

# Synthesis and Characteristics of Photoactive-Hydrogenated Rosin Epoxy Methacrylate for Pressure Sensitive Adhesives

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**ABSTRACT:** Hydrogenated rosin epoxy methacrylate (HREM), based on hydrogenated rosin and glycidyl methacrylate (GMA), was synthesized for use as an advanced tackifier in the UV-crosslinking pressure sensitive adhesives (PSAs) system. The HREM, as a tackifier, contained UV-curing sites; thus, allowed photopolymerization to occur by UV irradiation. This UV-curable tackifier, HREM, can improve the curing rate and adhesion performance of UV-crosslinking PSAs. The characteristics of HREM were analyzed by GPC and DSC and its synthetic mechanism studied using FTIR and <sup>1</sup>H NMR; the characteristic peaks

of hydrogenated rosin and GMA vanished, but new peaks for HREM appeared. The PDI and the  $T_g$  by DSC were 1 and  $-25.6^\circ\text{C}$ , respectively. The photopolymerization of HREM was studied using photo-DSC. Heat flow was observed during UV irradiation, and the curing rate and conversion both increased with rising photoinitiator content. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1172–1176, 2009

**Key words:** hydrogenated rosin epoxy methacrylates; tackifiers; UV-curing reaction

## INTRODUCTION

Rosin is a complex mixture of mutually soluble, naturally occurring high-molecular weight organic acids and related materials. The acidic constituents, which make up the major portion of rosin, are called resin acids. The major constituent of resin acids is abietic acid.<sup>1</sup>

Rosin is an effective adhesion promoter and viscosity controller, etc. All these useful properties are certainly related to the bulky alicyclic structure of rosin. Therefore, it is expected that adhesive, stable, transparent, and thermally stable polymer films will be obtained when the rosin moiety is incorporated into the polymer structure. However, rosin is a mixture of abietic acids and some isomers with C=C double bonds in different positions. It is easily oxidized at these C=C double bonds of rosin. As a result, rosin is used in a chemically modified form by means of hydrogenation, polymerization, or disproportionation.<sup>2</sup>

The Diels–Alder adduct of rosin and maleic anhydride (RMA) has been extensively used as a raw material for the elimination of the C=C double bond of rosin-containing polymers. Hydrogenated rosin is also widely used as an additive and modifier in vari-

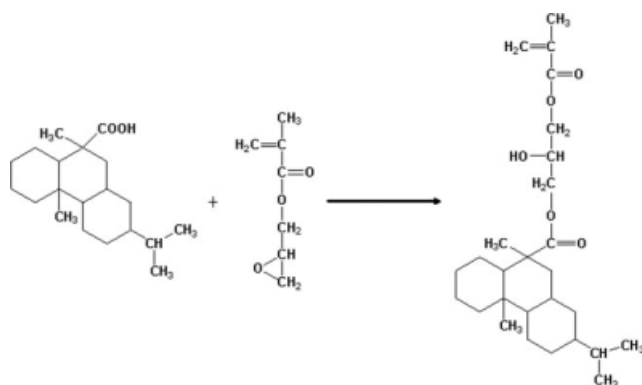
ous applications.<sup>3</sup> This has advantages over nonhydrogenated rosin; it is of light color, has improved stability, lower skin sensitization, and is suitable for UV irradiation. However, to utilize RMA and hydrogenated rosin in a UV-curing system, modification to the acrylate functionality, which can be converted to a photocurable polymer via UV irradiation, is required. There have been many investigations on modifying rosin with acrylates. To obtain a trifunctional rosin acrylate, the Diels–Alder adduct of RMA was esterified with 2-hydroxyethyl acrylate and fumaric acid. Monofunctional rosin acrylate was also obtained by esterifying RMA with 2-hydroxyethyl acrylate.<sup>4</sup>

Pressure sensitive adhesives (PSAs) have been manufactured by blending gums with tackifier resins. Gum is a linear polymer with a very low glass transition temperature ( $T_g$ ), such as natural rubber, synthetic rubber or block copolymer (SIS, SBS, SEBS, etc.), and the resin is a bulky compound, with a low molecular weight ( $\sim 1000$ ), such as rosins, terpene resins, and certain synthetic resins.<sup>5,6</sup>

Acrylic ester monomers are widely used to synthesize PSAs as acrylic PSAs possess superior properties, such as transparency, colorless, and resistance to yellowing under sunlight and oxidation. There have been many recent cases where acrylic PSAs were blended with tackifier resins to modify their adhesion properties.<sup>7</sup>

As these synthesized acrylic PSAs have a linear structure, crosslinkage between the polymer chains

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**Figure 1** Synthesis of hydrogenated rosin epoxy methacrylate (HREM).

is required to improve their mechanical and thermal stabilities.<sup>8</sup> Currently, UV-curing techniques are utilized to crosslink acrylic PSAs.<sup>9,10</sup> However, in a UV-curable acrylic PSAs blended with tackifiers system, the tackifiers act as fillers during UV-curing because most general tackifiers have no UV reactive site; thus, the UV-curing rate of PSAs become retarded. Therefore, it is necessary to incorporate UV-curable sites to tackifiers to improve the curing rate and adhesion performance.

In this study, monofunctional hydrogenated rosin epoxy methacrylate (HREM) was newly synthesized from hydrogenated rosin and glycidyl methacrylate (GMA). In addition, the effect of the photoinitiator concentration on the photopolymerization of the synthesized HREM was investigated using photocalorimetry (photo-DSC).

## EXPERIMENTAL

### Materials

Hydrogenated rosin (Foral AX-E, Eastman Chemical Co. Ltd., Netherlands) and GMA (Junsei Chemical Co., LTD., Japan) were used to synthesize a HREM in methyl ethyl ketone (MEK, Samchun Pure Chemical Co., LTD. Korea). Hydroquinone (HQ, Sigma Aldrich) and tetramethylammonium bromide (Sigma Aldrich) were used as an inhibitor and catalyst, respectively. Irgacure<sup>®</sup> 754 (oxy-phenyl-acetic acid 2-[2 oxo-2 phenyl-acetoxy-ethoxy]-ethyl ester and oxy-phenyl-acetic 2-[2-hydroxy-ethoxy]-ethyl ester, Ciba Specialty Chemicals) was used as a photoinitiator in the photopolymerization of HREM.

### Synthesis of HREM

HREM was synthesized from hydrogenated rosin and GMA in MEK. A mixture with equal moles of GMA and hydrogenated rosin was charged with tetramethylammonium bromide and hydroquinone dissolved in MEK into a 500 mL three-necked round bottom flask,

equipped with a thermometer, condenser and mechanical stirrer as 50% solid contents. The synthesis was performed at 80°C for 24 h, with the solution evaporated to remove the MEK, washed with 5% sodium hydroxide solution to remove the HQ and then dried in a vacuum oven at 40°C for 72 h. The final product was used as HREM. Figure 1 shows the synthesis procedure for the formation of HREM.

### Characterization of HREM

#### Molecular weight

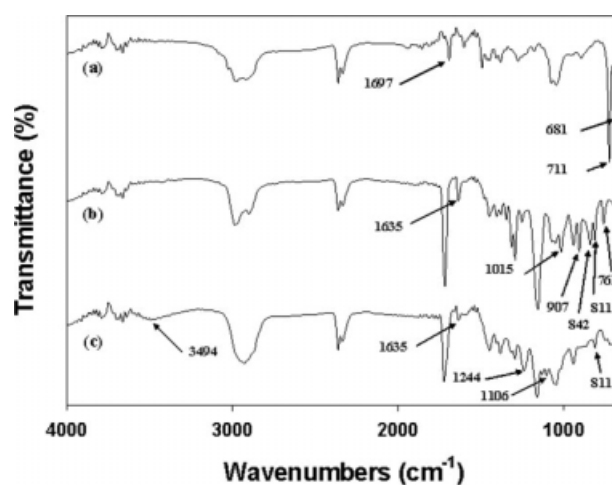
The average molecular weight ( $M_w$ ), number-average molecular weight ( $M_n$ ), and molecular weight distribution ( $M_w/M_n$ , MWD) of the synthesized HREM were determined at 40°C using gel permeation chromatography (GPC, Shimadzu Co. Ltd., Japan) coupled to an RID-10A refractive index detector, with tetrahydrofuran (THF) used as the solvent. An Asahi pack KF 804, 8 mm × 800 mm column was used, with ammonium acetate buffer THF used as the eluent, at a flow rate of 1.0 mL/min. The GPC system was calibrated using poly(methyl methacrylate).

#### FTIR spectroscopy

The infrared reflectance spectra were measured using a Fourier-transform infrared (FTIR) spectrometer, JASCO FTIR-6300, employing a Mylar beam splitter. Spectra were collected over 32 scans to reduce the noise, with a resolution of 8 cm<sup>-1</sup> between 650 and 4000 cm<sup>-1</sup>.

#### <sup>1</sup>H NMR

The <sup>1</sup>H NMR spectrum of the HREM was obtained at ambient temperature in CDCl<sub>3</sub> solution (10% w/v),



**Figure 2** FTIR spectra of (a) hydrogenated rosin, (b) GMA, and (c) HREM.

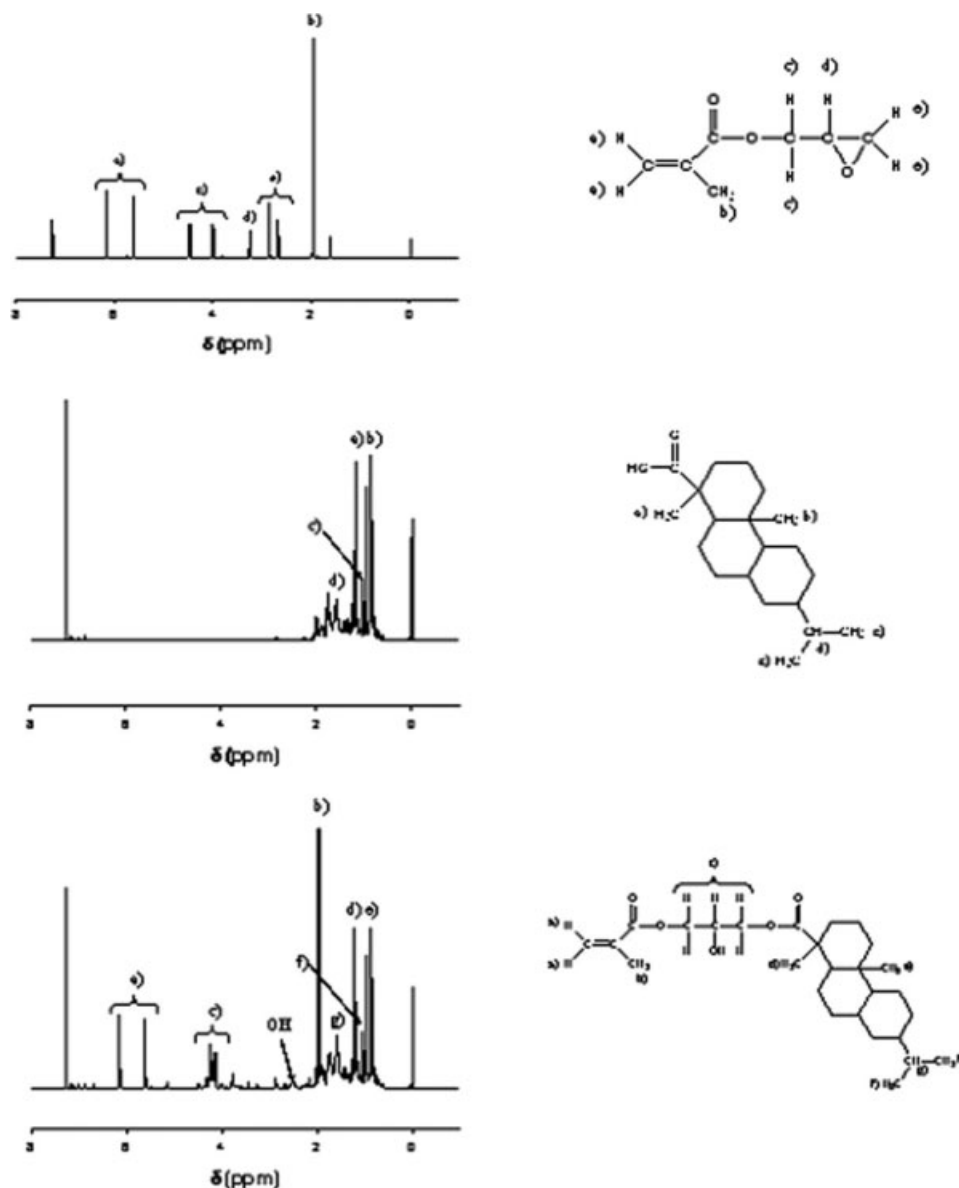


Figure 3  $^1\text{H}$  NMR spectra of (a) hydrogenated rosin, (b) GMA, and (c) HREM.

using an AVANCE 600 FT NMR (600 MHz, Bruker, Germany) spectrometer, with tetramethylsilane (TMS) as the internal standard.

### Photopolymerization of HREM

The photopolymerization of HREM was carried out using a TA differential scanning calorimeter (DSC, Q-1000 TA Instruments), equipped with a photocalorimetric accessory (Novacure<sup>®</sup> 2100). Light from a 100 W high-pressure mercury lamp was used for the photopolymerization, with the light intensity determined by placing an empty DSC pan on the sample cell. The light intensity was  $\sim 0.5$  W/cm<sup>2</sup>, over the wavelength range 320–500 nm. Approximately 2 mg of a sample mixture was placed in the aluminum DSC pan.

## RESULTS AND DISCUSSION

### Synthesis of HREM

The hydrogenated rosin was reacted with GMA, as shown in Figure 1. The reaction occurred between the epoxy ring of GMA and the carboxylic acid of hydrogenated rosin. The PDI of the synthesized HREM was about 1 ( $M_w$ : 470,  $M_n$ : 467). Figure 2(a) shows the FTIR spectrum of hydrogenated rosin. The bands at 711 and 681 cm<sup>-1</sup> were due to the in-plane vibration of the O—CO in the carboxylic group, and the broad absorption region at 3200–2500 cm<sup>-1</sup> was assigned to —OH stretching vibration. The band at 1697 cm<sup>-1</sup> was due to C=O stretching vibration. Figure 2(b) shows the characteristic band of GMA, where the bands at 842, 907, and 1015 cm<sup>-1</sup> were assigned to epoxy ring stretching

vibration,  $\text{—C—O—C—}$  symmetric stretching vibration and  $\text{C—O—C—}$  asymmetric stretching vibration, respectively. The band at  $811\text{ cm}^{-1}$  was attributed to  $\text{CH}_2=\text{CH—}$  twisting vibration and  $\text{C=C}$  stretching vibration in the acrylic double bond. The characteristic bands at  $681, 711, 842, 907, 1015,$  and  $1697\text{ cm}^{-1}$  disappeared in HREM, but new bands were created. Figure 2(c) shows the newly created bands at  $1106, 1244,$  and  $3494\text{ cm}^{-1}$ . The band at  $1106\text{ cm}^{-1}$  was due to the stretching vibration of  $\text{—C—O—}$  in the secondary alcohol group, and those at  $1244$  and  $3494\text{ cm}^{-1}$  to  $\text{C—H}$  deformation vibration and newly created hydrogen-bonded  $\text{O—H}$  stretching vibration of the secondary alcohol ( $\text{—CH—OH}$ ).<sup>11</sup>

Figure 3 shows the  $^1\text{H}$  NMR of (a) GMA, (b) hydrogenated rosin, and (c) synthesized HREM. The signals at  $5.61$  and  $6.14$  ppm in Figure 3(c) were associated with the protons of the acrylic double bond. The signals at  $2.67$  and  $3.25$  ppm for the epoxy in Figure 3(a) shifted to  $4.31$  and  $4.1$  ppm [Fig. 3(c)], respectively, as a result of the epoxy ring opening reaction with carboxylic acid. In addition, the broad signal at  $2.5$  ppm in Figure 3(c) was due to the formation of the hydroxyl group.<sup>12</sup>

### Photopolymerization of HREM

Photopolymerization experiments were performed with HREM by varying the photoinitiator concentration from  $0.5\%$  to  $5\%$ , followed by photo-DSC under identical temperature and light intensity conditions ( $50^\circ\text{C}$  and  $0.5\text{ W/cm}^2$ ).

Heat flow versus time (DSC thermogram) curves were recorded in an isothermal mode, under a nitrogen flow of  $50\text{ mL/min}$ . The heat of reaction liberated during the polymerization was directly proportional to the number of vinyl groups reacted in the system. By integrating the area under the exothermic peak, the conversion ( $C$ ) of the vinyl groups or the extent of reaction could be determined according to the following equation

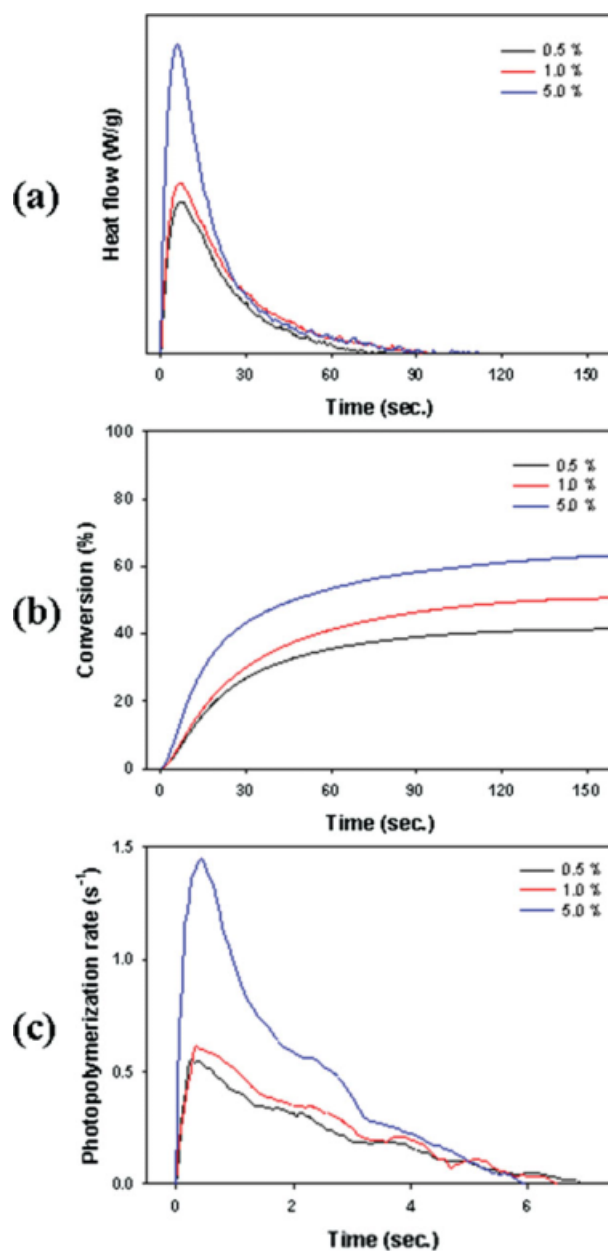
$$C(\%) = \frac{\Delta H_t}{\Delta H_0^{\text{theor}}}$$

Where  $\Delta H_t$  is the reaction heat evolved at time,  $t$ , and  $\Delta H_0^{\text{theor}}$  the theoretical heat for complete conversion. For a methacrylic double bond,  $\Delta H_0^{\text{theor}} = 56\text{ kJ/mol}$ .

The rate of photopolymerization,  $R_p$ , is directly related to the heat flow ( $dH/dt$ ) by the following equation:

$$R_p = \frac{dC}{dt} = \frac{dH/dt}{\Delta H_0^{\text{theor}}}$$

Comparisons of the rate of photopolymerization with different photoinitiator concentrations are pre-



**Figure 4** (a) Photo-DSC profiles, (b) conversion versus time, and (c) rate versus time, for polymerization of HREM with different photoinitiator concentrations. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

sented in Figure 4(a). The initiator efficiency was constant at low conversions, but decreased when the segmental mobility of the medium decreased, as this prevents the initiator radicals from escaping the surrounding solvent cage. In the early stages of the photopolymerization of HREM, the molecules increase in size, branch, physical crosslink, which reduce the mobility of the molecular segments and raise the  $T_g$ . Once the  $T_g$  of the material exceeds the isothermal curing temperature, the material vitrifies, freezing in the mobility of the reactive vinyl groups

and radicals and preventing further reaction.<sup>13</sup> With a very low photoinitiator concentration (0.5 wt %), 6.95 s were required to reach the rate of polymerization ( $dC/dt$ ) becomes essentially zero [Fig. 4(c)]. This is because a very low initiator concentration yields few radicals due to the incident light; thus, leads to the requirement of a long time period to form the polymer structure, which then produces the maximum polymerization rate.

From a simple kinetic treatment of free radical polymerization, the maximum rate is expected to occur soon after the light is turned on; when the free-radical concentration has reached a steady state value and the concentration of unconsumed monomer is greatest.<sup>14</sup> The time to reach the rate of polymerization to zero decreased from 6.55 to 5.95 s on increasing the photoinitiator concentration from 1 to 5 wt %.

The correlation between conversion and photopolymerization rate, and their dependency on initiator concentration are shown in Figure 4(b,c), where the maximum photopolymerization rate occurred with high conversion at initiator concentration 5.0%, and final conversions increased to 41.1, 50.6, and 63.2%, respectively, with increasing photoinitiator concentration. In the case of photopolymerization, initiation rate was very high and the conversion increased with photopolymerization rate. This is known as "autoacceleration," which results from a decrease in the mobility of polymer radicals with increasing viscosity of the medium, and causes a reduced termination rate. The reduced rate of termination causes an increase in the radical concentration, which increases the polymerization rate. After the rate of polymerization reached its maximum, it then started to decrease due to autodeceleration, where branches and physical crosslink restricted and stopped the propagation reaction altogether. As the polymerization rate increased, the volume relaxation was unable to keep pace with the conversion and lead to an increased free volume formation. The free volume in excess of equilibrium values causes higher mobility, which results in increased conversion. Thus, these systems can not be in volumic equilibrium because the volume shrinkage rate is much smaller than the rate of the chemical reaction. This difference generates a

temporary excess of free volume, which increases the mobility of the residual double-bond, leading to a higher conversion.

## CONCLUSIONS

HREM was synthesized via an epoxide ring opening reaction with the carboxylic acid of hydrogenated rosin. The heat flow generated in the Photo-DSC test showed that HREM caused photopolymerization to occur, as it contains UV-curing sites. The time to reach the maximum polymerization rate decreased and the final conversion increased with increasing the photoinitiator concentration. The rate of photopolymerization increased with increasing initiation rate, as the high initiation rate induced temporary lower volume shrinkage. This caused the segmental mobility of the polymers to increase, which extended the time to reach autodeceleration of the polymerization reaction.

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