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ORIGINAL PAPER

Curing Characteristics and Thermal Properties of Epoxidized Soybean Oil Based Thermosetting Resin

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Abstract Epoxidized soybean oil (ESO) was thermally cured using methylhexahydrophthalic anhydride (MHHPA) curing agent in the presence of 2-ethyl-4-methylimidazole (EMI) catalyst. The curing characteristics of ESO/MHHPA/EMI systems were characterized using Fourier transform infrared spectroscopy (FTIR), a dynamic mechanical analyzer (DMA) and a differential scanning calorimeter (DSC). FTIR spectra showed that the polyesterification rate in ESO/MHHPA/EMI systems increased with increasing of the catalyst concentration. DSC thermograms indicated that EMI-catalyzed ESO/MHHPA systems experienced enthalpy relaxation at low EMI concentration whereas the extent decreased with increasing of the EMI concentration. There is a direct relationship between the degree of conversion and crosslink density of the thermal cured ESO/MHHPA/EMI systems with EMI concentration. The curing characteristics of thermal curable ESO thermosetting resins were found to have influence on the thermal properties of the ESO systems. It was determined that the glass transition temperature (T_g) and storage modulus (E') of cured ESO increased with increasing the EMI concentration whereas the damping properties of the ESO/MHHPA/EMI systems exhibited the reverse trend. It was found that the thermally curable ESO thermosetting resins experienced a two-stage thermal decomposition process.

Keywords Oleochemistry · Biobased products · Thermal analysis · Epoxidized soybean oil · Curing characteristics · Thermosetting resins

Introduction

In recent years, attention has been paid to develop biopolymers from vegetable oil derivatives. This is attributed to the environmental friendliness and cost effectiveness of vegetable oils. Epoxidized vegetable oil (EVO) have been predominantly used to replace and toughen fossil-fuel based polymers, for example, cycloaliphatic epoxy/epoxidized palm oil (EPO) blends [1], diglycidyl ether of bisphenol-A (DGEBA) resin/epoxidized soybean oil (ESO) blends [2], and epoxy blends/EPO system [3].

In the published literature, there are several curing techniques and approaches used to synthesize epoxidized vegetable oil based thermosetting materials, e.g. thermal curing of epoxidized linseed oil (ELO) under the influence of catalysts and anhydride hardeners [4], thermal curing of EVO and *N*-benzylquinoxalinium hexafluoroantimonate (BQH) thermal latent initiator [5], thermal curing of ESO with maleinated linseed oil [6], thermal curing of ESO under the catalytic reaction of a pyridine catalyst [7], ultraviolet (UV) curing of EVO/cationic photoinitiators in the presence of substituted benzyl alcohol [8], UV curing of epoxidized sunflower oil using hybrid photoinitiators [9] and UV induced cationic photopolymerization of naturally occurring epoxidized triglyceride oils in the presence of diaryliodonium salt photoinitiators [10].

Although the EVO based thermosetting materials are more environmental friendly, they have some limitation, such as long curing schedules, high curing temperature and poor thermo-physical properties. To overcome some of

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these problems, our aim was to synthesize a thermal curable ESO thermosetting resin in the presence of the 2-ethyl-4-methylimidazole (EMI) catalyst. EMI was selected to be used as the catalyst in this study since this type of nucleophilic catalyst exhibits an excellent balance of pot life and is more efficient and fast curing than that of tertiary amines. It is hypothesized that the ESO thermosetting resin could be prepared using a shorter curing schedule and a lower curing temperature. The thermal properties and curing characteristics of the ESO thermoset will be correlated and a plausible mechanism will be proposed.

Experimental

Materials

Epoxidized soybean oil (ESO) with 6.1 wt% epoxy oxirane content and an average molecular weight of about 950 g/mol was purchased from the Shangdong Longkou Longda Chemical Industry Co. Ltd., China. The methylhexahydrophthalic anhydride (MHHPA) curing agent was bought from CAPE Technology Sdn Bhd., Malaysia. The 2-ethyl-4-methylimidazole (EMI) catalyst was supplied by Sigma-Aldrich, USA.

Preparation of Thermally Curable ESO Thermosetting Resin

Methylhexahydrophthalic anhydride was pre-mixed with EMI catalyst at a predetermined ratio. The ESO and the MHHPA/EMI mixture were then mixed at room temperature and stirred mechanically. The mixture was then poured into the cavities of the mold and subjected to a thermal curing process in an oven at 140 °C for 3 h.

Thermal Characterization of ESO Thermosetting Resin

The curing profile of ESO thermosetting resin was examined using a DSC Diamond Analyzer (Perkin Elmer, USA). Approximately 20 mg of the sample was placed in the DSC aluminium pans, followed by thermal scanning from 30 to 300 °C at a heating rate of 10 °C/min, in a nitrogen gas atmosphere. The onset curing temperature (T_{onset}), the temperature where maximum cross-linking reaction takes place (T_{peak}) and the total heat released during curing reaction (ΔH) of the thermally cured ESO thermosetting resin were determined. The dynamic mechanical properties of cured ESO thermosetting resin were determined using DMA 8000 (Perkin Elmer, USA). The specimen with dimensions of 25 mm × 10 mm × 2 mm was heated from −100 to 200 °C at a heating rate of 2 °C/min in nitrogen atmosphere. The specimen held in a single cantilever mode was fixed at one end and the other end was vibrated by the bending stress at a frequency of 1 Hz with a displacement of 0.05 mm. The glass transition temperature (T_g), storage modulus (E') and damping properties ($\tan\delta$) of the cured ESO were studied with DMA. The thermal stability of the thermal cured ESO thermoset was characterized using TGA Pyris 6 (Perkin Elmer, USA). Approximately 5 mg of the specimen was heated from room temperature to 600 °C at a heating rate of 10 °C/min under a nitrogen gas atmosphere.

Curing Characteristics

The curing characteristics of ESO/MHHPA/EMI thermosetting resins which had been thermally cured for 1, 2 and, 3 h were determined using Fourier transform infrared ray spectroscopy (FTIR, Perkin Elmer, USA). The FTIR spectra of the thermal curable ESO specimen from the wavelength of 4,000–550 cm^{-1} was recorded as the infrared radiation was transmitted through the specimen. The carbonyl index (C.I.) values of the specimens were calculated based on the ratio of absorbance (A) at two different wave-numbers as shown in Eq. 1.

$$\text{C.I.} = \frac{A_{1700}}{A_{1456}} \tag{1}$$

where A_{1700} represents the absorbance band at 1,700 cm^{-1} due to the presence of a carbonyl stretch of the aromatic acid whereas A_{1456} represents the band at 1,456 cm^{-1} corresponding to the absorbance from the presence of a methyl group, which is taken as reference band.

The degree of conversion of ESO thermosetting resin was determined using a DSC Diamond Analyzer (Perkin Elmer) and calculated based on Eq. 2 [11]. The crosslink density (v_c) and molecular weight between cross-linking (M_c) of the cured ESO were determined using DMA 8000 (Perkin Elmer) and calculated based on Eq. 3 [12] and Eq. 4 [4], respectively.

$$\alpha = \frac{\Delta H_c - \Delta H_r}{\Delta H_c} \times 100\% \tag{2}$$

$$v_c = \frac{E'}{3RT} \tag{3}$$

$$M_c = \frac{d}{v_c} \tag{4}$$

where α is the degree of conversion, ΔH_c is the total exothermic heat generated for a fully cured system and ΔH_r is the total residual exothermic heat generated during a specified period of time. v_c is the crosslink density for epoxy network, E' is the storage modulus of the thermoset in the rubbery plateau region at $T_g + 40$ °C, R is the gas constant, T is the absolute temperature, d is the density

(1.1 g/cm^3) and M_c is the molecular weight between crosslinks.

Results and Discussion

Curing Characteristics of ESO Thermosetting Resin

FTIR Characterization

Figure 1 shows the FTIR spectra of the EMI catalyst, the MHHPA curing agent and the mixture of MHHPA/EMI. One can see that the FTIR spectrum of MHHPA/EMI mixture consists of a new 1,700 cm^{-1} shoulder peak. The appearance of this new peak is mainly associated with the carbonyl stretch (C=O) of the aromatic acid, which indicates the asymmetric cleavage of the MHHPA functional group by the EMI to form the zwitterion (internal salt betaine). The amount of the carbonyl group present and the extent of the anhydride ring opening are estimated according to the carbonyl index value obtained from the FTIR study (c.f. Table 1). It is proposed that the ring opening of the MHHPA curing agent by the EMI catalyst involves the S_N2 reaction, in which a lone electron pair in EMI acting as a nucleophile attacks the electron deficient electrophilic carbon center in anhydride, removes the electronegative oxygen leaving group and takes its place. Though the exact absorbance band represents the zwitterion is undetected from FTIR spectrum, the intensity reduction of the infrared absorbance bands that appear at approximately 1,856, 1,775, and 887 cm^{-1} in FTIR spectrum is a good indicator that supports the phenomenon of anhydride ring opening by the EMI catalyst. This is due to the fact that they are the characteristic bands for the conjugated cyclic anhydride which can be assigned to the C=O and C–O stretches. Considering these phenomena, a plausible hypothesis that zwitterions are generated during the pre-mixed reaction could be made.

It is clear that the carbonyl stretch, corresponding to the aromatic acid, increases with increases in the EMI catalyst concentration in the MHHPA/EMI mixture. This can be evidenced by the increment in the carbonyl index as shown in Table 1. While, the absorbance assignable to the C=O

Table 1 Curing characteristics of ESO thermosetting resins

Curing characteristics	ES_0.3I	ES_0.6I	ES_0.8I
Carbonyl index[a]			
Pre-mix	0.64	0.87	0.89
Curing			
1 h	0.66	1.78	1.83
2 h	2.43	2.80	3.06
3 h	2.91	3.39	3.60
Degree of conversion[b] (%)	85.2	90.8	93.6
Crosslink density[c] (10^{-3} mol/cm^3)	0.105	0.170	0.208
M_c^c (g/mol)	10,476	6,471	5,289
Gel content (wt%)	93.0	94.2	95.9

[a] Calculated from FTIR analysis

[b] Calculated from DSC analysis

[c] Calculated from DMA analysis

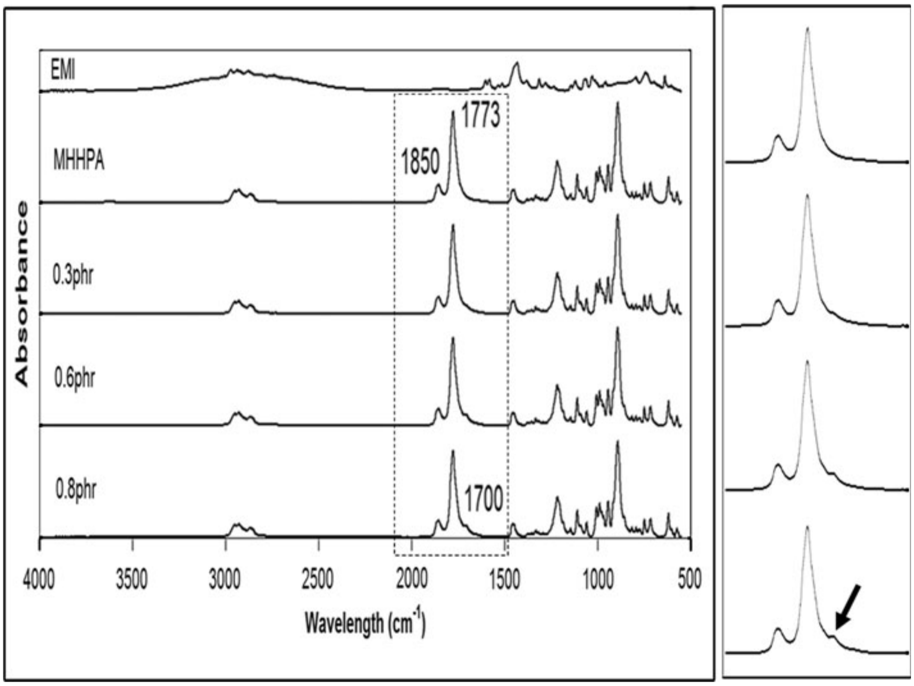

Fig. 1 FTIR spectra representing the ring opening of MHHPA curing agent with an EMI catalyst (Note: the *arrow* shows the 1,700 cm^{-1} shoulder peak)

and C–O stretches of the MHHPA curing agent show the reverse trend. This is a phenomenon that suggests the increased ring opening reaction between EMI catalyst and MHHPA curing agent as the former shows a greater ability to facilitate the anhydride ring opening at higher EMI concentration. However, only a low conversion of the zwitterions is achieved during the pre-mixed reaction. It has been experimentally determined in this study that no anhydride ring opening is observed and detected at low levels of EMI concentration (<0.3 phr). According to Kolar and Svitilova [13], the presence of *N*,*N*-dimethyl aniline catalyst speeds up the DGEBA/maleic anhydride cross-linking reaction by significantly lowering about 40% activation energy of the catalyzed chemical reaction.

During the heating reaction of ESO/MHHPA/EMI mixture at 140 °C in the oven, the zwitterions tend to react with the epoxy rings on the ESO backbone chains and form the alkoxide intermediates. The intermediates will then cleave the other MHHPA curing agents to yield carboxylate anions. The carboxylate anions will chemically react with the ESO monomers to generate the reaction intermediate products. After a 3-h curing reaction, the polyesterification reaction in the ESO/MHHPA/EMI mixture is complete. At this stage, the thermally cured ESO thermoset will consist preferably of polyester-type linkages. To support this curing mechanism and transformation, the curing characteristics of thermal curable ESO were evaluated using a FTIR study (Fig. 2).

From Fig. 2, it can be observed that the intensity of the absorbance bands corresponding to the C–O and C=O stretches of acid anhydride was further reduced with increases in the curing reaction time for the ESO/MHHPA/EMI. Additionally, it can be clearly seen that the stretching vibrations of the C–O–C and C–C–O functional groups in MHHPA appear in the range of 1,300–1,000 cm^{-1} and disappear gradually with curing time. The reduction in intensity of these absorbance bands indicates the polyesterification reaction of the MHHPA curing agent with alkoxide. The carboxylate anion derived from the chemical reaction eventually reacts with the ESO monomers to form the reaction intermediate products. The emergence of absorbance bands at 1,695 and 1,161 cm^{-1} which correspond to the C=O and O–C–C vibrations of the ester functional groups with curing time also indicates the polyesterification process in the ESO/MHHPA/EMI mixture. This is due to the fact that these absorbance bands are the representative bands for all esters. Also, as shown in Fig. 2, it is found that the polyesterification reaction of ESO/MHHPA/EMI mixture proceeds in a relatively slow manner after 2 h of thermal curing. This event takes place as the overall catalytic reaction in ESO system begins to change from kinetic to diffusion-controlled. The curing process in bisphenol-S epoxy resin/phthalic anhydride system changing from being kinetically controlled to diffusion controlled was also reported by Li et al. [14]. According to the information obtained from the FTIR spectra, the curing mechanism of thermally cured ESO thermosetting resin is proposed. Figure 3 shows the proposed mechanism for the ESO/MHHPA/EMI system.

Furthermore, the effect of the EMI catalyst concentration for the ESO/MHHPA/EMI systems is reported in Fig. 2. An intensity reduction in the representative bands

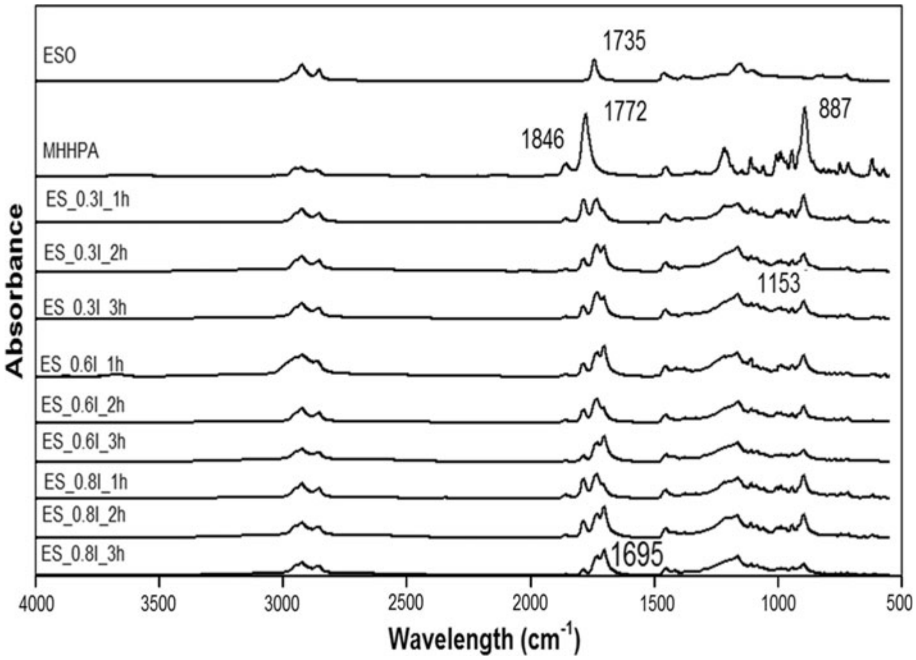

Fig. 2 FTIR spectra representing the curing characteristics of a ESO/MHHPA/EMI mixture

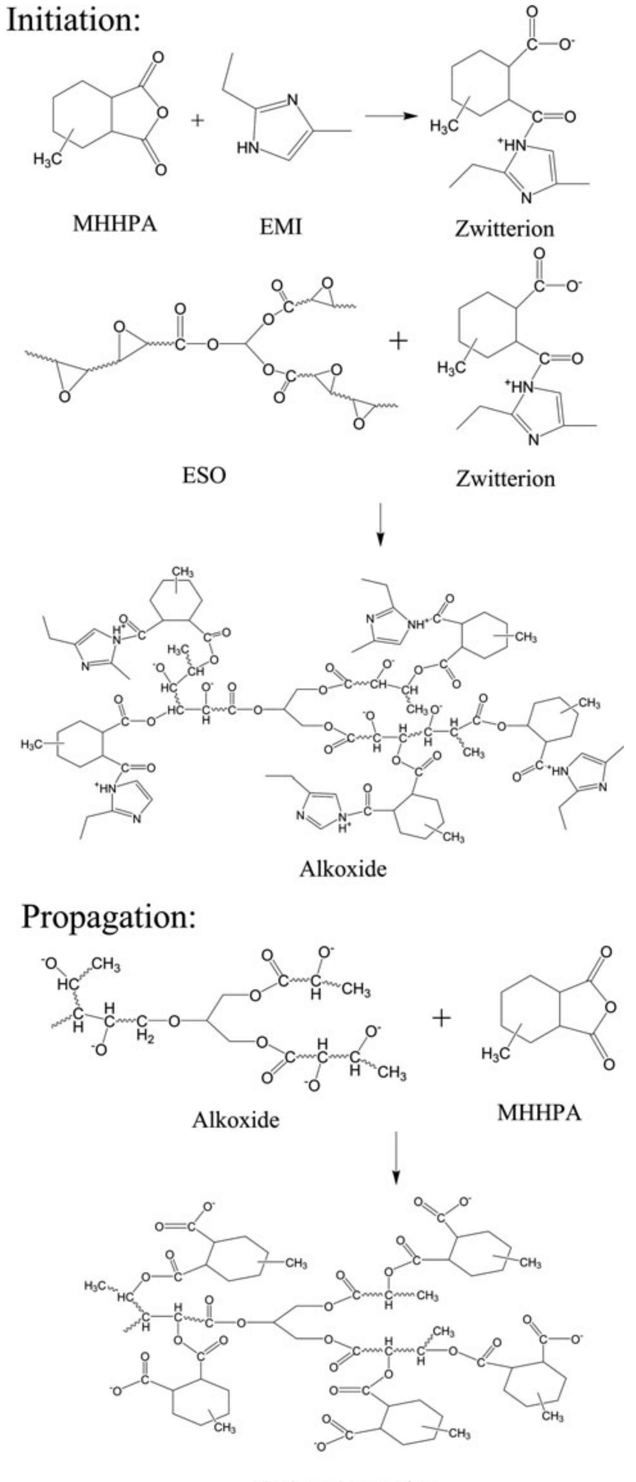

Fig. 3 Curing mechanism of thermally curable ESO thermosetting resins

for the MHHPA cross-linking agent and an increment in the absorbance bands intensities for the ester are observed when increasing the EMI catalyst concentration from 0.3 to 0.8 phr. These results indicate that rate of polyesterification is higher in cured ESO containing a higher EMI catalyst concentration. Lower levels of EMI catalyst concentration (<0.3 phr) were also investigated in this study, perhaps even a 0-level EMI experiment. However, it can be seen that the polyesterification reaction of the ESO/MHHPA/EMI system is highly unfavorable and the ESO mixture is incapable of being cured completely at a low level of EMI concentration. One possible explanation could be linked to a very limited or even complete lack of chemical reaction between the ESO monomers and the MHHPA curing agents in the absence of a catalyst.

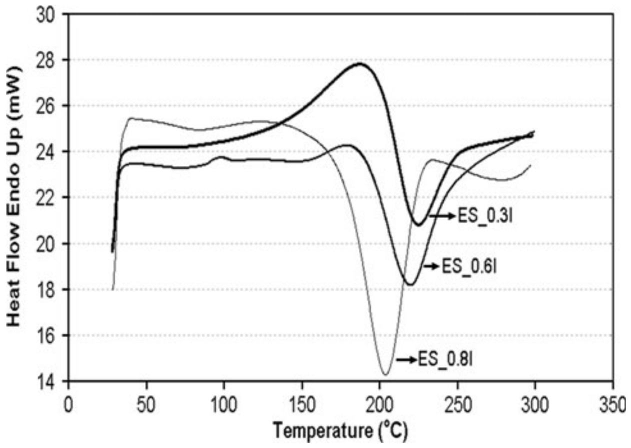

Fig. 4 DSC heating thermograms of ESO thermosetting resins

DSC Characterization

Figure 4 shows the DSC heating thermograms of the non-isothermal curing characteristics of the EMI-catalyzed ESO/MHHPA system. It can be observed that an exothermic peak representing the epoxy curing reaction is detected on the DSC heating curves. The enthalpy of epoxy/anhydride polymerization could be determined by integrating the exothermic peak. It is also experimental proven that ESO/MHHPA systems catalyzed with higher EMI concentration exhibits higher ΔH values. The differences in enthalpies of polymerization are mainly attributed to the extent of the conversion of ESO monomers to ESO thermosets in the presence of the MHHPA curing agent. This finding indicates that the higher the catalyst concentration, the greater the extent of polymerization of ESO/MHHPA and the higher degree of cross-linking formation seem to be. One possible explanation could be associated with the fact that a higher conversion of zwitterions is achieved during the pre-mixed reaction to initiate the polymerization reaction of ESO/MHHPA. From the DSC thermograms, second exotherm peaks or shoulders after the T_{peak} are not observable; this may give us a hint that the homopolymerization of epoxy monomers does not take place.

According to Boquillon and Fringant [4], a second shoulder exotherm peak after the main exotherm peak appearing at a lower temperature could be attributed to the epoxy homopolymerization. Hence, it can be concluded that ESO/MHHPA polymerization is the only chemical reaction occurring during the polyesterification process and the crosslinked ESO thermosetting resin does not contain any epoxy homopolymer.

It can also be seen that the T_{onset} and T_{peak} (c.f. Table 2) of the EMI-catalyzed ESO systems shift to a lower temperature as the EMI concentration is increased from 0.3 to 0.8 phr. The shifts of DSC heating thermograms to lower temperatures are mainly due to the increase in the crosslinking reaction rate. According to Liu et al. [15], increasing the catalyst concentration in epoxy-phenol/montmorillonite nanocomposites will shift the T_{onset} and T_{peak} to much lower temperatures. Furthermore, as shown in Fig. 4, thermally curable ESO experiences the enthalpy relaxation phenomenon at low EMI concentration and this progressively reduces at higher catalyst concentrations. The reduction in enthalpy relaxation is strongly believed to be related to the increase in cross-link density resulting from an increase in the extent of polymerization of ESO/MHHPA. Shin et al. [16, 17] suggested that the restriction of enthalpy relaxation is directly related to an increase in crosslink density and activation energy for the enthalpy relaxation.

The degree of conversion of the thermal curable ESO thermosetting resin is determined and calculated using Eq. 2. The influence of the EMI catalyst concentration on the degree of conversion of ESO/MHHPA/EMI systems is summarized in Table 1. An increment in the degree of conversion from 85.2 to 93.6% is observed when the EMI catalyst concentration is increased from 0.3 to 0.8 phr. These results indicate that the efficiency of an EMI catalyst to facilitate the ring opening of the MHHPA curing agent and create reactive sites on the anhydride (zwitterions) increases with EMI concentration. The increased number of zwitterions formed favors the polyesterification process in the ESO/MHHPA/EMI system and accounts for the increment in degree of conversion. This finding is in good agreement with the study on curing kinetics of bisphenol-F using benzyl dimethyl amine as the catalyst reported by Shokrolahi et al. [18] who found that the positive relationship between the catalyst concentration and the extent of conversion rate.

Table 2 Thermal properties of ESO thermosetting resins

Thermal properties	ESO thermosetting resins		
	ES_0.3I	ES_0.6I	ES_0.8I
T^{a}_{onset} (°C)	211.0	192.0	151.0
T^{a}_{peak} (°C)	226.0	220.0	205.0
T^{b}_{o1} (°C)	208.0	212.0	206.0
T^{b}_{o2} (°C)	361.0	359.0	358.0
T^{b}_{d} (°C)	453.0	463.0	462.0
T^{c}_{g} (°C)	49.1	52.0	60.8

[a] Detected from DSC

[b] Detected from TGA

[c] Detected from DMA

DMA Characterization

The crosslink density of the thermally cured ESO thermosetting resins determined and calculated based on Eq. 3 are reported in Table 1. An increase in the crosslink density from about 0.105×10^{-3} to 0.208×10^{-3} mol/cm^3 is obtained when the EMI concentration is increased from 0.3 to 0.8 phr. Crosslink densities obtained for the ESO/MHHPA/EMI systems are found to be lower than those of epoxidized vegetable oils/petrochemical-based epoxy blends [19], but close to those of triethylamine catalyzed ESO/anhydride systems [12]. A higher EMI concentration favors the ring opening of the anhydride functional group and promotes a higher number of reactive sites on the MHHPA curing agent. This will eventually result in an increase in the catalyzed reaction rate, extent of conversion, as well as crosslink density. It has been determined that there is a direct relationship between the degree of conversion and crosslink density of the ESO thermosetting resins with EMI concentration. Figure 5 further illustrates a linear relationship between the degree of conversion and crosslink density. This observation seems to contradict the previous finding reported by Boquillon and Fringant [4] who stated that the crosslink density decreases with the catalyst concentration as a result of the diffusional restrictions of the reagents at high catalyst concentration.

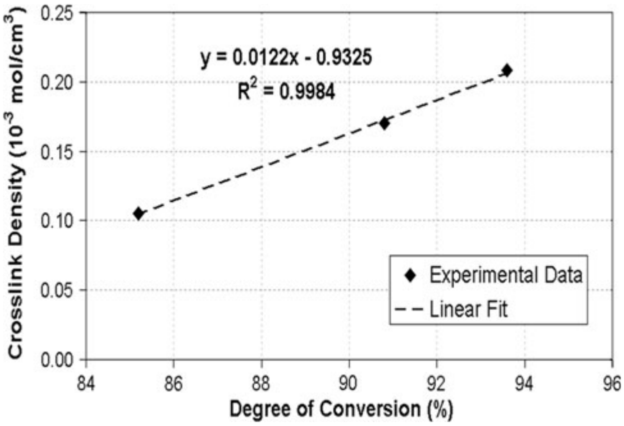

Fig. 5 Relationship between crosslink density and degree of conversion for ESO thermosetting resins

One possible explanation could be linked to the difference in the polymerization reaction rate in both systems. The relatively high 2-methylimidazole concentration in the ELO/tetrahydrophthalic anhydride system [4] gives rise to a fast gelling of the system. Consequently, the diffusion of the reagents is relatively low and results in a lower extent of conversion. While, in our work, the ESO/MHHPA system catalyzed with relatively low EMI catalyst concentration, the diffusion restriction associated with vitrification is less hindered. Hence, the extent of conversion and consequently crosslink density increase with the catalyst concentration.

Thermal Properties of ESO Thermosetting Resin

Dynamic Mechanical Analysis

The storage modulus (E') and tan δ of cured ESO as a function of temperature is shown in Fig. 6. As can be seen in Fig. 6, the E'–T curve shifts to a higher temperature as the EMI concentration is increased from 0.3 to 0.8 phr. The increment in E' as a function of the EMI concentration is attributed to the increase in crosslink density and the reduction in molecular weight between crosslinks (M_c) of the cured ESO. The reduction of M_c (c.f. Table 1) from about 10,476 to 5,288 g/mol for the 0.3–0.8 phr-EMI catalyzed ESO/MHHPA systems indicates a reduction in the chain's mobility and consequently an increase in stiffness and storage modulus. This is in line with the finding reported by Jin and Park [2] who found that the storage modulus of DGEBA/ESO blends was lower with increasing molecular weight between crosslinks.

From Fig. 6, it can be seen that the tan δ–T curve shifts to lower temperature as the EMI concentration is reduced. This can be ascribed to the depression of the glass transition temperature (T_g). It is noteworthy that the intensity of the tan δ peak increases with increasing the EMI concentration (see Fig. 6). In addition, the intensity of the tan δ peak for ES_0.3I (low concentration of EMI) is relatively broader and lower compared to that of ES_0.8I (high concentration of EMI). Commonly, one may find that the molecular motions become more restricted and the amount of energy that can be dissipated throughout the polymer decreases as the crosslink density increases, and subsequently, the tan δ peak height decreases. However, in our finding, the opposite trend is observed. According to Asif et al. [20], the lowering and broadening of tan δ peak intensity is presumable due to the heterogeneity of the cross-linked network structure and a broad distribution of chain segment mobility. A similar finding to the increase in tan δ peak intensity with crosslinking was also reported by Li et al. [21] and in our previous work [19].

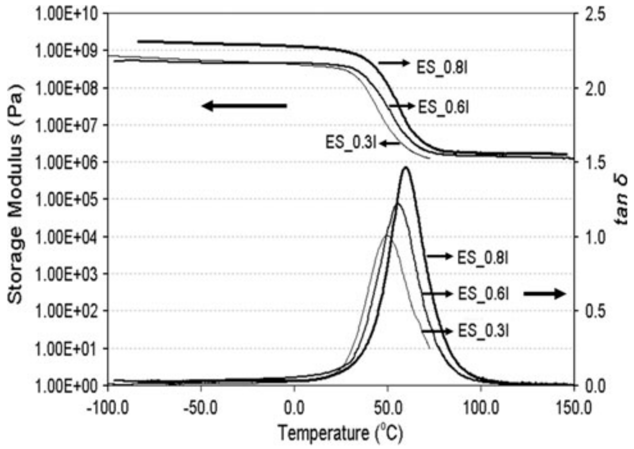

Fig. 6 Effect of EMI concentration on the storage modulus (E') and tan δ of the cured ESO thermosetting resins

Figure 6 shows the effect of EMI concentration on the glass transition temperature of thermally curable ESO thermosets. The T_g values obtained for the ESO/MHHPA/EMI systems are found to be comparative with or even higher than those found for existing epoxy resins based on ESO. An important increment in T_g from 49.1 to 60.8 °C is detected when increasing the EMI concentration from 0.3 to 0.8 phr. These changes in T_g values could be related to the increase in crosslink density of the curable ESO thermosets and the reduced amounts of unreacted ESO in the specimens. The increase in catalyst concentration causes an increase in crosslink density and a reduction in the degree of freedom for chain movements and internal rotation in the network structure. This explains the higher T_g value found. Also, the increase in catalyst concentration is expected to induce a more complete curing reaction in which most of the unreacted monomers are built into three-dimensional infusible cross-linked network structures of cured ESO thermosetting resins. It can be seen in Table 1 that an increase in EMI concentration leads to an increase in the amount of gel content. In other words, the amount of unreacted monomers was reduced accordingly. The presence of unreacted monomers in the ESO would plasticize the sample dramatically and lower the T_g. This is due to the fact that the plasticizing effect of unreacted monomers will improve flexibility and the degree of freedom for movement of the molecular chains in the network structure. Consequently, the T_g value detected is lower.

Thermogravimetric Analysis

Thermogravimetry analysis (TGA) was used in this study to determine the thermal stability of thermally curable ESO thermosetting resin. Figure 7 presents the TGA/DTG curves as a function of temperature for the cured ESO and Table 2 summarizes the TGA results [i.e., onset decomposition temperature (T_o) and the maximum decomposition

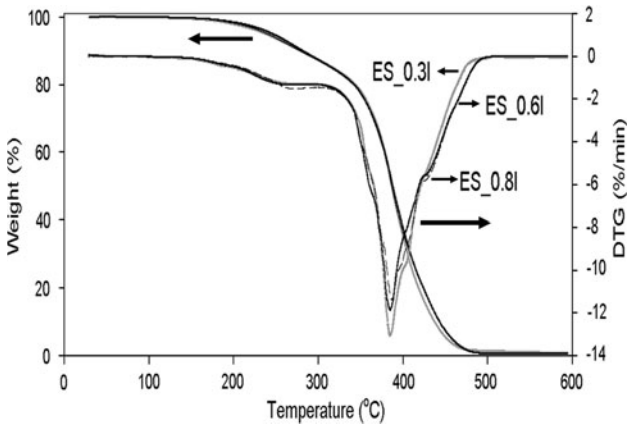

Fig. 7 TGA and DTG curves of ESO thermosetting resins

temperature (T_d)] for the cured ESO system. It can be clearly noticed in Fig. 7 that the cured ESO thermosetting resins experience two-stage thermal decompositions. The EMI-catalyzed system passes through T_{o1} at nearly 200 °C, T_{o2} at 350 °C and T_d at approximately 450 °C. With approximately 25 wt% of the thermally cured ESO decomposing during the first stage of decomposition and 71 wt% is lost during the second stage of decomposition. The remaining 4 wt% of the cured ESO residuals are decomposed completely as the heating temperature is further increased up to 500 °C.

The first stage of decomposition is believed to be due to the decomposition of the low-molecular-weight components such as the MHHPA curing agent or the EMI catalyst. It is believed that, generally, the low-molecular-weight compounds will show lower thermal stability. The second stage of major decomposition which takes place in the temperature range of 350–400 °C can be attributed to the thermal degradation of the relatively stable ESO component. A similar thermal decomposition behavior was reported by Gerbase et al. [12] for a ESO/dodecenylsuccinic anhydride/triethylamine mixture, which presented two different stages of thermal decomposition. Referring to Fig. 7, the first stage effect of the thermally cured ESO systems with different EMI concentration are found to be similar among each other. This suggests that increasing the catalyst concentration in the EMI-catalyzed ESO system does not greatly influence the initial decomposition of cured ESO thermosetting resins. However, the TGA curves diverge before the final decomposition. The T_d of the ES_0.6I and ES_0.8I are relatively higher than the ES_0.3I. These findings are strongly believed to be attributed to the increase in the degree of cross-linking as the catalyst concentration is increased. In general, a highly cross-linked network structure commonly exhibits greater thermal stability. In this connection, Yang et al. [22] who studied poly(epoxy-imide) crosslinked networks also reported that epoxy systems with higher crosslinking are more thermally stable than those with lower crosslinking at higher temperature. In addition, the relatively lower T_d value of ES_0.3I could be caused by the unreacted monomers present in the crosslinked network. Moreover, an increase in the number of unreacted monomers will cause an increase in free volume of the materials and result in reduced thermal stability [19, 23].

Conclusion

Based on this work devoted to studying the effect of 2-Ethyl-4-methylimidazole catalyst on the curing characteristics and thermal properties of thermal curable ESO thermosetting resins, the following conclusions can be drawn: Ring opening of MHHPA by EMI involves the S_N2 reaction. The rate of polyesterification is higher for cured ESO systems with higher EMI concentrations. Degrees of conversion and crosslink densities of the thermally cured ESO with higher EMI concentrations were found to be higher than that of systems with low catalyst concentrations. From the DMA study, it was found that cured ESO thermosetting resin catalyzed with a higher EMI concentration possessed a higher glass transition temperature (T_g) and storage modulus (E') but a lower tan δ. A cured ESO thermoset experienced two-stage thermal decomposition on being heated up to 600 °C.

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