The Study of Curing Behavior and Thermal Properties for Soybean Oil Fatty Acid-Modified Glycidyl Methacrylate

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SYNOPSIS

The characteristics of glycidyl methacrylate (GMA)–modifiers, including the polymerization properties, curing properties, and thermal stability, were studied. The degree of cross-linkage for (GMA–modifier)polyols increases with increasing hexamethoxymethylmelamine (HMMM) content and reaches maximum when HMMM content is about 40 wt %. The gels obtained from thermal free-radical polymerization for GMA-modifier monomer decrease with increasing acid value. UV curing experiments indicate that the energy of ultraviolet might be insufficient to promote the curing reaction through transetherification with short-term irradiation. Kinetic parameters for the thermal decomposition of the polymer were measured with TG thermograms. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Unsaturated drying and/or semidrying oil fatty acids were previously usually used in alkyd resins and acrylic paints. Films were dry-coated by air oxidation to achieve desirable water resistance, saltwater spray resistance, and adhesion.

Glycidyl methacrylate (GMA), an ethylenic group monomer with an oxirane group, could be used to modify the unsaturated vegetable oil fatty acid such as soybean oil fatty acid, linseed oil fatty acid, safflower oil fatty acid, and tall oil fatty acid. The adduct of the oil fatty acid–modified GMA with a hydroxyl group can be used as one of the components for emulsion paint to improve the emulsion film property.[1-3] For instance, the Nippon Paint Co. reported that the modifier from the reaction of GMA and linseed oil fatty acid was incorporated into the component of emulsion polymerization comonomers; the modifier renders the film obtained by coating curable at room temperature.[2]

The resulted adduct of the reaction of GMA and fatty acid is a trifunctional monomer that has a vinyl group, a hydroxyl group, and an alkenyl double bond of fatty acid. The aim of the present study is to understand the characteristics of the modifier obtained from the reaction of GMA and soybean oil fatty acid, including polymerization properties, curing properties of the hydroxyl group and hexamethoxymethylmelamine (HMMM), UV-curing properties, and the thermal degradation behavior.

EXPERIMENTAL

Synthesis of GMA–Modifier

Soybean oil fatty acid, 60 g (acid value = 200) was placed in a 250 mL three-necked round-bottom flask equipped with a thermometer, reflux condenser, and magnetic stirrer. GMA solution, 20 g, containing 0.2 g hydroquinone and 0.1 g tetraethylammonium chloride was added into the flask. The reaction mixture was then heated to 140°C under a nitrogen atmosphere. When the temperature reached 140°C, a 0.4 g sample was taken from the flask every 30 min and was dissolved in 10 mL xylene. The samples were titrated with a 0.1 N KOH alcoholic solution to trace the acid value until the acid value reached a constant.
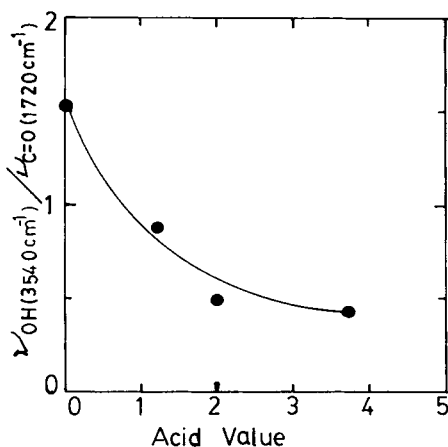
Preparation of (GMA–modifier)polyol

Benzoyl peroxide, 0.2 g, and xylene, 15 mL, were added to each of the various acid value GMA–mod-

Scheme 1 structures:

$$R_1COOH + CH_2\text{—}CH\text{—}CH_2\text{—}O\text{—}\overset{\overset{O}{\|}}{C}\text{—}\overset{\overset{CH_3}{\|}}{C}{=}CH_2 \xrightarrow[140°C]{TEAC}$$

$$R_1\overset{\overset{O}{\|}}{C}\text{—}OCH_2\text{—}\underset{\underset{OH}{|}}{CH}\text{—}CH_2O\overset{\overset{O}{\|}}{C}\text{—}\overset{\overset{CH_3}{\|}}{C}{=}CH_2$$

$R_1 = CH_3\text{—}(CH_2\text{—})_4CH{=}CH\text{—}CH_2\text{—}CH{=}CH\text{—}(CH_2\text{—})_7$

or $= CH_3\text{—}(CH_2\text{—})_7CH{=}CH\text{—}(CH_2\text{—})_7$

Scheme 1

ifiers (about 40 g). The GMA–modifier solution was then polymerized at 80°C for 3 h under a nitrogen atmosphere. After polymerization, the mixture was cooled to room temperature and the polyol product was obtained. To determine the solid content of polyol, we took an appropriate amount of the polyol sample and baked it at 110°C for 3 h. The dried product was weighed to calculate the solid content.

Thermal Curing of (GMA–modifier)polyol

(GMA–modifier)polyol, 4 g, was obtained from each of the samples, which had different acid values, and was mixed thoroughly with different weight fractions of HMMM (10, 20, 30, and 40 wt % based on pure polyol). Then, the mixtures were cured at 210°C for 2 h. To determine the gel fraction, the cured products were weighed in advance and placed in 700 mL of acetone in a 1 L flask. The solutions were heated to reflux for 24 h; then the samples were taken out to be dried at 50°C under vacuum for 24 h. The dried products were weighed to calculate the gel fraction that was defined as follows:

Gel fraction

$$= \frac{\text{weight of cured products after extraction}}{\text{weight of cured products before extraction}}$$

$$\times 100\%$$

UV curing of GMA–Modifiers

A solution of 0.05 g (1 wt %) benzoin ethyl ether UV sensitizer in 3 mL acetone was introduced into each of the GMA–modifiers, separately. After being thoroughly mixed, evacuated acetone and the samples were painted on a preweighed aluminum foil that was then irradiated with a 600 W UV high-pressure mercury lamp (HI-6NK Western Quartz made in the U.S.A.) at a distance of 20 cm. Samples

were taken from the UV chamber (Chi-Cheng UC-600) every 10 min. They were then weighed and extracted.

Thermal Analysis

Thermal analysis was carried out with a DuPont 951 thermogravimetric analyzer coupled to a 1090B programmer–recorder. The 5 mg samples were heated at heating rates of 5, 10, 15, and 20°C/min under a nitrogen atmosphere from ambient temperature to 650°C. The chart recorded the change in both temperature and sample weight percentage.

RESULTS AND DISCUSSION

Synthesis of GMA–Modifiers

The reaction of GMA and soybean oil fatty acid is shown in Scheme 1.

Scheme 1 shows that the reaction of a carboxylic acid group and an oxirane group generates a hydroxyl group. The more the carboxylic groups react with the oxirane groups, the more hydroxyl groups and the lower acid value. The relationship between the acid value and the reaction time for various ratios of fatty acid/GMA is shown in Figure 1. Figure 1 shows that the acid value for respective composition decreases with the increase of the reaction time and the decrease of the ratio of fatty acid/GMA.

Figure 1   The relationships between acid value and reaction time for various ratios of soybean oil fatty acid to GMA, i.e., soybean oil fatty acid/GMA: (○) 60/35; (●) 60/30; (□) 60/25; (■) 60/20. The time $t = 0$ corresponds to the first sample taken when the temperature reached 140°C.
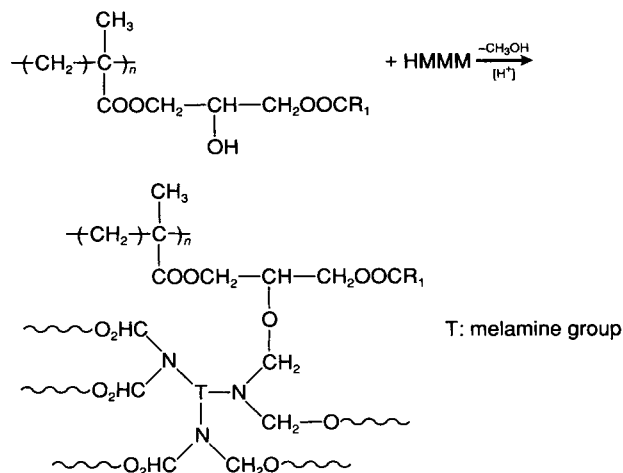
We have now established that as fatty acid reacts with GMA the lower the acid value the more hydroxyl groups. To confirm this, another series of experiments for a smaller ratio of fatty acid/GMA were conducted and the intensity ratio of $\nu_{OH(3540\,cm^{-1})}$ to $\nu_{C=O(1720\,cm^{-1})}$ from IR spectrometry (JASCO A202) for each composition was determined. The relationship between $\nu_{OH(3540\,cm^{-1})}/\nu_{C=O(1720\,cm^{-1})}$ from the IR spectrum and the acid value is shown in Figure 2, which points out that the larger the acid value, the smaller the intensity ratio, i.e., the smaller the number of the hydroxyl groups. This result is consistent with the results shown in Figure 1. In addition, when the acid value approaches zero in the reaction, it implies that the fatty acid is completely reacted.

Curing of (GMA-modifier)polyols

Hexamethoxymethylmelamine (HMMM) is used to reduce the viscosity of high-solid paint systems. HMMM and polyols can undergo polycondensation under acidic conditions. Kooistra suggested that the reaction pathways of HMMM exist in the presence of an acid catalyst.[4] Blank reported that the self-condensation reaction of HMMM-type melamine resin is accelerated by water.[5] Holmberg proposed a SN_2-type reaction on the basis that the curing speed depends upon the hydroxyl content of the system.[6] Nakamichi et al. studied the reactivity of HMMM using the reference mode of FTIR in conjunction with a heating unit.[7] The curing reaction of (GMA-modifier)polyol with HMMM is presented in Scheme 2.

Scheme 2

The gel content obtained from the curing reaction of the various (GMA-modifier)polyols with HMMM is shown in Figure 3. The degree of cross-linking for polyols increases with increasing amount of HMMM. The amount of gel content reaches maximum when the HMMM content is approximately 40 wt %. Thus, our study focused on polyol/HMMM = 1/0.4. Figure 4 shows the relationship between gel content and curing time for various acid values of GMA-modifiers. The amount of gel content increases with the curing time. In addition, at the initial stage of the reaction, the gel content increases with decreasing acid value, because there are plenty of hydroxyl groups when the acid value is low. But when the acid value approaches zero, the reaction shows abnormality. Since there is scarcely

Figure 2   The intensity ratio of IR spectra for various acid values of GMA-modifiers.
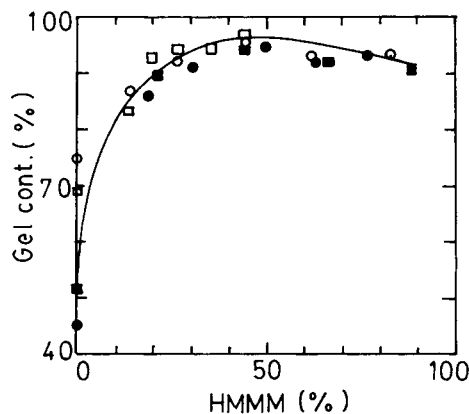
Figure 3   The relationship between the gel content and the weight percent of HMMM introduced into (GMA-modifier)polyols. Acid values: (O) 2.09; (●) 8.24; (□) 17.4; (■) 39.0.
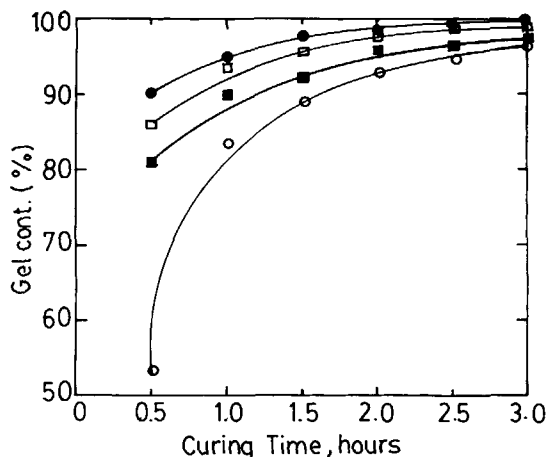
Figure 4 The relationship between gel content and curing time for various acid value (GMA–modifier)polyols. Conditions: HMMM/(GMA–modifier)polyol = 40 wt %, baking temperature = 210°C, baking time = 2 h. Acid values: (○) 2.09; (●) 8.24; (□) 17.4; (■) 39.0.

any ionized hydrogen (H^+) that can be used as a catalyst when the acid value is very low, the rate of the reaction slows down. However, the gel content of every sample remains essentially the same even when the curing time approaches 3 h.

Polymerization of GMA–Modifier

Each 5 g GMA–modifier sample was dissolved in a 20 mL xylene solution containing 1 wt % benzoyl peroxide. The polymerization reaction proceeded at 80°C for 48 h under a nitrogen atmosphere. After polymerization, the reaction mixture was poured into excess methanol to precipitate. The precipitate was extracted using acetone to remove unreacted fatty acid. It was then dried and weighed. The gel content in each fraction is plotted against the corresponding acid value in Figure 5. Figure 5 shows that the gel content from the GMA–modifier decreases with increasing acid value. The gels resulting from thermal polymerization can be attributed to the reaction of chains of unsaturated fatty acid with oxygen in the air, as shown in Scheme 3.[8]

UV Curing of GMA–Modifiers

In Figure 6, the relationship between gel content and irradiation time after UV irradiation is shown. The gel content increases as the irradiation time increases. Moreover, the smaller the acid value, the higher the gel content. This is a result of the higher concentration of the GMA–modifier monomer. On

the other hand, for the system containing 40 wt % HMMM, the relationship between irradiation time and gel content is shown in Figure 7. Comparing the results in Figures 6 and 7, it is clear that the energy of UV light may be insufficient to promote the curing reaction through transetherification for polyol and HMMM in the absence of the acid condition. In addition, a comparison between Figures 5 and 6 reveals that the degree of cross-linking from the thermal polymerization reaction is about 20% higher than that from UV curing.

To observe the structural change of the GMA–modifier monomer after UV irradiation, we coated the monomer film on a KBr plate, irradiated it for 10 min, and observed the IR spectrum change using JASCO A202 IR spectrometry. Figure 8 shows the IR spectra of GMA, the GMA–modifier, and the UV-cured polymer of the GMA–modifier. The characteristic peak of GMA is situated at 910 cm^{-1} (Oxirane ring) and 1640 and 810 cm^{-1} (C=C). After modifying, the peak at 910 cm^{-1} disappears while a 3540 cm^{-1} peak (—OH) appears. With the modifier irradiated, the 1640 and 810 cm^{-1} absorption bands of the acrylic double bond disappear completely. This indicates that the polymerization occurs only at the acrylic double bond by UV irradiation for 10 min. To further observe the cross-linking reaction of HMMM and the GMA–modifier (acid value: 2.09), the mixture of these reactants was coated on a KBr plate and then cured by UV irradiation for different curing times (3, 6, and 9 min). The changes of their infrared spectrum were shown in Figure 9. From the changes of the absorption ratios of the triazine group ($\nu_{820\,cm^{-1}}$) and methoxy groups ($\nu_{909\,cm^{-1}}$) contained in HMMM in Figure 9, the reaction rate of methoxy groups with the hydroxyl
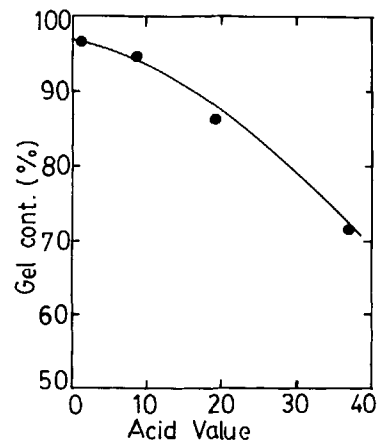
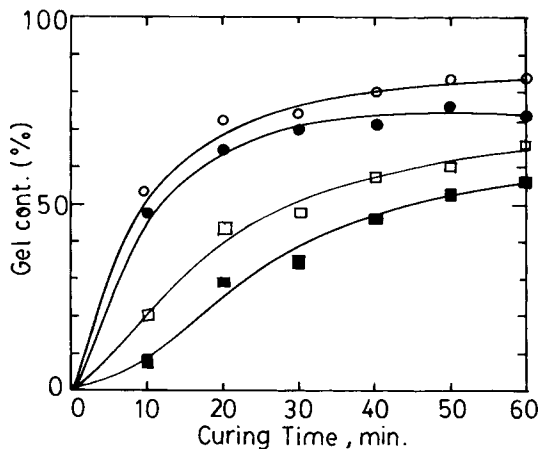**Figure 5** The relationship between gel content and acid value for GMA–modifier polymerized at 80°C for 48 h.

Polymerization Reaction:

Gel Formation:

GMA backbone

www = Alkenyl group R_2=CH_2—CH—CH_2—
                                              |
                                             OH
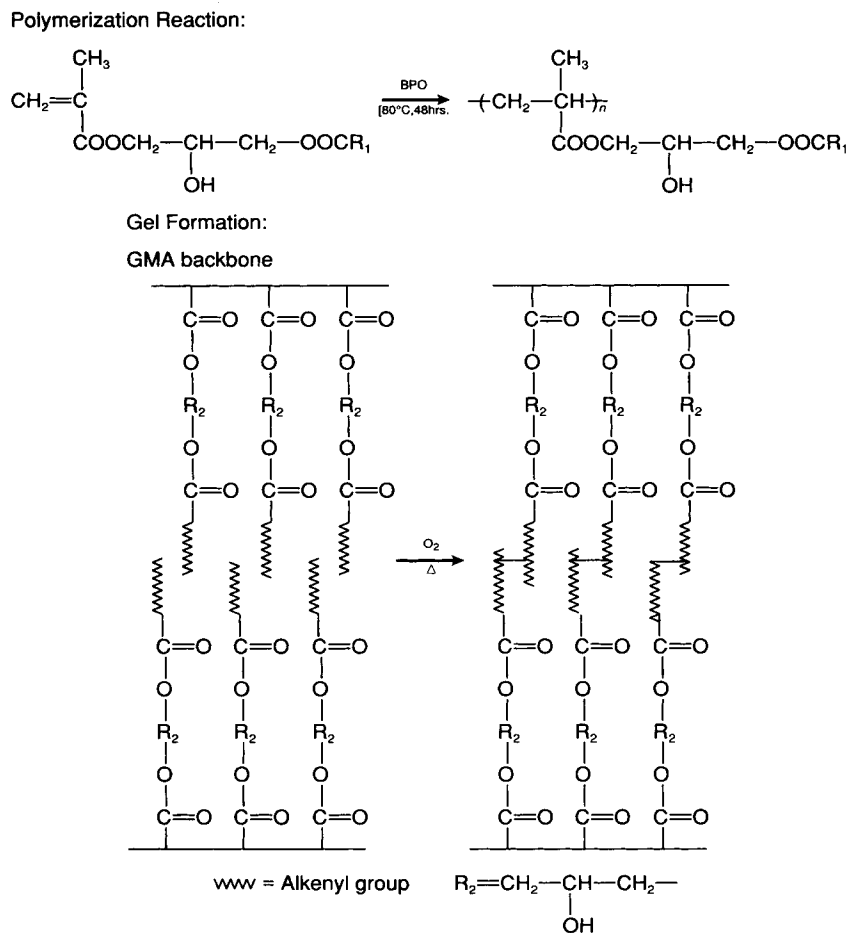
Scheme 3

groups contained in the GMA–modifier can be observed. The ratios of transmittance intensity of triazine peak and methoxy peak irradiated by dif-
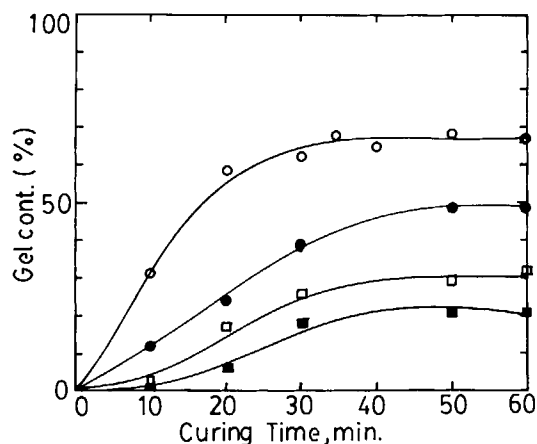

Figure 6 The relationship between gel content and UV curing time for GMA–modifier. Acid values: (O) 2.09; (●) 8.24; (□) 17.4; (■) 39.0.

ferent irradiation time are shown in Table I. It shows that the ratios of $v_{909\ cm^{-1}}/v_{820\ cm^{-1}}$ decrease slowly with the irradiation time. The tendency of the decrease of $v_{909\ cm^{-1}}/v_{820\ cm^{-1}}$ is very small. For example, after a 9 min irradiation, only 8.68% of the methoxy groups took part in the reaction. This indicates that only a small fraction of HMMM and the GMA–modifier took part in transetherification under UV irradiation.

TG Curve Characteristics of Poly(GMA–modifier)

The thermal degradation of 5 mg samples with various acid values was carried out at a heating rate of 5°C/min under nitrogen atmosphere. (The highest acid value of 39.0 was excluded because its gel content is too low.)

An example of a TGA thermogram of poly(GMA–modifier) is shown in Figure 10 with related definitions listed in Table II. The TG curve contains all the information necessary to show the maximum

Figure 7 The relationship between gel content and UV curing time for GMA–modifier added 40 wt % HMMM. Acid values: (○) 2.09; (●) 8.24; (□) 17.4; (■) 39.0.

rate of weight loss, the temperature interval of the degradation (ΔT), and the weight loss (ΔW).

The TG thermograms for various GMA–modifier polymers exhibit a major-stage degradation and

show a maximum rate of weight loss at 420.8, 420.3, 424.0, and 413.3°C shown by derivative thermograms for acid values of 17.4, 8.28, 2.09, and 2.09 (UV curing), respectively. The corresponding weight percentages remaining at 650°C are 2.6, 3.8, 5.2, and 7.5, respectively.

The weight loss and decomposition temperature ranges are pointed out in Table III, which also shows that the weight loss at the stage of the thermal degradation increases with the decrease of the acid value. However, at an acid value of 2.09, the polymers obtained by different polymerization methods show different results.

As a criterion of heat stability of the polymer, we take the temperature of the start of intense degradation (T_{start}) and the temperature corresponding to a 50% weight loss ($T_{50\%}$) at 5°C/min for various acid value polymers. The results are presented in Table IV. Table IV shows that the temperature of thermal degradation of GMA–modifier polymers increases with decreasing acid value. The stability of such polymers obtained by free-radical polymerization is higher than that obtained by photoinitiated
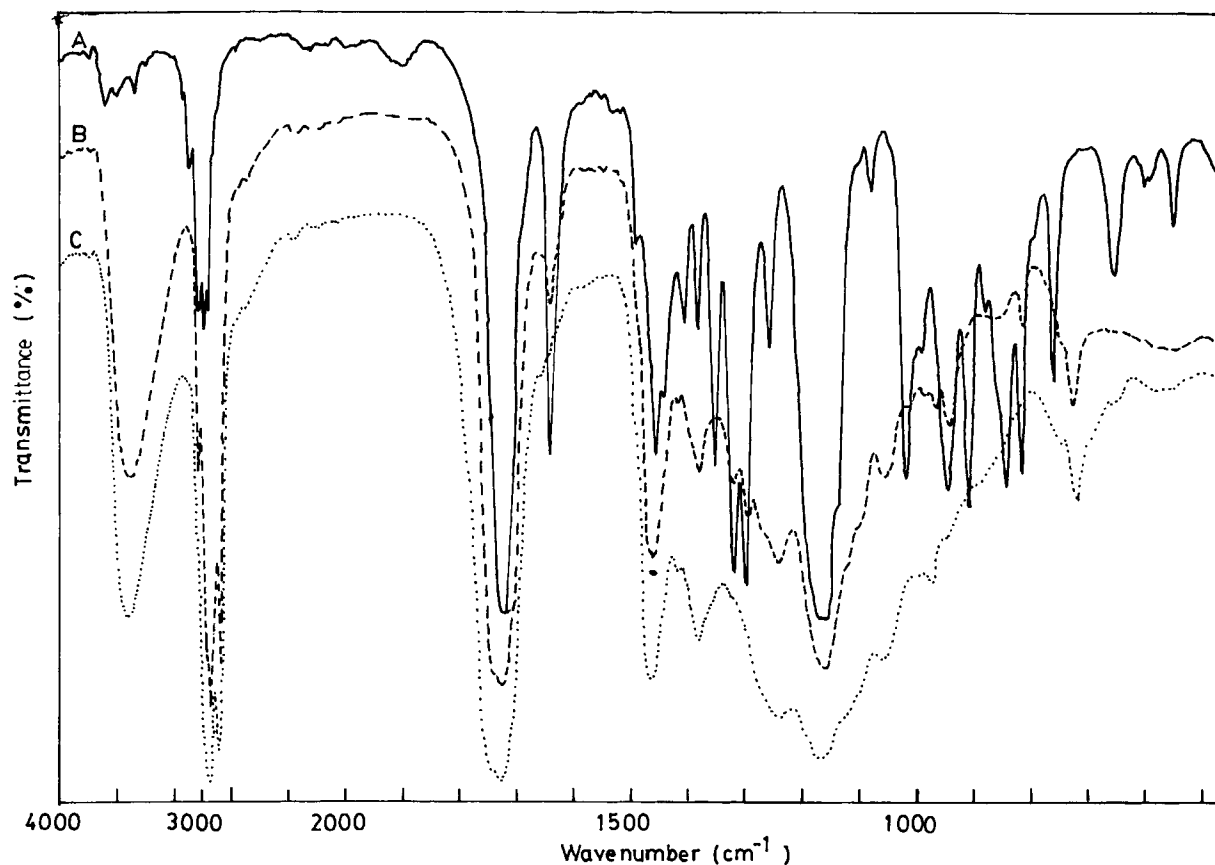
Figure 8 IR spectra of GMA, GMA–modifier, and UV-cured polymer of GMA–modifier: [A (—)] GMA; [B (– –)] GMA–modifier; [C (----)] UV-cured polymer.
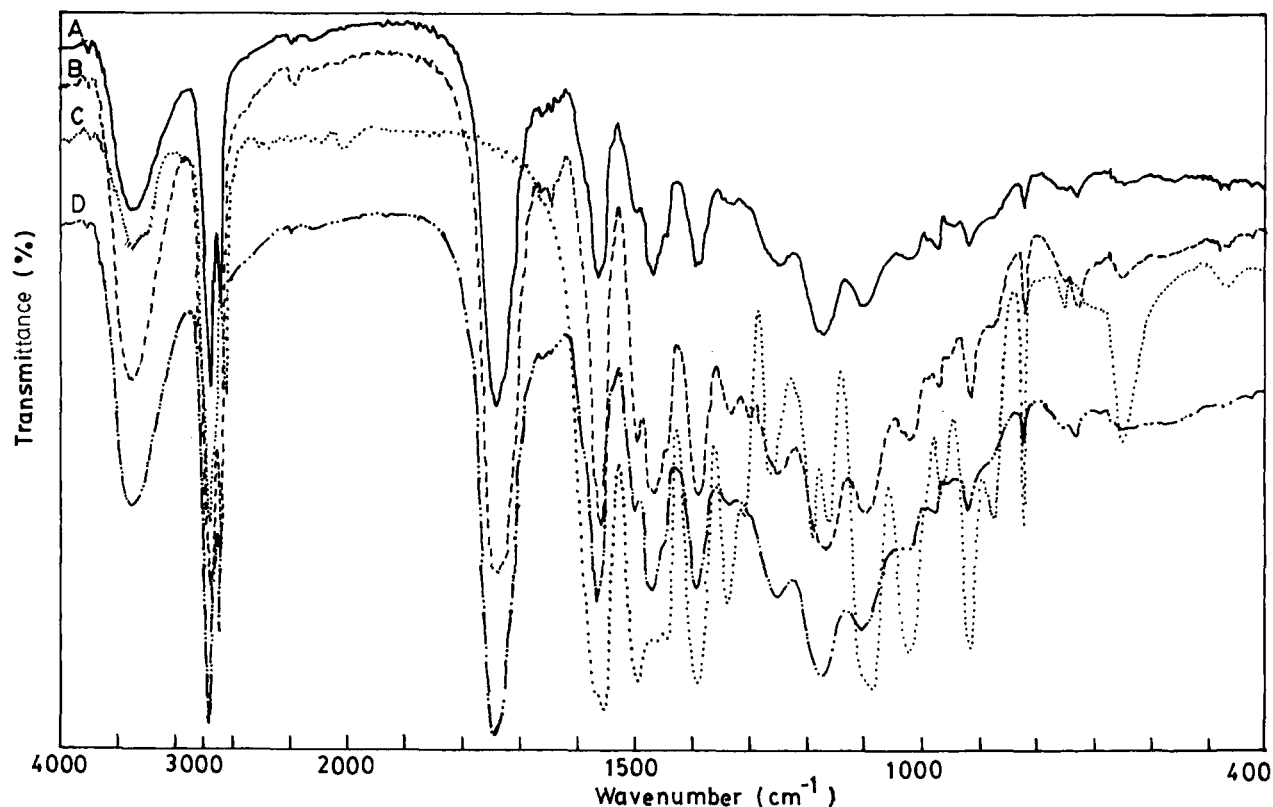
Figure 9 IR spectrum of the GMA–modifier/HMMM (1/0.4) at different times.
[A (—)] 6 min; [B (- - -)] 3 min; [C (----)] HMMM; [D (- · · -)] 9 min.

polymerization when the acid value is equal to 2.09. The above results point out that the thermal stability is related to cross-linkage—the higher the cross-linkage, the higher the thermal stability.

Determination of Kinetic Parameters for Thermal Degradation of GMA–Modifier Polymers

The results from the thermogravimetry of GMA–Modifier polymer (acid value = 8.28) at different heating rates under a nitrogen atmosphere are plotted against the absolute temperature in Figure 11.

The apparent activation energy was determined by Ozawa's method for a given value of the weight fraction (W %).[9] According to it, the weight decreases to a given fraction at temperature T_1 for the heating rate of β_1, at T_2 for β_2, and so on. The following equation could be derived[9]:

$$-\log \beta_1 - 0.457 \frac{E_1}{RT_1} = -\log \beta_2 - 0.457 \frac{E_2}{RT_2} \quad (1)$$

where E is the activation energy and R is the ideal gas constant. From Figure 11, the logarithm of the

Table I   The Transmittance Intensity Ratios of the Methoxy Group and the Triazine Group in HMMM at Different Irradiation Times

Time (Min)	$\nu_{909cm^{-1}}/\nu_{820cm^{-1}}$	Methoxy Group Reacted (%)
0	0.852	—
3	0.843	1.06
6	0.786	7.75
9	0.778	8.68

Table II   Definitions of Variables and Constants

$\Delta W = (W/W_0) \times 100$ (%)

ΔT	decomposition range at major stage (°C)
W_0	initial weight (%)
W	weight loss between decomposition range at major stage (%)
ΔW	weight change between decomposition range at major stage (%)
T_s	extrapolated temperature at start of the intense degradation (T_{start}) (°C)
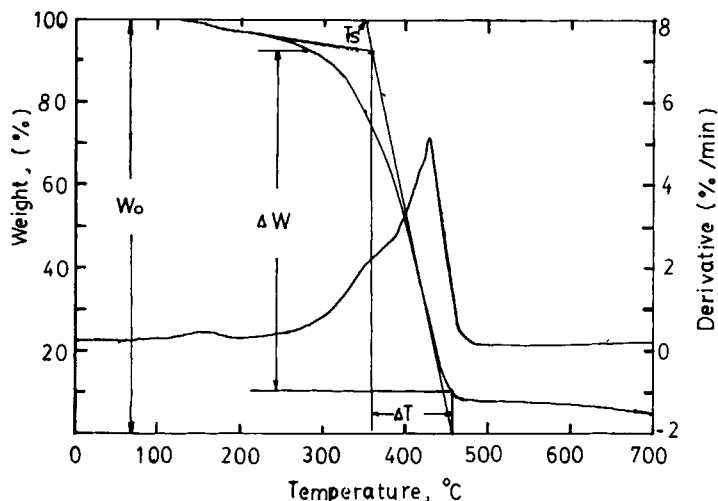
Figure 10   Example of TGA thermogram of poly(GMA-modifier) with definition of temperature of the start (T_s) of intense degradation, weight loss (ΔW), and total weight loss.

heating rates could be plotted vs. the reciprocal absolute temperature until the weight of the sample decreases to a given fraction. The results are shown in Figure 12. Straight lines are drawn using the linear regression method. The activation energy (E) and the logarithm of preexponential factor ($\log A$) determined from these lines are 167.1 kJ/mol and 12.5 min^{-1}, respectively.

The kinetic order of the reaction could be derived by using eq. (1)[9,10]:

$$\log|\ln(1 - C)| = \log(AE/\beta R) - 2.35$$

$$- 0.4567(E/RT) \quad \text{for } n = 1 \quad (2)$$

where A is the preexponential factor; β, the heating rate; R, the ideal gas constant; and E, the activation energy.

The conversion (C) is defined by

$$C = 1 - W/W_0 \quad (3)$$

where W_0 and W represent the initial weight and weight at any time, respectively, and n is the reaction order. The logarithm of $|\ln(1 - C)|$ can be plotted vs. the logarithm of heating rate (β) as shown in Figure 13. From Figure 13, a good linear relationship was obtained at constant temperatures of 350 and 450°C. These results mean that the apparent kinetic order is unity under a nitrogen atmosphere.

**Effect of Heating Rate on the Thermodegradation Kinetic Parameters**

The effect of the heating rate on the thermodegradation kinetic parameters for the acid value 8.28

Table III   Weight Loss[a] of Degradation for Various Cured GMA—modifiers in a Nitrogen Atmosphere; Heating Rate = 5°C/Min

Acid Value	Major Stage T (°C)	Decomposition Range ΔT (°C)	Weight Loss (%)	T_{max} (°C)	Weight Remaining (%) at 650°C
17.4	354.0–450.0	96.0	79.0	420.8	2.6
8.28	348.1–447.4	99.3	81.0	420.3	3.8
2.09	360.5–448.6	88.1	84.5	424.0	5.2
2.09 (UV curing)	331.0–443.1	122.8	80.6	413.3	7.5

[a] The TGA results are an average of two runs.
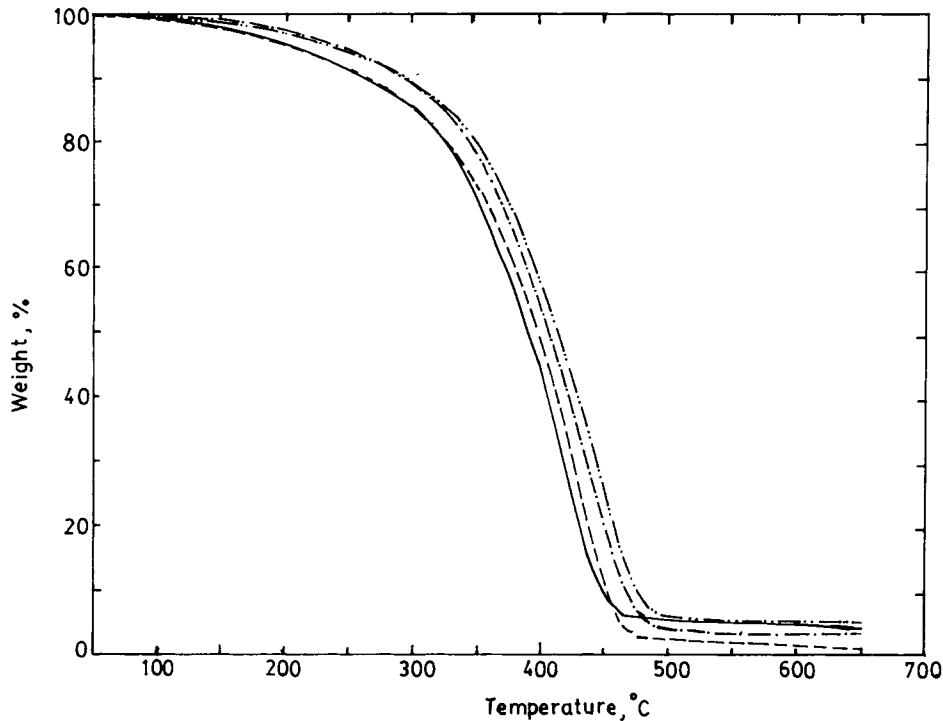
Figure 11   TG curves of acid value 8.28 cured GMA–modifier for various heating rates in a nitrogen atmosphere. Heating rates: (—) 5, (– –) 10, (– · –) 15, and (– · · –) 20°C/ min.

GMA–modifier polymer is determined by van Krevelen's method in a nitrogen atmosphere.[11] Using the method, T_m, a maximum reaction velocity, is measured at a certain temperature. When the reaction proceeds almost entirely within the range $0.9\ T_m < T < 1.1\ T_m$, the following equation could be derived[10-12]:

$$\ln|\ln(1 - C)| = \ln\left[\frac{A}{\beta}\left(\frac{0.368}{T_m}\right)^{E/RT_m}\frac{1}{E/RT_m + 1}\right]$$

$$\times \left(\frac{E}{RT_m} + 1\right)\ln T \quad (n = 1) \quad (4)$$

where E, R, A, C, and β are defined as previously,

Table IV   Thermal Stability for Various Cured GMA–modifiers in a Nitrogen Atmosphere; Heating Rate = 5°C/Min

Acid Value	T_{start} (°C)	$T_{50\%}$ (°C)
17.4	330	389
8.24	335	390
2.09	350	402
2.09 (UV curing)	320	385

and T_m is the temperature at the maximum weight loss rate, dC/dt. From eq. (4), the natural logarithm of $|\ln(1 - C)|$ can be plotted vs. the natural logarithm of the absolute degradation temperature (T) under a nitrogen atmosphere. The results are shown
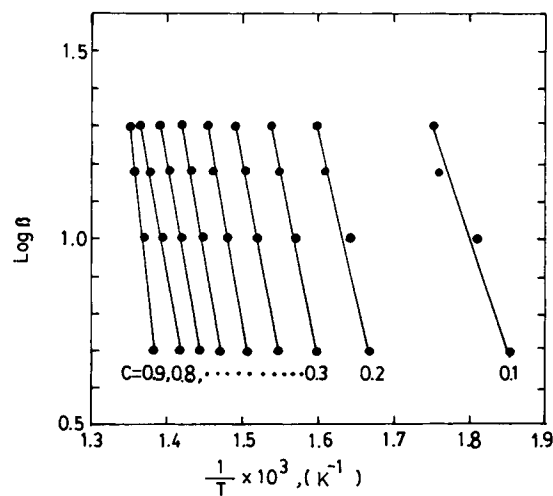
Figure 12   The plots of logarithms of heating rate vs. the reciprocal absolute temperature for indicated conversions of the degradation of acid value 8.28 of GMA–modifier polymer in a nitrogen atmosphere.
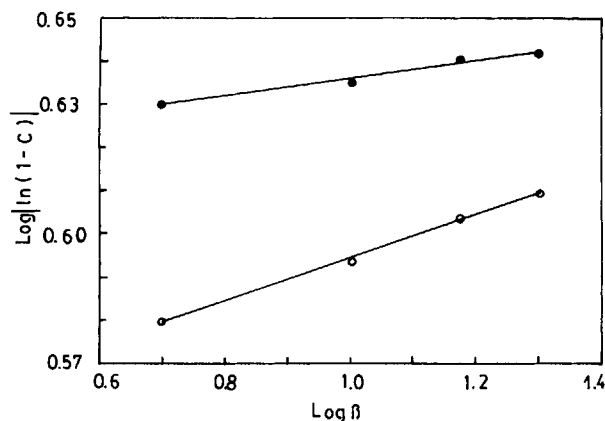
Figure 13 Relationship obtained by Ozawa's method for $n = 1$ in a nitrogen atmosphere: (●) 350°C; (○) 400°C.

Table V Comparison of Kinetic Parameters Obtained by van Krevelen's Method[11] under Different Heating Rates in a Nitrogen Atmosphere for GMA–Modifier Polymer with Acid Value 8.28

Heating Rate (°C/Min)	E (kJ/mol)	log A (min⁻¹)
5	78.72	4.36
10	78.25	5.28
15	70.55	4.72
20	69.68	4.71

in Figure 14, which points out that the reaction order shown by the linear relationship is unity. The activation energy and the preexponential factor calculated are listed in Table V, which shows that the heating rate exercises a significant effect on E values arrived at by using van Kreven's method. As the heating rate increases, the E value decreases from about 78 kJ/mol to about 69 kJ/mol. The log A values are not correlated with the heating rate. The variation in E values with the heating rates may be ascribed to the relaxation time for regrouping of the molecule or the heat capacity, thermal conductivity, and degree of fineness of the sample.[13] From the foregoing discussion, Ozawa's method, which yielded the E value of about 167 kJ/mol, represents an

overall degradation process. In comparison with Ozawa's method, van Krevelen's method represents a certain temperature degradation at a maximum reaction range and only yielded about one-half the value of 167 kJ/mol.

Effect of Acid Value for GMA–Modifier Polymer on the Kinetic Parameters

The kinetic parameters of various acid values of GMA–modifier polymers are calculated by using van Krevelen's method.[11] The relationship between natural logarithm of $|\ln(1 - C)|$ and ln T for each sample is shown in Figure 14, which confirms what is presented in Table VI in regard to the activation energies and preexponential factors.

Table VI shows that the effect of acid value on the activation energy and log A is not apparently
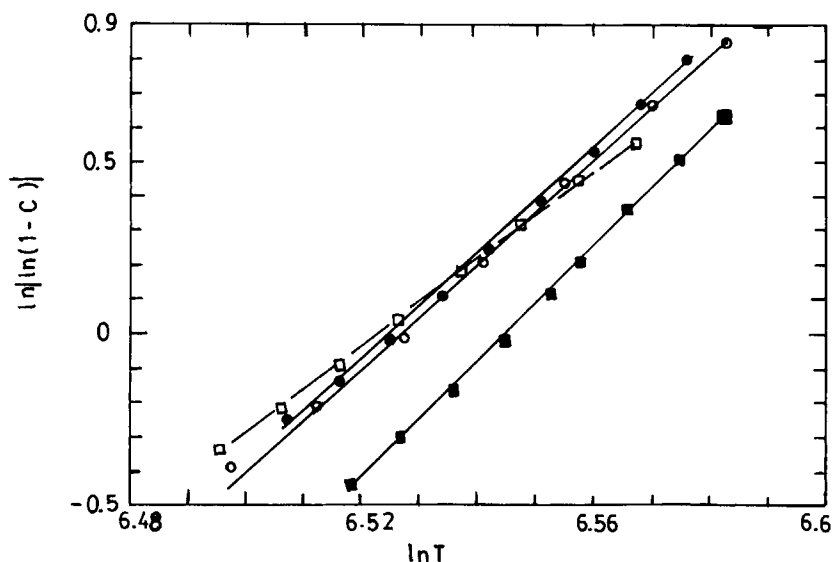
Figure 14 Application of van Krevelen's method to experimental data in a nitrogen atmosphere for various acid value samples. Acid values: (○) 17.4; (●) 8.24; (■) 2.09; (□) 2.09 (UV curing).

Table VI Kinetic Parameters Obtained by van Kreleven's Method[11] in a Nitrogen Atmosphere with Heating Rate of 5°C/Min

Acid Value	E (kJ/mol)	log A (min^{-1})
17.4	82.60	4.56
8.28	78.72	4.36
2.09	91.42	5.30
2.09 (UV curing)	67.07	3.42

regular. However, for the acid value of 2.09, it is apparent that both the activation energy E and log A values for polymer photoinitiated are much lower than free-radical-derived polymers. This result leads to the conclusion that the thermal behavior of the GMA–modifier is dependent on the polymerization method and gel fraction.

REFERENCES

1. Dainippon Ink and Chemicals, Inc., Jpn. Kokai 122,557 (1984).
2. Nippon Paint Co. Ltd., Jpn. Kokai 152,965, 149,913 (1984).
3. G. Y. Tilak, *Prog. Org. Coat.*, **13**, 333 (1985).
4. M. F. Kooistra, *J. Oil. Colour Chem. Assoc.*, **62**, 432 (1979).
5. W. Blank, *J. Coat. Technol.*, **56**, 61 (1979).
6. K. Holmberg, *J. Oil Colour Chem. Assoc.*, **61**, 359 (1978).
7. T. Nakamichi, F. Sakurai, and O. Ohe, *J. Jpn. Soc. Colour Mater.*, **58**, 522 (1985).
8. D. J. Love, *Polym. Paint Colour J.*, **180**, 48 (1990).
9. T. Ozawa, *Bull. Chem. Soc. Jpn.*, **38**, 18811 (1965).
10. W.-F. Lee, *J. Appl. Polym. Sci.*, **37**, 3263 (1989).
11. D. W. van Krevelen, C. van Heerden, and F. J. Huntjens, *Fuel*, **30**, 253 (1951).
12. W.-F. Lee and S.-P. Su, *Tatung J.*, **17**, 167 (1987).
13. A. E. Newkirk, *Anal. Chem.*, **32**, 1558 (1960).