

A novel flame retardant UV-curable vinyl ester resin monomer based on industrial dipentene: Preparation, characterization, and properties

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ABSTRACT: A novel bio-based and flame-retardant UV-curable vinyl ester resin (VER) monomer named Diglycidyl ester of maleinized dipentene modified with dibutylphosphate and methacrylic anhydride (MDDMD) was synthesized from industrial dipentene via Diels-Alder reaction, glycidylation, epoxy ring-opening reaction, and esterification. Its chemical structures were characterized by Fourier transform infrared (FTIR) analysis and proton nuclear magnetic resonance (¹H-NMR). In order to improve its flexibility, we prepared a series of copolymers under UV light radiation by mixing it with certain proportions of poly(ethylene glycol) dimethacrylate-200 (PEGDMA-200) which contained flexible groups. Their tensile property, curing degrees (CD), hardness, limiting oxygen index (LOI), dynamic mechanical thermal properties, and thermostability were all investigated. The cured mixed resins have a relatively high tensile strength of 10.05 MPa and curing degrees up to 92.5%. Both hardness (range: 50 to 23 HD) and LOI (range: 22.8% to 24.4%) of cured resins are improved with the increase of MDDMD content. Dynamic mechanical analysis (DMA) shows that their glass transition temperatures rise with the increase of MDDMD content. Thermogravimetric analysis (TGA) shows that the thermal stability of cured resins is enhanced with the increase of PEGDMA-200 content, as the main thermal initial decomposition temperatures are all above 260 °C and char yield at 800 °C are above 18.10%. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, , 44084.

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INTRODUCTION

Vinyl ester resins (VERs), representatives of thermosetting polymers and unsaturated polyester resins, are usually prepared from the reaction of an unsaturated carboxylic acid and an epoxy resin. Their molecular structures contain unsaturated double bonds, and their curing-mechanism is typical of unsaturated polyester resins.^{1–3} The UV-curable VERs possess the excellent properties of both epoxy resins and unsaturated polyesters, such as excellent mechanical electrical properties, chemical stability, and heat resistance.⁴ Therefore, UV-curable VERs are extensively used in coatings, electronic appliances, aviation, construction, sports, pharmacy, optical fiber coating, printed circuit board, and other fields.^{5–11}

Along with the intensification of fossil fuel depletion and environmental pollution, many efforts have been made to develop new eco-friendly polymers from renewable resources to replace nonrenewable and petroleum-based products.^{12,13} Moreover,

researchers are interested in exploring renewable resources from agricultural and forestry feedstock, and have identified many bio-based polymers, such as epoxidized soybean oil, myrcene-based VER monomer, and tung-oil-based resin.^{14,15} As for bio-based VERs, however, their further development is largely hindered by the poor flame retardancy because some applications require high flame retardancy.^{16,17} Nevertheless, the introduction of reactive flame groups could bestow VERs with excellent flame retardancy and high thermal stability.^{18,19} There are diverse flame retardants, such as P—, Si—, N—, or halogen-containing flame retardants.^{20–23} In particular, P-containing flame retardants, such as 9,10-dihydro-9-oxa-10-phosphaphenanthren-10-oxide, dibutylphosphate, and 3-hydroxy phenyl phosphate acid ester, are very effective for VERs because P promotes both carbonization and inhibits combustion.^{24–26}

Industrial dipentene, a colorless or light yellow oily liquid, is mainly obtained from the camphor preparation and pulp-paper industry. Industrial dipentene is also a volatile mixture of cyclic

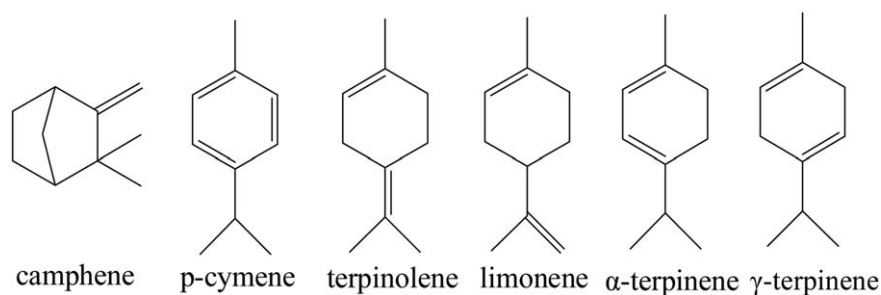


Figure 1. Chemical constituents of industrial dipentene.

monoterpene hydrocarbons ($C_{10}H_{16}$). Figure 1 shows its typical components, such as isomers of camphene, *p*-cymene, terpinolene, limonene, α -terpinene, and other menthadienes.^{27–30} Now, industrial dipentene has received more attention because of high output, low price, and the potential use as an unartificial and renewable feedstock in the fine chemical industry.³¹ As a green and eco-friendly resource, industrial dipentene can be used to prepare various novel bio-based products. For instance, α -terpinene, one of the most promising and valuable products, can be prepared from the catalytic dehydrogenation of industrial dipentene. In this work, starting from industrial dipentene as raw material, we prepared a bio-based and flame-retarding VER monomer via Diels-Alder reaction, glycidylation, epoxy ring-opening reaction, and esterification. To improve its flexibility, we mixed it with poly(ethylene glycol) dimethacrylate-200 (PEGDMA-200), and explored the tensile and thermal properties, hardness, and flame retardancy of the cured materials as-prepared.

EXPERIMENTAL

Materials

Industrial dipentene was purchased from Nanjing Yixin Chemical Industry Co., Ltd., China and used as received, the content of limonene, camphene, *p*-cymene, α -terpinolene, and γ -terpinolene were 58.04, 5.98, 11.10, 17.54, and 2.78%, respectively. Maleic anhydride, hydroquinone, and benzyltriethylamine chloride were purchased from Nanjing Kowloon Chemicals Co., Ltd., China. Epichlorohydrin, methacrylic anhydride, and calcium oxide were purchased from the Shanghai Group chemical reagent Co., Ltd., China. Sodium hydroxide and ethyl acetate were purchased from Shanghai Lingfeng chemical reagent Co., Ltd., China. Dibutylphosphate, dimethoxybenzoin, and PEGDMA-200 were purchased from Shanghai Aladdin Industrial Co., Ltd., China.

Synthesis of Retardant Diglycidyl Ester of Maleinized Dipentene (DMD) Modified with Methacrylic Anhydride

First, 0.29 g of iodine was dissolved into 280 g of industrial dipentene with a 0.5 L beaker, then 150 g of maleic anhydride was added into a 1 L four-necked flask equipped with a thermometer, a magnetic stirrer, a dropping funnel, and a reflux condenser, and then heated to 180 °C. Second, the mixture in the beaker was slowly added into the flask with a dropping funnel, after the mixture was added, the final mixture was heated to 200 °C with mechanical stirring and reacted for 2 h. Finally, the yellow liquid of terpinene maleic anhydride (TMA) was obtained by vacuum distillation.

Then 150 g of TMA was added into a 1 L four-necked flask with a thermometer, a magnetic stirrer, a dropping funnel, and a reflux condenser. Then, 13.5 g of distilled water was added into the flask and heated to 75 °C for 2 h until complete hydrolysis. After that, 555 g of epichlorohydrin and 0.14 g of benzyltriethylamine chloride were added to the TMA hydrolysate, and heated to 100 °C with mechanical stirring and reacted for 2 h. Then the mixture was cooled to 60 °C, and 48 g of sodium hydroxide and 67.2 g of calcium oxide were added to the flask with stirring for 3 h. Finally, the light yellowish viscous diglycidyl ester of maleinized dipentene (DMD) was obtained via filtering and evaporating.

Then 30 g of DMD, 29.5 g of dibutylphosphate, 0.08 g of hydroquinone and 0.29 g of benzyltriethylamine chloride were added into a four-necked flask, and heated to 120 °C with mechanical stirring for 2 h, and then a yellow viscous liquid ester diglycidyl ester of maleinized dipentene modified with dibutylphosphate (DDMD) was obtained. After that, 10.95 g of methacrylic anhydride was added into the flask with 30 g of DDMD, 0.06 g of hydroquinone and 0.2 g of benzyltriethylamine chloride were heated to 120 °C and maintained the temperature at 120 °C for 2 h with mechanical stirring. Finally, the dissociative methacrylic acid was removed by washing with weak alkali and distilled water, and the residual water was removed by vacuum distillation, and then a yellow viscous liquid resin (MDDMD) was obtained (yield: 90%). The synthesis route is shown in Figure 2.

Preparation of Copolymers Containing MDDMD and PEGDMA-200

The cured samples were prepared by changing the weight ratio of MDDMD to PEGDMA-200. Then dimethoxybenzoin (3 wt % of the total resin weight) was added as the photoinitiator and the mixture were mixed uniformly. Cured samples were prepared by casting the above mixture into a vertical gasket molds. Then the molds were put in the Intelli Ray 400 UV light curing box for 3 min with the irradiation intensity of 100 mW/cm². The prepared copolymers were denoted as follows: MDDMD90/PEGDMA-200 10 means a mixture of 90 wt % of MDDMD and 10 wt % of PEGDMA-200.

Characteristics

Fourier Transform Infrared (FTIR) Spectroscopy Analysis. Infrared spectroscopy was performed on an IS10 FTIR instrument (Nicolet, America). Samples were analyzed as liquid films on a ZnSn window. Each samples was scanned from 4,000 to 400 cm⁻¹.

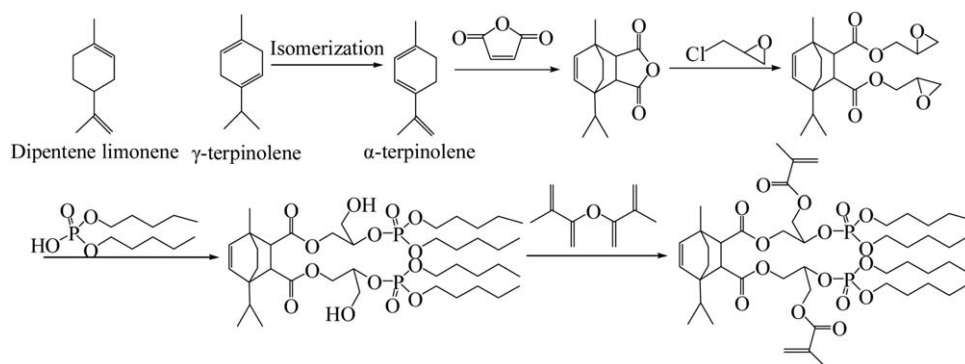


Figure 2. The synthesis route of MDDMD VER monomer.

Proton Nuclear Magnetic Resonance ($^1\text{H-NMR}$) Analysis. $^1\text{H-NMR}$ spectra of prepared samples were recorded in CDCl_3 on an ARX300 spectrometer (Bruker, Germany) operating at 300 MHz. Chemical shifts are given in ppm.

Tensile Properties Analysis. Tensile properties were measured by a CMT4303 universal test machine (SANS, China) following ASTM D638-03. The test speed of machine was 10 mm/min and test region of the samples was $50 \times 13 \times 3.18$ mm. Five sample pieces were prepared for the sake of accuracy and the samples were tested at 25°C .

Curing Degree (CD) Analysis. The curing degrees (CD) of copolymers were tested with solvent elution method. About 1.0 g of copolymer was cut into tiny pieces and all the pieces had an approximate dimensions of $2.5 \text{ mm} \times 5 \text{ mm} \times 0.2 \text{ mm}$, then these tiny pieces were wrapped up in filter paper with filament, and then the wrapping paper was put into a 250 mL elution device equipped with a reflux condenser. Finally, the sample was eluted for 24 h with acetone and then dried to a constant weight in the oven. In this experiment, each sample was tested three times. The sample's curing degree (CD) was calculated as:

$$\text{Curing degree (CD)} = \frac{(M_3 - M_1 + M_i)}{(M_2 - M_1)} \times 100\% \quad (1)$$

where M_i is the weight loss of filter paper (g); M_1 is the original weight of filter paper (g); M_2 is the weight of wrapping paper (g); and M_3 is the weight of wrapping paper after eluting (g).

Hardness Analysis. The hardness of copolymers were measured using TH 210 Shore D durometer (TIME, China) at 25°C .

LOI Analysis. The limiting oxygen index (LOI) values of copolymers were measured by a JF-3 oxygen index meter (Nanjing, China) according to ASTM D2863-97, with sheet dimensions of $130 \times 6.5 \times 3.2 \text{ mm}^3$.

The Dynamic Mechanical Analysis (DMA). The dynamic mechanical thermal properties of copolymers were measured by a Q800 dynamic mechanical thermal analyzer (TA, America) in stretch test mode. All samples had a dimension of $60 \times 10 \times 4 \text{ mm}^3$ and were swept from -70 to 120°C at a heating rate of $3^\circ\text{C}/\text{min}$ as well as a frequency of 1 Hz.

Thermogravimetric Analysis (TGA). Thermal stability of copolymers was measured by a 409PC thermogravimetric

analyzer (Netzsch, Germany). Each of samples was tested from 25 to 800°C at a rate of $15^\circ\text{C}/\text{min}$ under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Characterization of MDDMD Resin Monomer

The Fourier transform infrared (FTIR) spectra of DDMD and MDDMD are shown in Figure 3. The spectrum of DDMD shows several characteristic peaks at $3,380 \text{ cm}^{-1}$ (O—H absorption), $1,737 \text{ cm}^{-1}$ (C=O of ester groups), $1,254 \text{ cm}^{-1}$ (P=O absorption), $1,030 \text{ cm}^{-1}$ (P—O absorption), and $1,176$ and 909 cm^{-1} (P—O—C absorption). However, the absorption peak of epoxy group at about 830 cm^{-1} and the absorption peak of P—OH at about $2,600 \text{ cm}^{-1}$ both disappear, indicating DDMD has reacted with dibutylphosphate. The FTIR spectrum of MDDMD does not show the peak of O—H at $3,380 \text{ cm}^{-1}$, but shows a new intense peak of C=C at $1,636 \text{ cm}^{-1}$, indicating that DDMD has reacted with methacrylic anhydride. All these evidences indicate the successful synthesis of the target product.

The proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra of DDMD and MDDMD are shown in Figure 4. As for DDMD, the peaks at about 5.59 and 2.85 ppm corresponding to the protons in the hexatomic ring indicate the occurrence of the Diels-Alder reaction. Moreover, the $^1\text{H-NMR}$ signal of the hydroxyl group appearing at 2.38 ppm proves the occurrence of

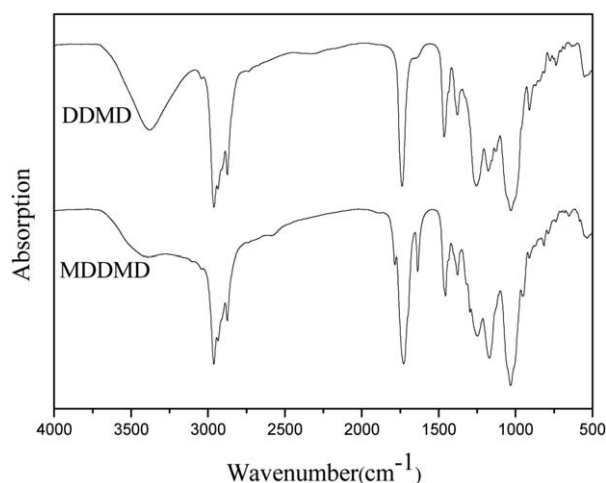


Figure 3. FTIR spectra of DDMD and MDDMD.

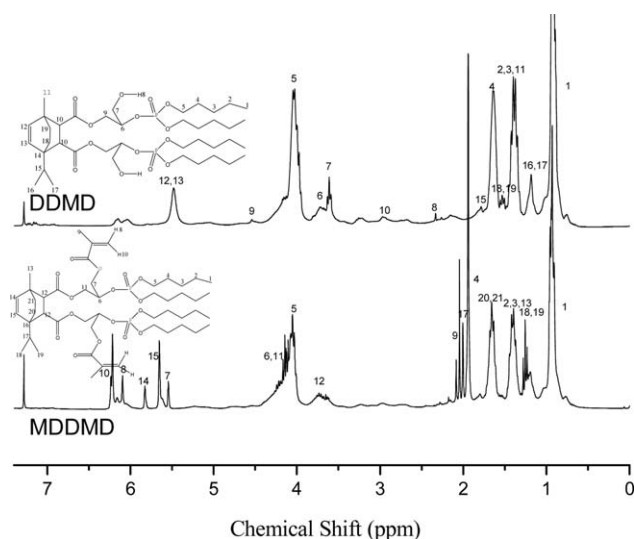


Figure 4. $^1\text{H-NMR}$ spectra of DDMD and MDDMD.

epoxy ring-opening. The peaks at about 3.85–4.41 ppm corresponding to the protons on the glycid ester also indicate the occurrence of epoxy ring-opening. As for MDDMD, the $^1\text{H-NMR}$ signal of the hydroxyl group at 2.38 ppm disappears, which proves the success of esterification. The appearance of new peaks at 6.24 and 6.05 ppm corresponding to the protons of $-\text{CH}=\text{CH}-$ further confirms the occurrence of esterification. All these $^1\text{H-NMR}$ results indicate that the target product has been successfully synthesized.

Mechanical Properties of MDDMD

The tensile stress–strain curves of copolymers with different weight ratios are shown in Figure 5 and the details are summarized in Table I. The pure cured sample (100% MDDMD) exhibits the lowest tensile strength of 0.63 MPa and the lowest elongation at break of 1.86%, which indicate the characteristics of brittle materials. With the increase of PEGDMA-200 content, the tensile strength and elongation at break of copolymers are generally improved, which could be attributed to the long-chain

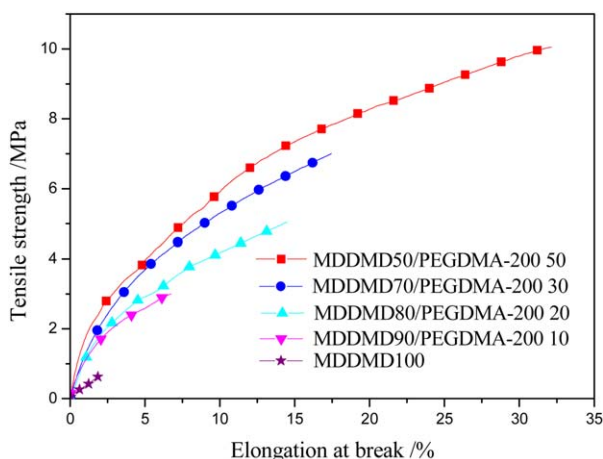


Figure 5. Tensile stress–strain curves of copolymers with different weight ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. The Detailed Data of the Cured Materials

Sample	Tensile strength (MPa)	Elongation at break (%)
MDDMD50/PEGDMA-200 50	10.05	32.15
MDDMD70/PEGDMA-200 30	8.54	17.45
MDDMD80/PEGDMA-200 20	6.05	14.50
MDDMD90/PEGDMA-200 10	5.41	6.75
MDDMD100	0.62	1.85

flexible structures of PEGDMA-200. On the contrary, the presence of much rigid bridge-ring structure in the MDDMD monomer improves the steric hindrance and thus reduces the curing degree and crosslinking density in the curing reaction, so the cured pure MDDMD has a low elongation at break. The major influence factors on the tensile strength of cured materials include the chemical structure and crosslinked states of monomers, and the mixing proportion. In the pure MDDMD polymerized system, all MDDMD molecules could covalently link with each other on the crosslinking point via chemical crosslinking after free-radical polymerization. When the content of PEGDMA-200 is low, PEGDMA-200 molecules are copolymerized crosswise. PEGDMA-200 has smaller molecular structure, when the content of PEGDMA-200 is high up to 50 wt %, the crosslinking point increases in copolymerized system, overmuch PEGDMA-200 molecules could form a relatively single bridge connection structure in copolymerized system, resulting in a well-crosslinked structure.

Curing Degree Density and Shore Hardness

As shown in Figure 6, the curing degree density of cured materials rises while the shore hardness declines with the increase of PEGDMA-200 content. The reduction of shore hardness is attributed to the increased proportion of long-chain flexible structure from PEGDMA-200 and the decreased proportion of rigid alicyclic hexatomic structure from MDDMD. The decrease of curing degree is attributed to the reduction of crosslinking

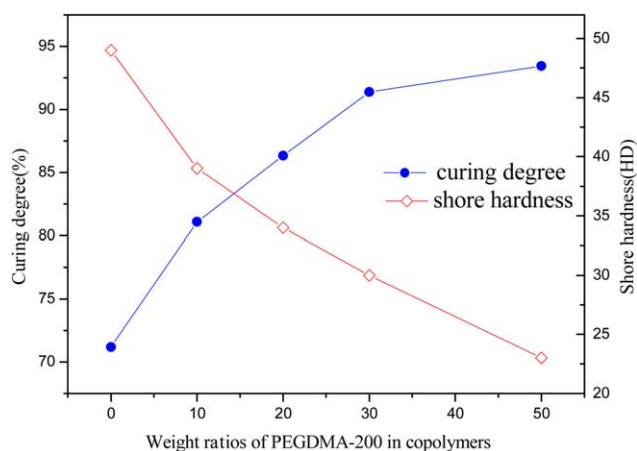


Figure 6. Curing degree and Shore hardness of cured materials. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. The LOI Values of Cured Materials

Sample	P (wt %)	LOI
MDDMD50/PEGDMA-200 50	3.33	22.8
MDDMD70/PEGDMA-200 30	4.69	23.4
MDDMD80/PEGDMA-200 20	5.36	23.7
MDDMD90/PEGDMA-200 10	6.03	24.0
MDDMD100	6.70	24.5

point and steric hindrance effect of bridge-ring structure in MDDMD monomer. The curing degree is low in the cured pure MDDMD, but is generally above 81% in all the cured copolymers. The curing degree increases sharply when the PEGDMA-200 content is up to 0–30 wt %, indicating that PEGDMA-200 plays a dominant role in the copolymerized system, so the cured materials has an excellent crosslinked structure. When the PEGDMA-200 content is 30–50 wt %, the curing degree increases (though at relatively slow) and reaches 93.44% in the copolymer with 50 wt % PEGDMA-200.

However, compared with the mechanical property tests, higher curing degree can bestow copolymers with lower shore hardness (rigidity) and higher elongation at break. The reasons are complex, for different curing systems, the curing degree and the molecular structure of mixed monomers can affect the tensile property and rigidity of cured materials simultaneously. MDDMD monomer has much rigid bridge-ring structure, the molecular structure is the main factor to affect the rigidity of the copolymers under this condition. Although the curing degree increases with the weight ratio of PEGDMA-200, the content of rigid bridge-ring structure decreases greatly, and then the rigidity decreases at the same time.

Flame Retardancy

The flammability of polymers can be evaluated by the limiting oxygen index (LOI). The LOIs of all the UV-cured materials are summarized in Table II. Clearly, the LOIs of the MDDMD/PEGDMA-200 system increase from 22.8% to 24.4% when the P content rises from 3.3 wt % to 6.7 wt %. The reason is that P promotes both carbonization and inhibits combustion, so the excellent charring interaction with the incorporated P-containing group enhances the flame retardancy of VERs. However, according to the LOIs, the high P content from MDDMD cannot remarkably improve the flame retardancy of VER cured product.

Dynamic Mechanical Analysis (DMA) of Copolymers

The storage modulus (E') and $\tan \delta$ curves of copolymers with different weight ratios are presented in Figure 7. The lowest concentration of crosslinkable dimethacrylates and the rigid alicyclic structure of pure MDDMD account for the high brittleness of pure cured MDDMD and the MDDMD90/PEGDMA-200 10 copolymer. Consequently, these two samples both break down under very low temperature below 0 °C, so their DMA data are not detected.

DMA, an extremely versatile thermal analysis technique, is used to study the viscoelastic behaviors of cured copolymers and quantify E' and $\tan \delta$. The E' curves of all the cured

copolymers show a similar trend: at very low temperature, E' remains at a very high level from 3,250 to 4,000 MPa; within -70 to 40 °C, E' decreases sharply and finally becomes constant (Figure 7). With the temperature rising from 10 to 50 °C, however, the E' curve increases and decreases alternately for all the cured copolymers, mainly because the introduction of the flexible chain segment facilitates the movement of the molecular chain of copolymers. In addition, E' is largely affected by the chemical structure and crosslinking state of the monomers.

Based on the theory of rubber elasticity, the crosslink density (ν_e) of a rubbery-state crosslinked polymer can be computed from E' as follows:

$$\nu_e = \frac{E'}{3RT} \quad (2)$$

where T is the absolute temperature and R is the gas constant.

To ensure the cured resins are at the rubbery state, we set E' at $T_g + 20$ °C. The data of ν_e of the cured copolymers are listed in Table III. The ν_e of the copolymers is improved with the increase of PEGDMA-200 content, probably because the late stage of curing reaction is dominated by diffusion.³² In the curing progress, the viscosity of samples is improved quickly (Figure 8). The PEGDMA-200 monomer is more curable than the MDDMD monomer because it contains more functional groups and has a higher congruent crosslinking point.

The peak temperature of $\tan \delta$ corresponds to the glass transition temperature (T_g). As showed in Figure 8, each of the copolymers has a very clear single T_g , which indicates all the cured systems have a homogeneously crosslinked structure. T_g is relatively low in MDDMD50/PEGDMA-200 50 (35.52 °C) and then it increases with the decrease of PEGDMA-200 content. T_g of cured copolymers is affected by the crosslinked state and chemical structure of monomers. In the same curing system, the mixed proportion of all monomers remains constant, the heat resistance of cured materials is decided by the curing degree of mixed monomers. However, for different curing systems, the curing degree and the different molecular structure of mixed monomers can affect the heat resistance of cured

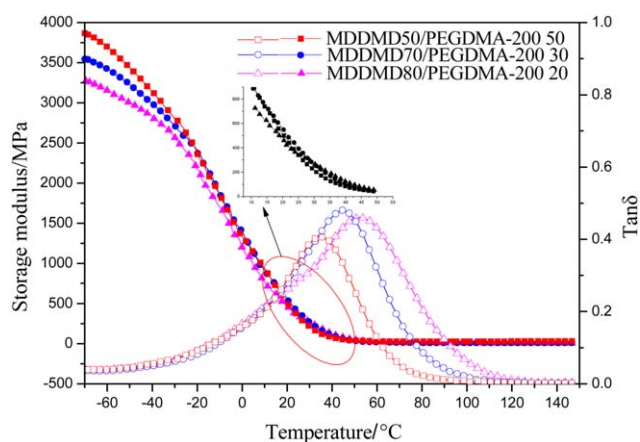


Figure 7. DMA curves of copolymers with different weight ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. The Crosslink Densities of Copolymers with Different Weight Ratios

Sample	T_g (°C)	E' at T_g+20 °C (MPa)	v_e (mol/m ³)
MDDMD50/PEGDMA-200 50	35.5	33.3	3869
MDDMD70/PEGDMA-200 30	44.6	17.6	2090
MDDMD80/PEGDMA-200 20	51.9	12.1	1476

Table IV. TGA Data of Copolymers with Different Weight Ratios

Samples	First thermal event			Second thermal event			Third thermal event			Char yield at 800°C
	T_i (°C)	T_{max} (°C)	T_f (°C)	T_i (°C)	T_{max} (°C)	T_f (°C)	T_i (°C)	T_{max} (°C)	T_f (°C)	
MDDMD50/ PEGDMA-200 50	330.4	361.0	500.0	—	—	—	—	—	—	18.10
MDDMD70/ PEGDMA-200 30	290.6	323.9	500.0	—	—	—	—	—	—	18.27
MDDMD80/ PEGDMA-200 20	280.0	306.7	330.0	330.0	338.9	500.0	—	—	—	20.25
MDDMD90/ PEGDMA-200 10	271.0	290.1	341.0	341.0	346.2	500.0	—	—	—	19.70
MDDMD100	259.8	280.0	348.0	348.0	360.1	380.0	380.0	389.1	480.0	20.38

materials simultaneously. MDDMD monomer has much rigid bridge-ring structure, the molecular structure is the main factor to decide the heat resistance of material under this condition. Although the curing degree of copolymers increases with the weight ratio of PEGDMA, the content of rigid bridge-ring structures shows downtrend, and then the glass transition temperature (T_g) decreases at the same time. The results agree with the mechanical property and shore hardness tests. Thus with the increase of PEGDMA-200 content, the introduction of more flexible chain segments allows the molecular chain of copolymers to move early, so the T_g of MDDMD 50/PEGDMA-200 50 is lower than that of MDDMD80/PEGDMA-200 20.

Thermogravimetric Analysis (TGA) of Copolymers

The TGA curves of copolymers with different weight ratios are showed in Figure 9. The initial decomposition temperature (T_i), temperature of maximum rate of mass loss (T_{max}), final decomposition temperature (T_f), and the char yield at 800°C are all listed in Table IV. These TGA data are the best evidences to evaluate the thermal stability of copolymers. Clearly, when the PEGDMA-200 content is 0 (cured pure MDDMD), 0–30 wt %, and above 30 wt %, the TGA trace shows a three-step, two-step, and single-step decomposition behavior, respectively.

The cured pure MDDMD has a three-step decomposition within 250–500°C, the first thermal event exhibits a catastrophic degradation within 250–348°C, the decomposition of the cured pure MDDMD starts at only 259.8°C, accelerates within 260–348°C, which may be attributed to the thermal degradation of dibutylphosphate group on MDDMD monomer, the rupture of ester groups and the C—C groups from the MDDMD monomer. From the variation trend of TG curves (the temperature from 348 to 480°C) and the special structure of MDDMD

monomer, the second thermal event might be attributed to the thermal degradation of the middle section of bridge ring. From the thermal weightlessness ratio between the second and the third thermal event, the third thermal event might be attributed to the thermal degradation of alicyclic structure from the dipentene.

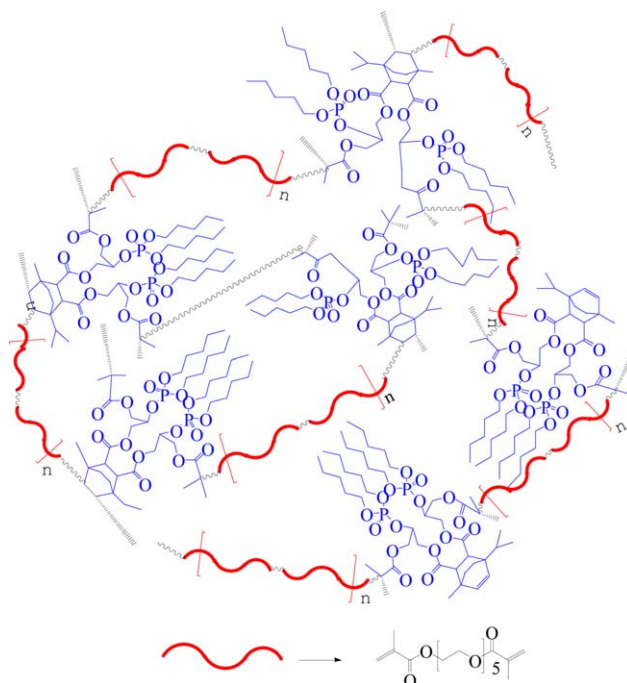


Figure 8. The possible crosslinking schematic diagram of copolymerized system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

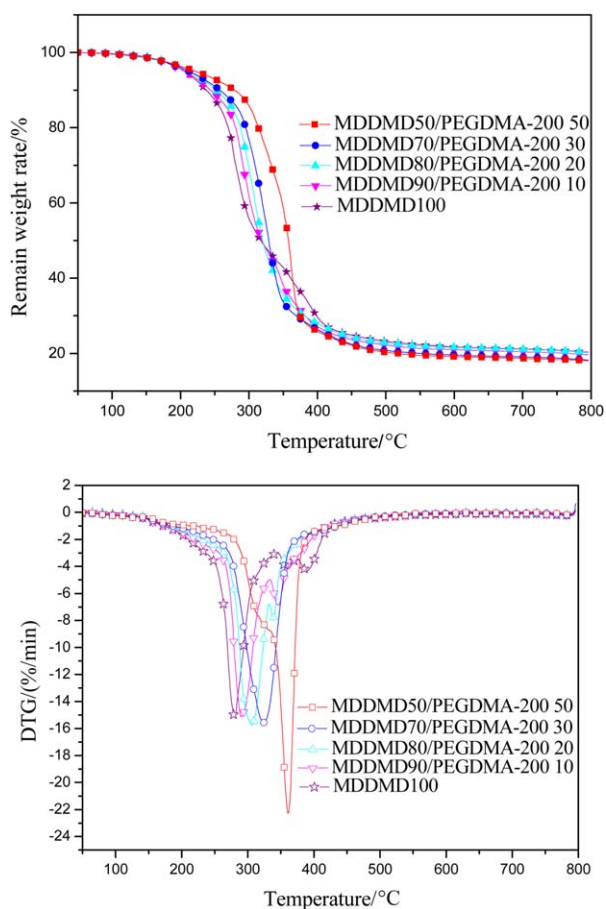


Figure 9. TGA curves of copolymers with different weight ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The PEGDMA-200 monomer is relatively rich in crosslinkable dimethacrylates as previously discussed. The copolymers could be cured equably with the increase of PEGDMA-200 content, probably because the low viscosity of PEGDMA-200 allows the two monomers to mix uniformly to form a good single cross-linked system, so the decomposition temperature range of every part in copolymerized system is very closed and makes the degradation process overlap. This result is also agreed with the study on crosslinking density and curing degree.

The T_i of copolymers is above that of cured pure MDDMD, probably because the presence of voluminous methyl group of MDDMD makes vinyl esters unstable and thermally degradable. In other words, the copolymers containing more PEGDMA-200 are thermally more stable. The char yields of the copolymers at 800 °C are all above 18.10%, which indicates that all the copolymers have excellent flame retardancy. This result also agrees with the flame retardancy tests.

CONCLUSIONS

A flame-retardant MDDMD VER monomer was successfully synthesized from industrial dipentene. Compared with the cured pure MDDMD VER, the MDDMD/PEGDMA-200 copolymers have excellent tensile properties, relatively low hardness, and

high elongation at break, which indicate a well-crosslinked structure. The curing degrees of copolymers reach 92.5%. The hardness of cured resins ranges from 50 to 23 HD and the LOIs vary from 22.8% to 24.4% with the increase of MDDMD content. DMA shows that the glass transition temperatures of all the copolymers range broadly from 30 to 50 °C. TGA shows that the copolymer containing more PEGDMA-200 is thermally more stable, and the main thermal initial decomposition occurs above 260 °C for all the cured resins, which prove the high thermal stability of all the copolymers.

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