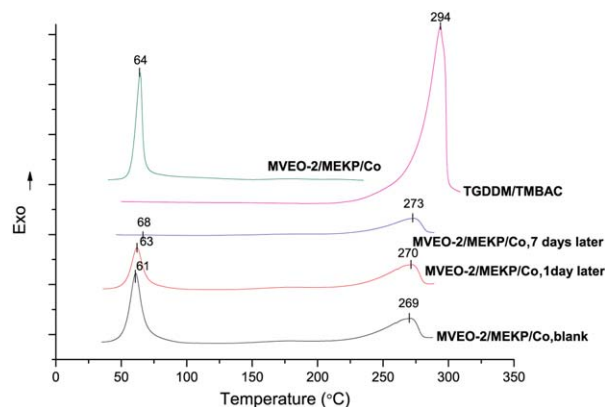


Figure 7. DSC scanning of vinyl ester groups initiated by MEKP/Co versus time for MVEO-2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Curing Program 1: Vinyl Ester Groups of MVEO-2 Curing Initiated by MEKP/Co without MeTHPA

The curing behavior of MVEO-2 is shown in Figure 7 when only MEKP and cobalt octoate are added. DSC curve of TGDDM/TMBAC exhibit a single exothermic peak. The curve of MVEO-2 initiated MEKP/Co exhibits two exothermic peaks. Based on the close correspondence of peak temperature in Figure 7, the lower temperature exotherm at 64°C which was attributed to vinyl ester initiated by MEKP/Co, the second peak at approximately 270°C was because of epoxy cured by TMBAC but is not by MeTHPA. Epoxy/MeTHPA curing exothermic peak did not appear in the DSC spectrum at about 150°C, which indicated that epoxy group did not cure without MeTHPA at this temperature.

The trends of polymerization enthalpy and peak temperature of MVEO-2/ MEKP/Co over time at 25°C are listed in Table VI. The heat of polymerization for vinyl ester groups of MVEO-2 is 224 J/g while the heat of cure of epoxy groups is 192 J/g. The polymerization enthalpy for MVEO-2 at lower peak decreases gradually with time because of the curing of vinyl ester groups at room temperature. The polymerization enthalpy for vinyl ester groups in MVEO-2 decreases from 224 to 134 J/g 1 day later, accounting for the degree of vinyl ester

Table V. Scanning DSC Results and Conversion of Vinyl Ester and Epoxy in MEVOs Cured with MEKP/Co and MeTHPA

Signal	Temperature of peak exotherm (°C)	Polymerization heat (J/g)	Calculated heat (J/g)	Conversion of vinyl and epoxy (%)
TGDDM	179	431	-	-
TGDDM/TMBAC	159	411	-	-
MVEO-1	144	332	-	-
MVEO-2	85	161	174	92.5
	147	196	216	90.7
MVEO-3	80	237	260	91.2
	169	82	108	75.9
MVER	64	347	-	-

Table VI. Heat of Polymerization and Peak Temperatures of the MEKP/Co Initiated Vinyl Esters in MVEO-2

Sample	Curing peak (°C)	ΔH (J/g)
0 day, 25°C	61	Peak1: 224
	269	Peak2: 192
1 day later, 25°C	63	Peak1: 134
	270	Peak2: 192
7 days later, 25°C	68	Peak1: 1.10
	273	Peak2: 195
MVER	64	347
TGDDM+TMBAC	294	920

groups cure attained 85%. The heat of polymerization for vinyl ester groups in MVEO-2 become 1.1 J/g 7 days later, representing the almost the end of the curing. The heat of polymerization for epoxy groups keeps stable at 192 J/g 7 days later.

All these results illustrate that vinyl ester groups cure independently in MVEO-2, which has no influences on the curing of epoxy groups without MeTHPA.

Curing Program 2: Epoxy Groups of MVEO-2 Cured by MeTHPA Without MEKP/Co

The curing behavior of MVEO-2 is shown in Figure 8 when MeTHPA is added. Figure 8 exhibits a broad peak at 156°C corresponds very closely to the curing exotherm in TGDDM/MeTHPA/TMBAC system (159°C). As there is residual esterification catalyst TMBAC in MVEO-2, the exotherm peak of MVEO-2 at 156°C is attributed to epoxy groups cured by MeTHPA and BTMAC. Vinyl ester curing exothermic peak did not appear at 64°C in the DSC spectrum because there is no MEKP/Co. The exotherm peak of epoxy groups shift from 156°C to 170°C after 1 day and shift to 181°C after 7 days, which is because of the partly cure of epoxy groups.

The trends of polymerization enthalpy and peak temperature of MVEO-2 cured by MeTHPA over time are listed in Table VII.

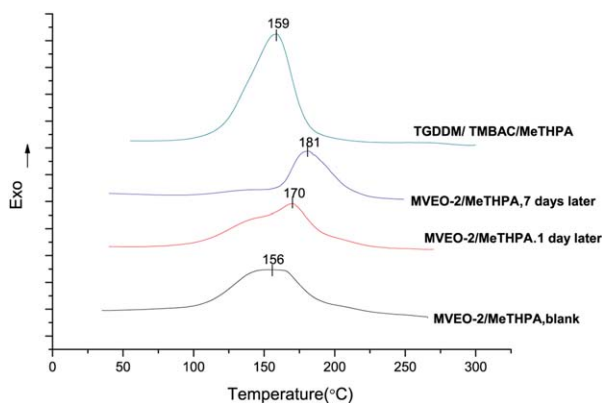


Figure 8. DSC scanning of epoxy groups cured by MeTHPA versus time for MVEO-2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table VII. Heat of Polymerization and Peak Temperatures of the MeTHPA-Cured Epoxy Groups in MVEO-2

Sample	Curing peak (°C)	ΔH (J/g)
0 day	156	368
1 day later, 25°C	170	325
7 days later, 25°C	181	171
TGDDM+TMBAC+MeTHPA	159	411

The polymerization enthalpy for epoxy groups of MVEO-2 is 368 J/g, then decrease gradually to 325 J/g after 1 day, and to 171 J/g after 7 days, respectively. The degree of epoxy groups cure attained 51% 7 days later.

Curing Program 3: Vinyl Ester of MVEO-2 Curing Initiated by MEKP/Co and Epoxy Cured by MeTHPA Simultaneously

The DSC curves of MVEO-2 cured by MEKP/Co and MeTHPA, vinyl ester groups initiated by MEKP/Co and epoxy groups cured by MeTHPA are shown in Figure 9. In Figure 9, the DSC curve of epoxy groups/MeTHPA exhibits single broad peak. In Figure 9, MVEO-2/ MEKP/Co/MeTHPA system exhibits two distinct exotherm peaks: the lower exotherm peak at 85°C can be attributed to vinyl ester initiated by MEKP/Co, and the second peak at approximately 147°C can be attributed to the cure of epoxy/MeTHPA. The curing exotherm peak of vinyl ester shifted from 64°C to 85°C as a result of dilution of epoxy and MeTHPA. The epoxy exotherm shifted from 159°C to 147°C because of the heat releasing from vinyl ester. Two different kinds of curing programs have influenced each other which make the exothermic peaks overlapped.

The polymerization enthalpy and peak temperature of MVEO-2 cured by MEKP/Cobalt and MeTHPA simultaneously are listed in Table VIII. The total polymerization enthalpy for MVEO-2 cured by MEKP/Cobalt and MeTHPA simultaneously is 357 J/g, which is close to the heat (368 J/g) for epoxy groups of MVEO-

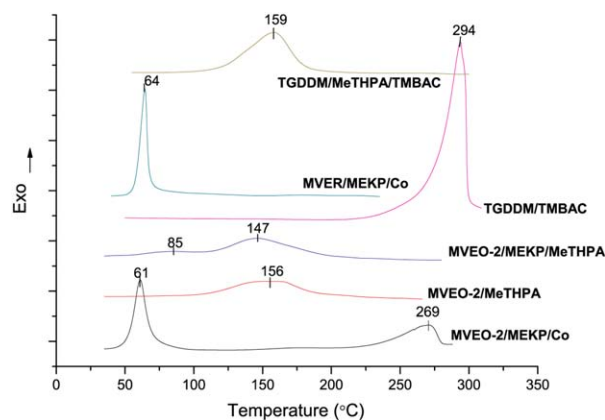


Figure 9. DSC scanning of MVEO-2 cured by MEKP/Co solely, MeTHPA solely, MEKP/Co/MeTHPA simultaneously and the parent resin system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table VIII. Heat of Polymerization and Peak Temperature of MVEO-2

Sample	Curing peak (°C)	ΔH (J/g)
MEKP/Co	61	224
	269	192
MeTHPA	156	368
MEKP/Co/MeTHPA	85/147	357

2 cured by MeTHPA without MEKP/Co. The similar total polymerization enthalpies account for thermal cure of vinyl ester groups in MVEO-2 has happened. The heat for epoxy groups of MVEO-2 cured by MeTHPA (368 J/g) actually include two parts: one is the exotherm from epoxy groups cured by MeTHPA, and the other is the exotherm from vinyl ester groups thermal cured without initiator. The thermal cure of vinyl ester in MVEO-2/MeTHPA system is because of the temperature rising.

CONCLUSIONS

The introducing of unsaturated vinyl ester groups at the end of TGDDM backbone by esterification of epoxy groups with AA can produce a new kind of oligomers (MVEOs) containing two different reactive groups depending on which the optimum properties can be derived. The content of double bonds and ester groups increased and content of epoxy groups decreased with more amount of AA in the reactant. Two distinct exothermic peaks were observed in the MVEOs which could be attributed to the radical polymerization of vinyl ester/styrene and condensation polymerization of epoxy/MeTHPA, respectively. The accelerated reaction rate of epoxy/MeTHPA for MVEO-1 and MVEO-2 was attributed to the exotherm releasing of vinyl ester curing and the H-bonding between OH groups and epoxide groups of MVEOs. Two different kinds of curing programs have influenced each other which make the exothermic peaks overlapped. The changes of vinyl ester and epoxy groups in MVEOs resulted in different peaks temperature and polymerization enthalpy. The DSC scan of MVEO-2 indicated that the radical initiated curing reaction of vinyl ester won't notably affect the curing of epoxy without MeTHPA. However, the thermal curing of vinyl ester without initiator would be occurred with the temperature rising.

ACKNOWLEDGMENTS

The authors sincerely acknowledge the Shanghai key R&D Program (12dz1100400), Shanghai Engineering Research Center of New Anticorrosion Material (13DZ2280900) and Anhui Collaborative Innovation Center for Petrochemical New Materials.

REFERENCES

- Lee, H.; Neville, K. *Handbook of epoxy resins*; McGraw-Hill: New York, **1982**.
- Ellis, B. *Chemistry and Technology of Epoxy Resins*; Blackie Academic and Professional; Chapman & Hall: Glasgow, **1993**.

- Chen, P.; Liu, S. P.; Wang, D. Z. *Epoxy resin and its Application*; Chemical Industrial Press: Beijing, **2011**, p 176.
- Chonkaew, W.; Sombatsompop, N.; Brostow, W. *Eur. Polym. J.* **2013**, *49*, 1461.
- Sprengerm, S. *Polymer* **2013**, *54*, 4790.
- Hodgkin, J. H.; Simon, G. P.; Varley, R. J. *Polym. Adv. Technol.* **1998**, *9*, 3.
- Day, R. J.; Lovell, P. A.; Wazzan, A. A. *Compos. Sci. Technol.* **2001**, *61*, 41.
- Scott, T. F.; Cook, W. D.; Forsythe, J. S. *Eur. Polym. J.* **2002**, *38*, 705.
- Sultania, M.; Yadaw, S. B.; Rai, J. S. P.; Srivastava, D. *Mater. Sci. Eng.* **2010**, *527*, 4560.
- Sperling, L. H. *Interpenetrating Polymer Networks and Related Materials*; Plenum Press: New York, **1981**; p 26.
- Cherian, A. B.; Varghese, L. A.; Thacil, E. T. *Eur. Polym. J.* **2007**, *43*, 1460.
- Lin, M. S.; Liu, C. C.; Lee, C. T. *J. Appl. Polym. Sci.* **1999**, *72*, 585.
- Karikal Chozhan, C.; Rajasekaran, R.; Alagar, M.; Gnanasundaram, P. *J. Polym. Mater.* **2008**, *57*, 319.
- Shaker, Z. G.; Browne, R. M.; Stretz, H. A.; Cassidy, P. E.; Blanda, M. T. *J. Appl. Polym. Sci.* **2002**, *84*, 2283.
- Mukherjee, C. S.; Saraf, M. N. *J. Polym. Sci. Part B: Polym. Phys.* **1995**, *33*, 855.
- Zhang, Z. Y. Study on the synthesis and properties of resins containing epoxy-vinylester bifunctional oligomers. M.D. Thesis, East China University of Science and Technology, June 2014.
- Abadie, M. J.; Mekhissi, K.; Burchill, P. J. *J. Appl. Polym. Sci.* **2002**, *84*, 1146.
- Martin, J. S.; Laza, J. M.; Morras, M. L.; Rodriguez, M.; Leon, L. M. *Polymer* **2000**, *41*, 4203.
- Ziaee, S.; Palmese, G. R. *J. Polym. Sci. Part B: Polym. Phys.* **1999**, *37*, 725.
- Pal, N.; Srivastava, A.; Agrawal, S.; Rai, J. S. P. *Mater. Manuf. Process.* **2005**, *20*, 317.
- Sultnia, M.; Rai, J. S. P.; Srivastava, D. *Eur. Polym. J.* **2010**, *2019*.
- Scala, J. J. L.; Orlicki, J. A.; Winston, C.; Robinette, E. J.; Sands, J. M.; Palmese, G. R. *Polymer* **2005**, *46*, 2908.
- Yang, T.; Zhang, C. F.; Zhang, J. Y.; Cheng, J. *Thermochim. Acta* **2014**, *577*, 11.
- Dean, K.; Cook, W. D.; Zipper, M.; Burchill, P. *Polymer* **2000**, *42*, 1345.
- Dean, K.; Cook, W. D.; Burchill, P.; Zipper, M. *Polymer* **2001**, *42*, 3589.
- Nowers, J. R.; Narasimhan, B. *Polymer* **2006**, *47*, 1108.
- Mustata, F.; Tudorachi, N.; Bicu, I. *Compos. Part B* **2013**, *55*, 470.
- Chen, F.; Cook, W. D. *Eur. Polym. J.* **2008**, *44*, 1796.
- Jin, S. R.; Widmaier, J. M.; Meyer, G. C. *Polymer* **1988**, *29*, 346.

30. Lin, M. S.; Chang, R. J. *J. Appl. Polym. Sci.* **1992**, *46*, 815.
31. Lin, M. S.; Jeng, K. T.; Huang, K. Y.; Shih, Y. K. *J. Polym. Sci. Polym. Chem. Ed.* **1993**, *31*, 3317.
32. Lin, M. S.; Yang, T.; Huang, K. Y. *Polymer* **1994**, *35*, 594.
33. Asmussen, S.; Schroeder, W.; dell'Erba, I.; Vallo, C. *Polym. Test.* **2013**, *32*, 1283.
34. Hua, F. J.; Hu, C. P. *Eur. Polym. J.* **1999**, *35*, 103.
35. Dean, K.; Cook, W. D. *Macromolecules* **2002**, *35*, 7942.