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Curing characteristics of carboxyl functionalized glucose resin and epoxy resin

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Abstract

The curing characteristics of carboxylic functionalized glucose resin (glucose maleic acid ester vinyl resin: GMAEV) and epoxy resin have been studied using DSC and FTIR methods. Exothermic reactions attributed to esterification and etherification reactions of the hydroxyl and carboxyl functionalities of GMAEV with the epoxy groups were identified. Exothermic reactions showed very different patterns according to the degree of carboxyl group substituent of GMAEV. The results showed that esterification reaction occurs in the early stage of cure and then etherification followed after completion of the esterification. A cured matrix containing epoxy resin and 50 wt.% of GMAEV was prepared and characterized. The cured matrix showed thermal stability up to 300 °C. The average glass transition temperature and storage modulus of the matrix were as high as 95 °C and 2700 MPa, respectively. The cured matrix of epoxy resin and GMAEV with higher degree of carboxyl group was found to have a lower density due to the formation of bulky groups in the crosslinks.

Keywords: Epoxy resin; Carboxyl functionalized glucose resin; Curing characteristics

1. Introduction

Epoxy resins are widely used for many important applications such as coatings, adhesives, reinforced plastics, and matrix resins for advanced composites, due to their high thermal resistance, high tensile strength and modulus [1]. Epoxy resins have also been investigated as a polymer matrix for biocomposites with natural fibers in order to apply them in automobile and construction industries [2,3]. The wide range of applications can be attributed to the fact that epoxy resins can be crosslinked with a variety of functionalized compounds that contain hydroxyl, carboxyl and amine groups [4].

The incorporation of biodegradable materials into an epoxy resin has advantages for the development of environmentally friendly biocomposites [5]. Glucose maleic acid ester vinyl resin (GMAEV) as a carboxyl functionalized glucose resin has been developed as a biodegradable adhesive for the paper and packaging industry [6]. Since GMAEV contains reactive carboxyl and hydroxyl functional groups in its structure, GMAEV can be crosslinked with epoxy resins and used as a part of polymer matrix for biocomposites [7].

The relative reactivity of hydroxyl and carboxyl groups with epoxy has been of great interest to researchers [8,9]. Shechter et al. has studied the reactivity of different alcohols and carboxylic acids towards different epoxide groups such as styrene oxide, phenyl glycidyl ether and benzyl oxide [10]. Wu et al. has investigated the crosslinking reactions for hydroxyl and carboxyl functionalized acrylic copolymer with cycloaliphatic epoxy resin [4]. The purpose of this research is

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to investigate the curing mechanisms between epoxy resin and GMAEV that have both hydroxyl and carboxyl groups in its structure and to determine if this matrix can be used in biocomposites.

2. Experimental

2.1. Materials

Epoxy resin, Tactix 123, based on diglycidyl ether of bisphenol A (DGEBA) was purchased from Ciba Chemical Co. The viscosity of the resin is 5000 cps at 25 °C and the epoxy equivalent weight is 172–176 g/mol. The structure of the monomer is shown in Structure 1.

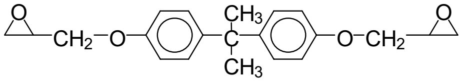
GMAEV was obtained from EcoSynthetix Inc. and used as received. The structure of GMAEV is shown in Structure 2. The average degree of polymerization of glucose (DP) and substitution of the maleic ester group (DS) of the samples used for this research are summarized in Table 1. Sample denoted as GMAEV-0 is hexyl-α -D-glycoside that does not have any carboxyl group in its structure.

GMAEV starts to decompose at 165 °C and degrades at temperatures over 110 °C. Comparison of the FTIR spectra between original GMAEV and the degraded GMAEV shows that the –C–O–C– peak characteristic of the glucose and vinyl groups peaks disappears. A new peak, due to the presence of free carboxyl group appears as the GMAEV degrades. It was also found that the broad peak for the hydroxyl group changed to a sharp peak when the glucose ring opened and formed free hydroxyl groups. These carboxyl and hydroxyl groups can now easily react with the epoxy group of the resin [7].

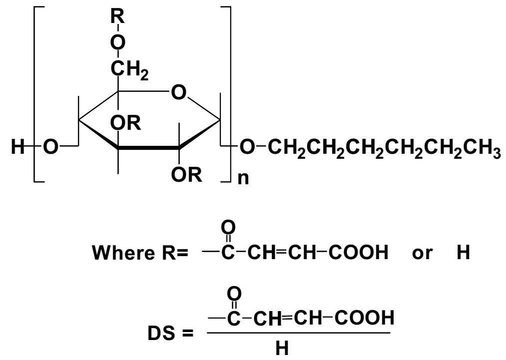
2.2. Sample preparation

2.2.1. Preparation of epoxy resin and GMAEV mixture

GMAEV and epoxy resin were heated to 90 °C separately and mixed by a melt-blending process. The formulation of 50 wt.% GMAEV and epoxy resin was used for all experiments. Once a homogeneous solution was obtained by mixing two solutions for 10 s, the solution was degassed at 90 °C for 10 min. Any curing reactions were not identified during the blending and degassing by FTIR examinations.



Structure 1. The DGEBA molecule.



Structure 2. GMAEV molecule.

Table 1
DP and DS of GMAEV samples

Samples	DP (n)	DS	Main functional groups of GMAEV for expected reaction with epoxy group
GMAEV-0	1.2	0	–OH
GMAEV-1.4	1.2	1.4	–OH/–COOH
GMAEV-2.0	1.2	2.0	–COOH

2.2.2. Preparation of samples for DSC and FTIR experiments

The blended solution was used to study the curing behavior of epoxy resin and GMAEV by DSC and FTIR in real time. The sample (6 ± 0.2 mg) was taken in the DSC aluminum pan at room temperature and heated from 30 to 320 °C with heating rate of 5 °C/min. The sample weight did not change before and after the DSC measurement.

For the FTIR, samples were prepared by casting a thin film of the blended solution onto a preheated sodium chloride plate at 90 °C and cooling down to room temperature immediately to prevent reaction. The sample was placed in a heating cell in the spectrometer and heated from room temperature to 170 °C to carry out the reaction.

2.2.3. Preparation of the cured samples of epoxy resin and GMAEV

The degassed solution was poured into a preheated silicone mold (1.2 cm × 7.5 cm × 0.3 cm) at 90 °C and cured in an air-circulating oven at a heating rate of 5 °C/min. The curing conditions were completed with heating the mixture at 175 °C for 2 h and 200 °C for 2 h, consecutively, allowing it to gradually cool down to room temperature. Thermomechanical properties of the cured samples of epoxy resin and GMAEV with different degrees of carboxyl group substitution were analyzed and compared.

2.3. Instrumental analysis

2.3.1. DSC monitoring of the reaction between epoxy resin and GMAEV

A DSC study was performed under a nitrogen atmosphere using a DSC2920 modulated differential scanning calorimeter from TA instruments. The base line was run and high purity indium was used to calibrate the calorimeter. Real time monitoring of the curing of epoxy resin and GMAEV was performed in an aluminum pan in the 30–320 °C temperatures ranges with heating rate of 5 °C/min.

2.3.2. FT-IR monitoring of the reaction between epoxy resin and GMAEV

Curing of epoxy resin with GMAEV was quantitatively analyzed by transmission FTIR spectroscopy using a Perkin Elmer FTIR system 2000 model, equipped with a conventional TGS detector. Samples were prepared by casting a thin film of resin onto a sodium chloride plate and placed in a heating cell in the spectrometer to carry out the reaction from 100 to 170 °C at a heating rate of 2 °C/min. The temperature of the heated cell was monitored with a DigiSense temperature controller from the Cole Parmer Co. The FTIR spectra were collected at different temperatures and compared to the FTIR spectra of fully cured samples prepared in an oven to confirm the presence of polymerization products.

The conversion of epoxy and hydroxyl functions in the formulation based on epoxy resin and GMAEV were calculated from the FTIR spectra. The 1509 $\mathrm{cm^{-1}}$ band was unchanged upon curing, and subsequently, was used as an internal standard [11]. The decrease of the band at 912 $\mathrm{cm^{-1}}$ assigned to the epoxy function permits accurate measurement of the monomer conversion via the following relation, where Π is the functional conversion and T is temperature. The epoxy function expresses the opening of the epoxy ring in the mixture. For the conversion of the hydroxyl function the maximum point of the hydroxyl peak in the region of 3666–3113 $\mathrm{cm^{-1}}$ was measured at each temperature. The hydroxyl function expresses the generation of the hydroxyl group in the mixture (Scheme 1).

$$\Pi(\text{epoxy}) = 1 - \frac{A_{912(T)} / A_{1509(T)}}{A_{912\,(T=25)} / A_{1509(T=25)}}$$

$$\Pi(\text{hydroxyl}) = 1 - \frac{A_{max(T)} / A_{1509(T)}}{A_{max(T=25)} / A_{1509(T=25)}}$$

Scheme 1.

2.3.3. Surface analysis

X-ray Photoelectron Spectroscopy examination was used to determine the functional groups on the surface of the cured matrix. A Perkin Elmer Physical Electronics PHI 5400 ESCA spectrometer equipped with standard magnesium X-ray source operated at 300 W (15 kV and 20 mA) was used for surface analysis.

2.3.4. Density measurement

Density of the cured matrix of epoxy resin and GMAEV with different degrees of carboxyl group substitution was measured using a NaBr solution method in a density measurement column of Techne Inc. [12].

2.3.5. Thermomechanical analysis

The glass transition temperature and the modulus of the cured matrix were measured by dynamic mechanical analysis in the single cantilever mode, at a frequency of 1 Hz. DMA runs were recorded with a DMA 2980 dynamic mechanical analyzer from TA instruments. The glass transition temperature was measured at the maximum of the Tan delta (δ) curve deduced from DMA experiments. Storage modulus of the matrix was determined at 40 °C.

2.3.6. Thermal stability analysis

Thermal stability of the cured matrix was analyzed under a nitrogen atmosphere using a TGA2950 thermal gravimetric analyzer from TA instruments.

3. Results and discussion

3.1. Curing behavior of epoxy resin and GMAEV

3.1.1. DSC investigation of epoxy resin and GMAEV mixture

Fig. 1 shows DSC scans for the mixture of epoxy resin and GMAEV with DS equal to 0, 1.4, 2.0. No exothermic reactions are observed in the $\mathrm{DS} = 0$ for the mixture of epoxy resin and GMAEV in the region of 100–300 °C. For the reaction of epoxy resin and GMAEV-1.4 three exothermal peaks are observed in the regions of 100–170 °C(A), 200–240 °C(B) and 260–300 °C(C), respectively. The exothermic peaks in the regions of 100–170 °C(A) and 260-300 °C(C) increase for the $\mathrm{DS} = 2.0$, however, the exothermic peak in the region of 180–240 °C(B) disappears. From this result it is postulated that the exothermic reaction observed in the

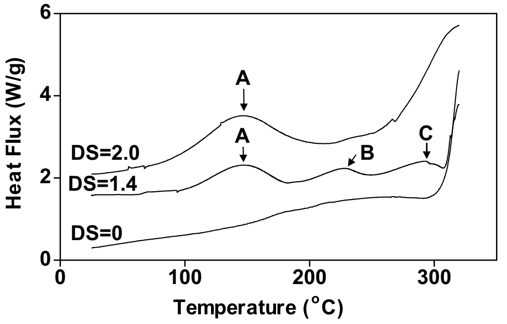


Fig. 1. DSC scans for mixture of epoxy resin and GMAEV with different degree of carboxyl group.

regions of 100–170 °C is attributed to the exothermic reaction of epoxy with carboxyl groups. This is coincident with the results of Nakamura et al. [13] that show an exothermic reaction between epoxy resin and carboxyl group of 1,3,5-triacetoxybenzene in the region of 100–180 °C.

Oh et al. [14] has studied the reaction between epoxy resin and hydroxyl groups of hyperbranched polymers. The research shows that the reaction between the epoxy group and the hydroxyl group of hyperbranched polymers has an exothermic reaction in the range of 250–350 °C. From these results the peak in the region of 260–300 °C can be explained as a exothermic reaction peak resulting from the reaction of an epoxy group of the epoxy resin and hydroxyl group of GMAEV.

Shechter et al. [10] showed that noncatalyzed, the alcohol–glycidyl ether reaction is rather sluggish; a temperature of 200 °C or higher temperature is required to realize a conveniently rapid rate [10]. Therefore, no exothermic reaction peaks and a slow increase of the slop for DSC curve for the mixture of epoxy resin and GMAEV-0 in the region of 100–300 °C can be explained that the reaction between hydroxyl group of GMAEV and epoxy group of epoxy resin is progressed slowly without any carboxylic groups. It means that the carboxyl groups also act as a catalyst.

3.1.2. FTIR spectra of epoxy resin and GMAEV curing

The curing behavior of epoxy resin and GMAEV with different degrees of carboxyl group substitution was monitored in real-time while heating the mixtures from room temperature to 170 °C by FT-IR. FTIR spectra were obtained at 25, 100 and 170 °C for each mixture of epoxy resin and GMAEV. Spectra from samples with different degrees of carboxyl group substitution are compared in Fig. 2.

The mixture of epoxy resin and GMAEV, shown in Fig. 2, indicates how the hydroxyl peak changes from a broad to a sharp peak and shows the shift to higher frequencies with increasing temperature. A change from a broad to a sharp peak results from the opening of glucose ring and that produces free hydroxyl groups in the GMAEV structure. Peak sharpening can also be explained by changing the intermolecular hydrogen bonding between hydroxyl groups of glucose ring to intramolecular hydrogen bonding. Peak shifting to higher frequencies indicates that new ester or ether bonds are formed near hydroxyl group due to crosslinks between epoxy resin and GMAEV[15].

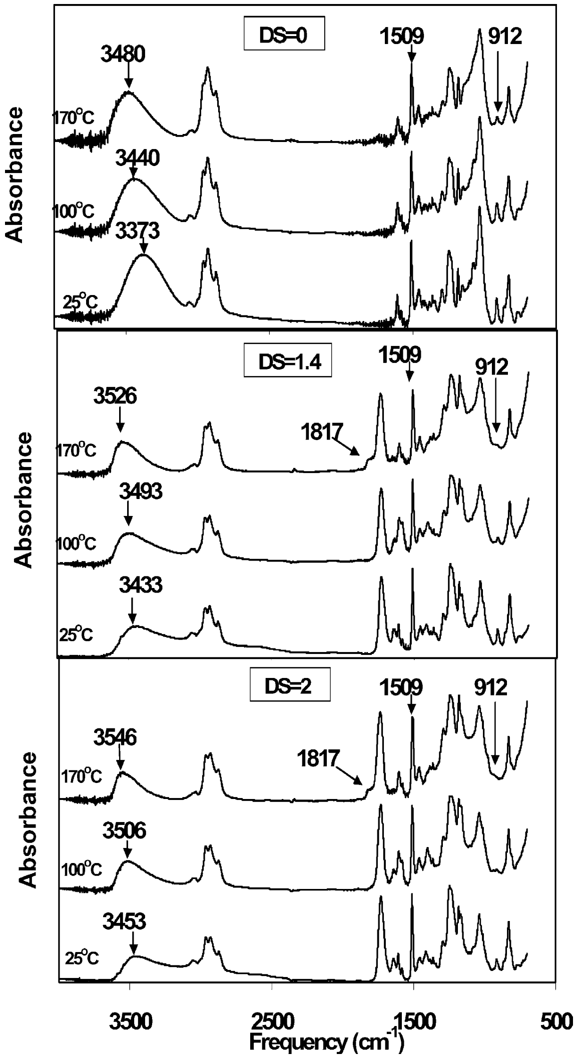


Fig. 2. FTIR Spectra of epoxy resin and GMAEV mixtures with different degree of carboxyl group substitution.

FTIR spectra for the mixture of epoxy resin and GMAEV-1.4 or GMAEV-2 shows a new peak formation in the region of 1780–1856 cm^{-1} when the mixture is heated above 160 °C. This peak can be explained as the formation of saturated carboxylic acid anhydride between carboxyl groups of GMAEV or saturated ali-

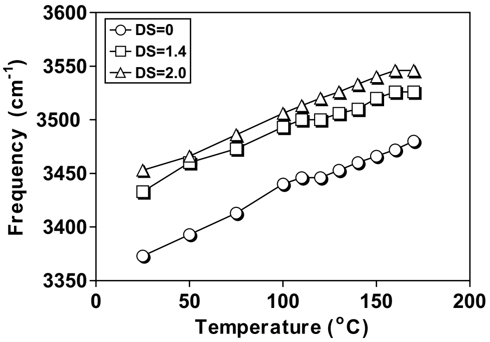


Fig. 3. The maximum point of hydroxyl peak for the mixture of epoxy resin and GMAEV with increasing temperature.

phatic acid peroxide during the curing of epoxy resin and GMAEV [15]. This peak appears and increases faster for the mixture of epoxy resin and GMAEV-1.4 comparing to that of epoxy resin and GMAEV-2.0. This indicates that the peak usually results from the formation of aliphatic acid peroxide. The reaction between the carboxyl group and hydroxyl group can proceed faster than the reaction between two carboxyl groups in the mixture. This peak was also observed in the cured matrix at temperatures higher than 170 °C. The increase in the peak near 1200 cm^{-1} is due to the stretching of –C–O–C– groups generated from crosslinks between epoxy resin and GMAEV [16].

The characteristic peak for the epoxy ring is also identified at 912 cm^{-1} in Fig. 2. As the cure reaction proceeded, the intensity of this peak decreases due to the opening of epoxy ring. This peak disappeared faster in the mixture of epoxy resin and GMAEV with a higher degree of carboxyl group substitution (DS = 2.0) resulting from the easy opening of epoxy ring under acidic conditions. However, this peak can be observed in the mixture of epoxy resin and GMAEV-0 when the mixture is heated to 170 °C.

Fig. 3 shows the shift of maximum hydroxyl peak of the mixture with increasing temperature. The maximum peak shifts to the higher frequencies with the higher DS in the mixture of epoxy resin and GMAEV. The difference of frequencies between DS = 0 and DS = 2.0 is almost 100 cm^{-1} resulting from proximity of the carboxylic groups to the hydroxyl groups. Peak shifting to higher frequencies of a mixture of epoxy resin and GMAEV with increasing temperature indicates that new ester or ether bonds are formed near hydroxyl groups due to the formation of crosslinks during the curing process.

3.1.3. *Epoxy conversion of epoxy resin and GMAEV mixture*

Fig. 4 shows the epoxy conversion in the mixture of epoxy resin and GMAEV when the mixture is heated from room temperature to 170 °C. The epoxy conversion increases continuously with increasing temperature and reaches 100% at 170 °C for the mixtures of epoxy resin and GMAEV-1.4 and GMAEV-2.0. For the mixture of epoxy resin and GMAEV-0, however, the epoxy conversion reaches 60% at 170 °C. These results implied that the epoxy ring opens easily in acidic condition resulting from the catalytic effect of carboxylic group.

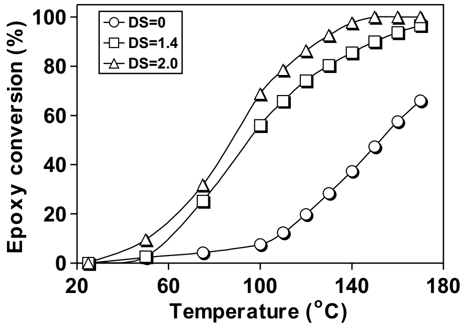


Fig. 4. Epoxy conversion in the mixture of epoxy resin and GMAEV with increasing temperature.

3.1.4. *Hydroxyl conversion of epoxy resin and GMAEV mixture*

Fig. 5 shows the hydroxyl conversion in the mixture of epoxy resin and GMAEV when the mixture is heated from room temperature to 170 °C. Because there is no carboxyl group in the mixture of epoxy resin and GMAEV-0, the epoxy ring opening is mainly caused by the reaction with the hydroxyl group of GMAEV-0. During the reaction, one hydroxyl group is generated with the opening of each epoxy ring as a result of the consumption of one hydroxyl group of GMAEV. Therefore, the change of the hydroxyl group concentration in the mixture is not substantial.

The decrease of hydroxyl conversion for the mixture of epoxy resin and GMAEV-0 below 100 °C can be explained that the amount of the hydroxyl groups generated from the epoxy rings is small and, the hence the hydroxyl groups of the glucose mainly initiated the cure process. Since the reactivity of the hydroxyl groups of glucose (primary alcohol) is somewhat higher than those generated from epoxy rings (secondary alcohol), the cure reaction proceeded better with free hydroxyl group of GMAEV-0 and that decreases the hydroxyl conversion. The slight increase of the hydroxyl conversion around 100 °C is attributed to the formation of free hydroxyl groups resulting from glucose degradation. Above 100 °C the generation and consumption of hydroxyl groups reaches a steady state due to the generation of one hydroxyl group with the opening of each epoxy ring as a result of the consumption of one hydroxyl group of GMAEV; therefore, the hydroxyl conversion remains constant. This result is consistent with the results of Oh et al. [14].

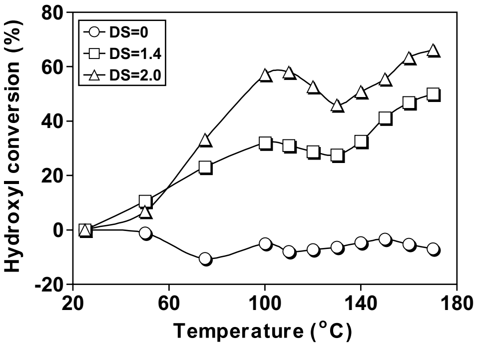


Fig. 5. Hydroxyl conversion in the mixture of epoxy resin and GMAEV with increasing temperature.

The data in Fig. 5 shows that curing of epoxy resin and GMAEV at DS equal to 1.4 increases the hydroxyl conversion from room temperature to 110 °C. Again this is a result of the easier epoxy ring opening and the formation of free hydroxyl groups resulting from glucose degradation in acidic condition. The esterification reaction between the carboxyl group and the hydroxyl group decreases the hydroxyl function in the range of 100–140 °C. Above 140 °C the esterification reaction between the carboxyl group and the epoxy group produces an increase of hydroxyl conversion. This results from the generation of hydroxyl group resulting from the opening of epoxy ring.

This pattern is more distinct in the mixture of epoxy resin and GMAEV-2.0. The hydroxyl conversion increases dramatically below 100 °C since production of the hydroxyl groups from the opening of epoxy ring and glucose degradation are easier in the acidic condition due to the catalytic effect of carboxylic group. The higher the hydroxyl group concentration is, the easier the esterification reaction between the carboxylic group and the hydroxyl group occurs. This produces a sharp decrease in hydroxyl conversion in the temperature range of 100–140 °C. The hydroxyl conversion increases again due to the epoxy ring opening that results from the esterification of carboxylic groups and epoxy. DSC and FTIR results show that the esterification reaction mainly occurs in the early stage of cure and then etherification proceeded after completion of the esterification. These results are comparable to the results of Park et al. [15].

3.1.5. Curing mechanisms of the epoxy resin and GMAEV mixture

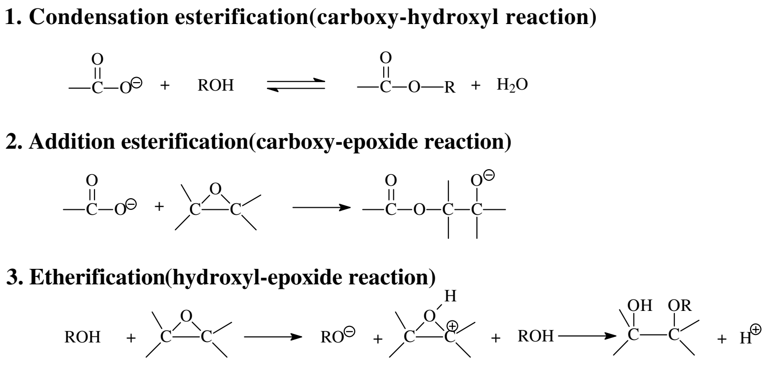
The reaction mechanisms between the epoxy group and, the carboxyl and hydroxyl groups have been studied and three different reactions—two esterifications and one etherification—are identified [9]. The results of DSC, FTIR and reaction mechanisms indicated that the curing process between the epoxy resin and GMAEV could be explained by condensation esterification (carboxyl–hydroxyl reaction), addition esterification (carboxyl–epoxy reaction) and etherification (hydroxyl–epoxy reaction) from lower temperature to higher temperature (Scheme 2).

3.2. Characterization of the cured matrix of epoxy resin and GMAEV

The mixture of epoxy resin and GMAEV was cured at 175 °C for 2 h and 200 °C for 2 h, consecutively. The properties for the cured matrix of epoxy resin and GMAEV with different degree of carboxyl group substitution were characterized and compared. The mixture of DGEBA and GMAEV-0 was not fully cured and was very brittle and sticky when the mixture was heated at 175 °C for 2 h and 200 °C for 2 h. Therefore, the mechanical properties of the mixture of epoxy resin and GMAEV-0 could not be investigated.

3.2.1. Thermal stability of the cured matrix of epoxy resin and GMAEV

Fig. 6 compares the thermal stability of the cured matrix of epoxy and GMAEV with different degrees of carboxyl group substitution. The cured matrices of



Scheme 2. Reaction mechanism between DGEBA and GMAEV.

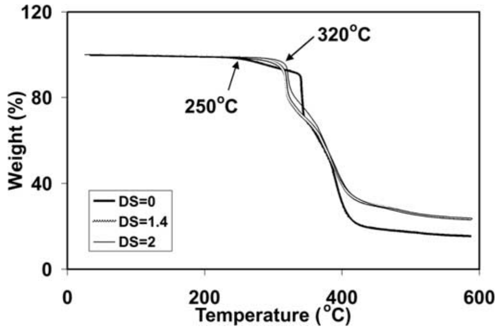


Fig. 6. TGA curves of the cured matrix for epoxy resin and GMAEV mixture.

epoxy resin and GMAEV-1.4 or GMAEV-2 show thermal stability up to 320 °C. However, the cured matrix of epoxy resin and GMAEV-0 starts to decomposes around 250 °C and shows a fast decomposition at 370 °C. The residues for the cured matrix of epoxy resin and GMAEV-0, GMAEV-1.4, GMAEV-2 after thermal decomposition over 500 °C are 15.4%, 23.3% and 23.8%, respectively. This means that the mixture of epoxy resin and GMAEV-0 could not be fully cured under the curing condition of 175 °C for 2 h and 200 °C for 2 h.

3.2.2. *Surface analysis of cured matrix of epoxy resin and GMAEV*

Surface analysis of the cured matrix of epoxy resin and GMAEV with different degrees of carboxyl group substitution is compared in Table 2. The atomic ratio of oxygen to carbon increased for the cured matrix of epoxy resin and GMAEV with the higher degree of carboxyl group substitution. Table 3 shows the changes of the carbon 1s and oxygen 1s of the cured matrix. The carbon 1s spectra is deconvoluted to four peaks that are assigned to –C–C*–C– (284.6 eV), –C*–O–H, –C*–O–C– (286.1 eV), –O–C*–O–, –C*(=O)– (287.6 eV) and –O–C*(=O)– (289.0 eV), respectively. The oxygen curve is deconvoluted to two peaks that are assigned –O–C–O*– (530.0 eV) and –C–O*H (532.0 eV).

Table 2
Atomic ratio of the cured matrix

Samples	[C] %	[O] %	[O]/[C]
GMAEV-1.4	75.7	24.3	0.322
GMAEV-2	74.1	25.9	0.349

Generally, C 1s and O 1s concentrations are similar in the cured matrix of epoxy resin and GMAEV-1.4 or GMAEV-2. Table 3 shows that C 1s concentration of the ether bonds increase with the cured matrix of epoxy resin and GMAEV-1.4 compared to the cured matrix of epoxy resin and GMAEV-2. On the other hand, the free hydroxyl groups are more abundant in the cured matrix of epoxy resin and GMAEV-2. From this result the curing of epoxy resin and GMAEV-1.4 proceeds to the formation of ether bonds resulting in compact crosslinks comparing to the formation of bulky crosslinks in the cured matrix of epoxy resin and GMAEV-2.

3.2.3. *Density of cured matrix*

Fig. 7 shows the density of the cured matrix of epoxy resin and GMAEV-1.4 or GMAEV-2 with different curing conditions. The cured matrix of epoxy resin and GMAEV-1.4 shows a higher density compared to that of the epoxy resin and GMAEV-2 under all curing conditions. This indicates that the curing process of epoxy resin and GMAEV with a higher degree of carboxyl group produces bulky crosslinks due to the formation of crosslinks between carboxyl groups or carboxylic and hydroxyl groups. However, the curing between epoxy resin and GMAEV-1.4 produces compact crosslinks like ether bonds in the network of the cured matrix.

The density of the cured matrix increases with increases in the curing temperature. This can be explained since the compact crosslinks such as ether bond forms easily with increasing temperature.

3.2.4. *Glass transition temperature and storage modulus of cured matrix of epoxy resin and GMAEV*

The glass transition temperature (T_g) and the storage modulus of the cured matrix of epoxy resin and GMAEV-1.4 or GMAEV-2 are compared in Fig. 8. The storage modulus of the cured matrix is not different much between GMAEV-1.4 and GMAEV-2; however, the T_g of the cured matrix of epoxy resin and GMAEV-2 decreased 10 °C. The decrease in T_g can be explained by considering that the cured matrix of epoxy resin and GMAEV-1.4 contains a higher concentration of dense bonds such as ether bonds in the crosslinks. The bulky

Table 3
Carbon 1s and oxygen 1s of the cured matrix

Samples	C1s concentration (%)				O1s concentration (%)	
	–C–C*–C–	–C*–O–H, –C–C*–O–	–O–C*–O–, C*(=O)–	–O–C*(=O)–C–	–C–O*–C–	C–O*H
GMAEV-1.4	38.0	24.2	9.6	3.8	11.0	13.7
GMAEV-2	38.4	25.8	6.5	3.4	10.0	15.8

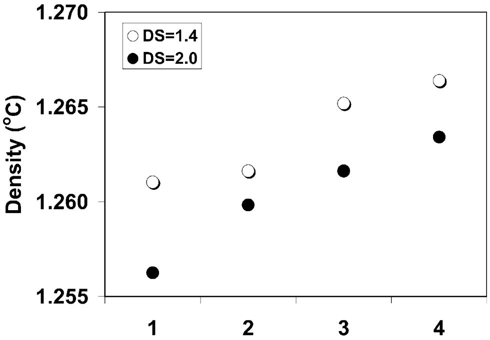


Fig. 7. Density of the cured matrix for DGEBA and GMAEV mixture with different curing conditions. (1) 175 °C for 2 h and 200 °C for 2 h, (2) 175 °C for 2 h and 220 °C for 2 h (3) 175 °C for 2 h and 240 °C for 2 h, (4) 175 °C for 2 h and 260 °C for 2 h.

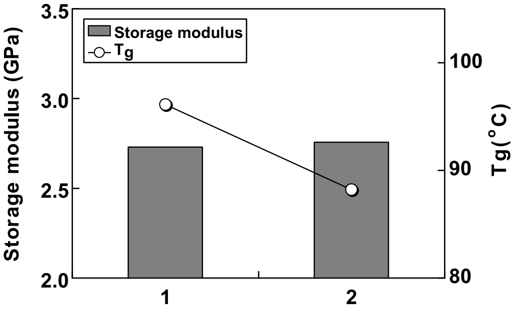


Fig. 8. Glass transition temperature of the cured matrix for epoxy resin and GMAEV mixture at 175 °C for 2 h and 200 °C for 2 h. (1) epoxy resin and GMAEV-1.4, (2) epoxy resin and GMAEV-2.

crosslinks of the epoxy resin and GMAEV-2.0 compared to the tight crosslinks of epoxy resin and GMAEV-1.4 gives flexibility to the chains, resulting in the T_g decrease.

4. Conclusion

An ecofriendly polymer matrix of epoxy resin and GMAEV has been investigated as a candidate matrix for biocomposites. Curing characteristics of epoxy resin and carboxyl functionalized glucose resin GMAEV have been studied by DSC and FTIR methods. The curing mechanism of the epoxy resin and GMAEV is identified as esterification and etherification reactions of the hydroxyl and carboxyl functionalities of GMAEV with the epoxy groups of the epoxy resin. The results showed that esterification reaction occurs in the early stage of cure and then etherification proceeded after completion of the esterification.

The cured matrix containing 50 wt.% of GMAEV with different degrees of carboxylic group substitution was prepared and characterized. The cured matrix with a higher degree of carboxyl group shows an increase in the atomic ratio of oxygen to carbon of the cured matrix and a decrease of density resulting from the bulky crosslinks. The cured matrix of epoxy resin and GMAEV showed a remarkable thermal stability up to 300 °C. The average glass transition temperature and storage modulus of the matrix with epoxy resin and GMAEV were as high as 95 °C and 2700 MPa, respectively. This study illustrated the potential for development of environmentally friendly polymer matrix based on epoxy resin and GMAEV for biocomposites. Biocomposites made from this matrix material could be used in durable goods applications such as those found in the automobile and construction industries.

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