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Thermal properties of anhydride-cured bio-based epoxy blends

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Abstract Epoxidized palm oil (EPO) (0–12 wt%) was added into petrochemical-based epoxy blends (diglycidyl ether of bisphenol-A (DGEBA)/cycloaliphatic epoxide resin/epoxy novolac resin) to develop a thermal curable bio-based epoxy system. The thermal behaviors of the EPO, epoxy blends (EB), and bio-based epoxy blends (EB/EPO) were characterized using differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMT) and thermo-mechanical analysis (TM). The glass transition temperature (T_g) and storage modulus (E') of the EB/EPO system was reduced with the increasing of the EPO loading. This is attributed to the plasticizing effect of the EPO. It was found that epoxy blends with higher loading of EPO possessed higher coefficient of thermal expansion (CTE) and tanδ value. This is due to the increase of the free volume and chain flexibility in the three-dimensional network of the epoxy blends. The internal thermal stresses of the EB/EPO were decreased as the increasing loading of EPO, owing to the reduction of crosslink density, modulus of elasticity, and T_g in the epoxy blends.

Keywords Epoxy blends · Epoxidized palm oil · Thermal properties · Internal stress · Thermal expansion

Introduction

Recently, renewable bio-based natural polymeric materials have been widely developed to overcome the disposal problems of non-biodegradable and synthetic epoxy resin materials which are difficult to deal with and give rise to relatively large quantities of waste generated day-to-day [1–3]. Polylactic acid (PLA), cellulosic plastics, polyhydroxy alkonate, thermoplastic starch, and vegetable oils (e.g., linseed oil, caster oil, corn oil, and soybean oil) are the examples of renewable resource-based biopolymers [4]. According to Jin and Park [5], epoxidized vegetable oils (EVO) is one of the potential candidates in substituting the petrochemical-based chemical feedstock as the EVO are renewable, more cost-effectives and capable to minimize the emission of carbon dioxide (CO_2) gas which will give rise to the global warming phenomenon [6–8].

In general, EVO which are synthesized by reacting carbon–carbon double bonds of the unsaturated fatty acids in the vegetable oils with peracids are granted priority in Malaysia due to their superior sustainability and availability [8–10]. However, Meyer et al. [9] and Clayton [11] reported that the natural vegetable oils with relatively high iodine value or high content of unsaturated fatty acid (e.g., flax seed oil, sunflower oils, soybean oils, jatropha oils, and safflower oil) are preferably selected to synthesize high epoxy functionality bio-based epoxies. Among those vegetable oils, it is determined that soybean and linseed oils are two different types of EVO utilized nowadays since, these vegetable oils are commercially available in huge quantities worldwide, and are readily chemically modified by epoxidization to fulfill industrial applications [3, 4, 12]. Although, Clayton [11] stated that approximately 90% of the market was commercially monopolized by the epoxidized soybean oils, Van et al. [13] believed that palm oil is estimated to come to the level with and pass soybean oils within the next few years.

The waste disposal problem, depletion of non-biodegradable resources and environmental issues are inspiring

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researchers worldwide to further explore the potential of bio-based polymeric materials from renewable resources [3, 5]. According to Park et al. [14], blending of highly cross-linked tetra-functional TGDDM epoxy resins with epoxidized soybean oil could overcome the brittleness of TGDDM resins. Amar et al. [15] reported that the impact strength of the epoxy resin system can be enhanced by blending the petroleum-based epoxies with epoxidized vegetable oils. However, Jin and Park [5] have reported that the increment of the amount of epoxidized vegetable oils induces the deterioration of the mechanical and thermal properties of the bio-based epoxies system. The thermal stability, pendulum hardness, and cure rate of the bio-based epoxies was reduced as the increasing loading of EVO [8, 16]. A balance of toughness and stiffness can be achieved by optimizing the ratio of EVO to petrochemical-based epoxy [15].

Although, there are plenty of studies have been done on blending the petrochemical-based epoxy with epoxidized vegetable oils [7, 8, 17, 18]; to the best our knowledge, there is lack of reports on the effects of epoxidized palm oil on the glass transition temperature (T_g), storage modulus, coefficient of thermal expansion (CTE), internal thermal stress, and thermal stability of the bio-based epoxy blends system. Thus, thermal analysis has been conducted in this present study to fully explore the suitability and the entire effect of epoxidized vegetable oils as a partial substitute of petrochemical-based epoxy resins in thermal curable resin system.

Experimental

Materials

The petrochemical-based epoxy resins (diglycidyl ether of bisphenol-A (DGEBA), cycloaliphatic epoxide, and epoxy novolac resin) and the methylhexahydrophthalic anhydride (MHHPA) crosslinking agent used in this present study were supplied by CAPE Technology Sdn Bhd (Malaysia). Epoxidized palm oil with a pH value of about 5–6 was supplied by Malaysian Palm Oil Board (MPOB, Malaysia). The acid value and viscosity at 25 °C of the EPO is 0.09 mg KOH g^{-1} and 70.7 cP, respectively.

Preparation of bio-based epoxy blends

The petrochemical-based epoxy resins were measured at a predetermined ratio followed by mechanical-mixing. The epoxy blends were then stirred until achieving a homogeneous ternary epoxy blends (EB) mixture. Next, the EB (Part A) and the crosslinking agent (Part B) with the mixing ratio of 1:1 were mechanical-mixed at room temperature until no phase separation observed. The mixture was then poured into the cavities of a silicone mold and subjected to curing process in an oven at 130 °C for 3 h.

Characterization of epoxidized palm oil

The thermal characteristics of the EPO were determined using a DSC Diamond Analyzer (Perkin Elmer, USA). Approximately 20 mg of the liquid EPO was initially heated from −40 to 150 °C at a heating rate of 20 °C min^{-1}, under nitrogen atmosphere. The sample was then held at 150 °C for 1 min, and afterward cooled down to −30 °C at a rate of 20 °C min^{-1}.

Thermogravimetry analysis (TG) of the EPO was carried out on a Perkin Elmer Pyris 6 thermogravimetry analyzer (USA). The EPO sample (approximately 2–3 mg) was heated from room temperature to 400 °C at a heating rate of 20 °C min^{-1} under nitrogen atmosphere.

The functional groups of liquid EPO were characterized using Fourier Transform Infrared Ray (FTIR) Spectrometer (Perkin Elmer, USA). FTIR spectra from the wavelength of 4,000–450 cm^{-1} were recorded as the infrared radiation transmitted through the EPO sample.

Characterization of epoxy blends

Differential scanning calorimetry

The glass transition temperature (T_g) of the cured epoxy system was determined using DSC Diamond Analyzer (Perkin Elmer, USA). The T_g was determined using the half-C_p method in which the specific heat (C_p) change is half of that of the complete transition. The DSC was conducted in the nitrogen atmosphere, using 10–12 mg cured sample sealed into aluminum pans. The samples were heated from 30 to 250 °C at a heating rate of 20 °C min^{-1}.

Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis (DMT) test was performed using DMA 8000 (Perkin Elmer, USA). The epoxy specimen with the dimension of 25 mm × 10 mm × 2 mm (length × width × thickness) was heated from 30 to 250 °C at a heating rate of 2 °C min^{-1}. DMT spectra were taken in single cantilever mode at 1 Hz frequency with the displacement of 0.05 mm.

Thermo-mechanical analysis

The coefficient of thermal expansion (CTE) and T_g of the epoxy blend system were determined using TMA Diamond

Analyzer (Perkin Elmer, USA). The epoxy samples with the geometry of 10 mm × 5 mm × 5 mm were heated from room temperature to 250 °C at the rate of 5 °C min^{-1} under the nitrogen gas atmosphere.

Fourier transform infrared ray spectroscopy

The functional groups of the uncured epoxy mixture and cured solid epoxy samples were characterized using FTIR Spectrometer (Perkin Elmer, USA). FTIR spectra from the wavelength of 4,000–450 cm^{-1} were recorded as the infrared radiation transmitted through the epoxy specimen.

Results and discussion

Characterization of epoxidized palm oils

FTIR characterization

Fourier transform infrared ray (FTIR) spectroscopy was utilized to identify the polymeric molecular structure and the chemical bonds of the organic EPO compounds. Referring to the FTIR spectrum as shown in Fig. 1, it can be summarized that the molecular chain of EPO consists of –CH bond (2922 and 2854 cm^{-1}), –C=O bond (1745 cm^{-1}), –C–O bond (1159 and 1112 cm^{-1}), –CH_3 bond (1466, 1415, and 1378 cm^{-1}), –OH group (3474 cm^{-1}) as well as epoxide group (826 and 843 cm^{-1}) [5, 18–20].

DSC characterization

The glass transition temperature (T_g), melting temperature (T_m) and cold crystallization temperature (T_c) of EPO were showed in Fig. 2. Chain motion of EPO is frozen at −40 °C since the epoxidized oil is cooled at the temperature lower than its glass temperature. EPO undergoes a second-order endothermic glass transition (step transition) at −18 °C when the sample is heated. Further heating of EPO up to −1.7 °C induces the exothermic cold crystallization reaction to take place in EPO specimen. It is believed that rotation, alignment and perfection of the internal order of the para-crystalline structure in EPO led to the cold crystallization process [21]. Also, cold crystallization process tends to occur because a part of the amorphous chains will rearrange themselves in the amorphous phase to form a crystalline phase when the specimen is heated [22]. This process commonly occurs at the temperature a few degrees above glass transition temperature as shown in Fig. 2. According to Michael and Patrick [23], the entirely amorphous substance possesses the capability to crystalline by heating at the temperature greater than its glass transition temperature. The EPO specimen then experienced melting transition from solid to the liquid phase at 27.3 °C. This is because the polymeric specimen obtained sufficient thermal energy to allow its chain to move freely and behave as a viscous liquid at the temperature greater than its melting temperature [24]. As shown in Fig. 2, it is observed that crystallization process takes place in the EPO at −0.97 °C which is in the range of temperatures between T_g and T_m when the sample is being cooled. There is one crystallization exothermic peak ($T_{c'}$) appears in DSC cooling curve because the randomly tangled molecular chains in the melt tend to rearrange and pack themselves into parallel array and form a three-dimensional ordered structure when the melt temperature is reduced below its melting temperature [24]. Thermal motion and chain entanglements during crystallization process will restrict the process to take place in the temperature range between T_g and T_m [24]. This finding of crystallization exothermic peak during cooling of EPO is identical to the finding reported by Xu et al. [25] who also found an exothermic crystallization peak in the cooling curve during cooling the hazelnut oil. Xu et al. [25] found in the DSC cooling curve that the hazelnut oil experiences onset of crystallization at −12.4 °C and a main exothermic crystallization step at −31.5 °C.

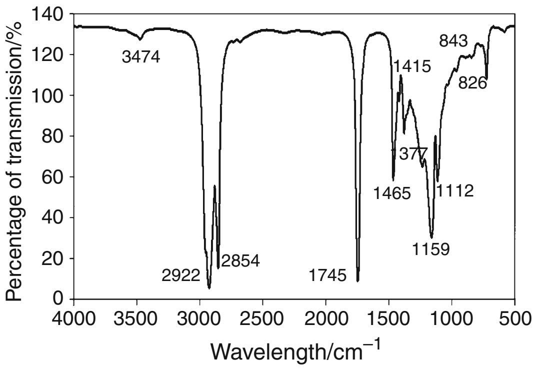

Fig. 1 FTIR spectrum of epoxidized palm oil

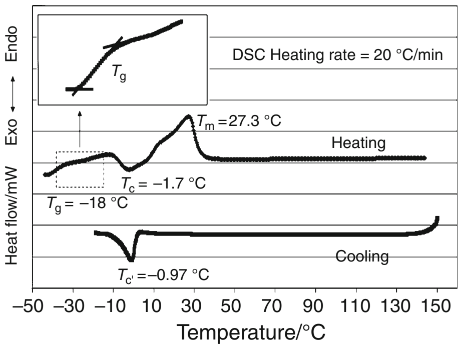

Fig. 2 DSC thermogram of EPO

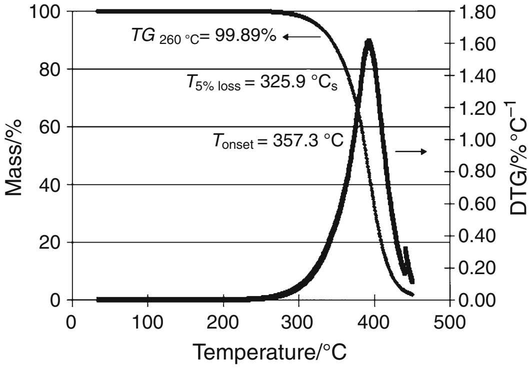

Fig. 3 TG curve of EPO

TG characterization

Figure 3 shows the TG curves as a function of temperature for EPO. Referring to the curves, the onset temperature (T_{onset}), the temperature at 5% loss of the sample ($T_{5\%\text{ loss}}$) and the thermal stability of the EPO at 260 °C were determined. It is shown in Fig. 3 that as the heating temperature is increased from room temperature to higher temperature at a heating rate of 20 °C/min; a loss in mass of the EPO sample will be noticed. However, it is found that the liquid EPO is relatively stable up to approximately 250 °C, since there is no any change in the DTG value observed. It is believed that mass loss of EPO sample will initiate as the temperature is increased beyond 250 °C. Mastura [26] had reported that a specimen will experience mass loss if subjected to increased temperatures. Hence, there is an approximately 0.11% mass loss of EPO at 260 °C and a 5% mass loss at 325.9 °C as shown in Fig. 3. It is believed that the mass loss curve obtained from TG experiment will shift to higher or lower temperature by changing the heating rate because mass loss during heating a material depends on both time and temperature.

Thermal characterization of epoxy blends

DSC characterization of epoxy blends

Figure 4 shows the effect of EPO loading on the glass transition temperature (T_g) of the epoxy blends system. Referring to Fig. 4, it can be observed that the T_g (detected by DSC) of the epoxy blends decreases as the loading of EPO increasing. This finding is believed to be caused by the plasticizing effect of EPO which will enhance the flexibility and the degree of freedom for movements of the molecular chains in the epoxy blends network structure [11, 16, 27]. On account of Robert [28] and Brydson [29] declared that polymers with less hindrance to internal rotation possess relatively low T_g values, the reduction in T_g value when the EPO content was increased in the epoxy blend system as shown in Fig. 4 could be justified.

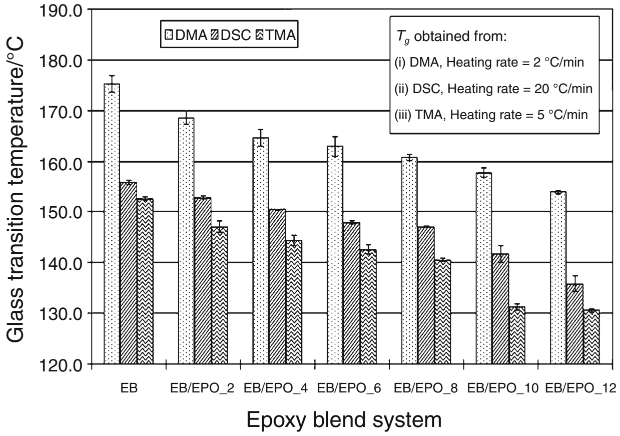

Fig. 4 T_g value of epoxy blends measured using different thermal analyzers

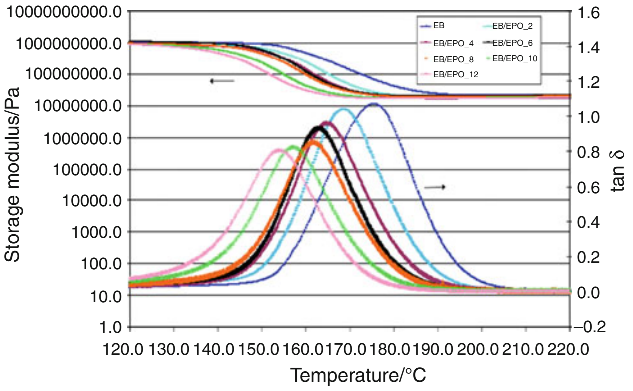

Fig. 5 Effects of EPO loading on the dynamic storage modulus and tanδ of the epoxy blends

DMT characterization of epoxy blends

The dynamic storage modulus and the damping for the epoxy blend system as a function of temperature is shown in Fig. 5. As shown in Fig. 5, it can be found that the storage modulus versus temperature curve shifted to lower temperature as the percentage of the EPO in the epoxy blends is increased. This reduction in storage modulus (E') by increasing EPO content is due to the decrease in stiffness of the epoxy blends. Blending of petroleum-based resins with epoxidized vegetable oils will give rise to the reduction in the stiffness of the epoxy blend system [15]. Since there is a positive relationship between storage modulus and crosslink density, the reduction in crosslink density by increasing the amount of EPO in the blend can lead to the decrease in storage modulus [16]. Besides, it is noticed in Fig. 5 that the tanδ versus temperature curve exhibits similar trend as storage modulus versus temperature curve. The shifting of the tanδ–T curve to lower temperature as the increasing amount of EPO in the epoxy blends could be due to the depression of the T_g of the thermal curable epoxy blends. Referring to Fig. 5, it is found that the tanδ of the epoxy system with high amount of EPO is higher than that of epoxy blend with no or low content of EPO because the former has lower elastic stiffness. According to Arcady et al. [30], the decrease in elastic constant will give rise to the improvement in damping properties. Thus, it can be concluded that epoxy system with high content of EPO will possess high damping value and vice versa. The T_g (detected by DMT) of the epoxy blends is shown in Fig. 4. It is noticed that the T_g for the epoxy blends decreases with increasing the loading of EPO. This phenomenon is believed to be contributed by the plasticizing effect of EPO. On account of the presence of flexible fatty acid backbone chain [31], EPO has the ability to reduce chain stiffness by enhancing the degree of freedom for chain movements in the epoxy blends network structure [15, 16]. Cowie [24] and Robert [28] reported that a flexible chain with less hindrance to internal rotation possesses lower T_g value. Accordingly, it can be justified that epoxy blends with higher concentration of EPO will exhibit lower T_g value.

TM characterization of epoxy blends

As shown in Fig. 6, it is clearly shown that the coefficient of thermal expansion (CTE) of the epoxy blends increases as the amount of the EPO increasing. Figure 6 also shows that the CTE before T_g (CTE 1) is lower than that of CTE after T_g (CTE 2). This finding is in agreement with the study reported by Jin and Park [16]. According to Jin and Park [16], the increment of the CTE of epoxy blends/epoxidized vegetable oil system was attributed to the increased freedom of movement of the macromolecules in the three-dimensional network structure. Erfan [32] reported that polymeric materials with high free volume experience higher degree of expansion. By the reason of increasing the EPO content in the epoxy blend system increase the free volume and chain flexibility [8, 33], epoxy blend system containing higher amount of EPO will possess higher CTE value. The CTE 2 of the epoxy blends is found to be higher than that of its CTE 1 value as displayed in Fig. 6. This is associated with the free volume and the freedom of motions of the molecules in both glassy region and rubbery region. The CTE 2 value of the epoxy blends (i.e., CTE value obtained after the T_g) tends to be greater than that of CTE 1 value (i.e., CTE value obtained before the T_g). This is due to the fact that the chain segments possess relatively high degree of movement and free volume in the rubbery state [24, 32]. Figure 4 shows the T_g (detected by TM) of the thermal curable epoxy blends. As shown in Fig. 4, there is a negative relationship between the T_g value and the content of EPO in the epoxy blends. The epoxy blends with higher amount of EPO content had lower T_g value due to the plasticizing effect of the EPO and the lower crosslink densities of the EB/EPO system [27, 34–36]. It is believed that low chain flexibility and high crosslink density could eventually contribute to high T_g value and thus, EB/EPO system with higher EPO content exhibits lower T_g value.

FTIR characterization of epoxy blends

Fourier transform infrared ray (FTIR) spectroscopy is a common technique used for material characterization, since this approach studies easily for a thin coating of irradiated film [37]. In the present study, FTIR was used to study the curing behavior of the thermal curable epoxy blend system. Figure 7 displays the FTIR spectra of the epoxy blends before and after the curing process. As shown

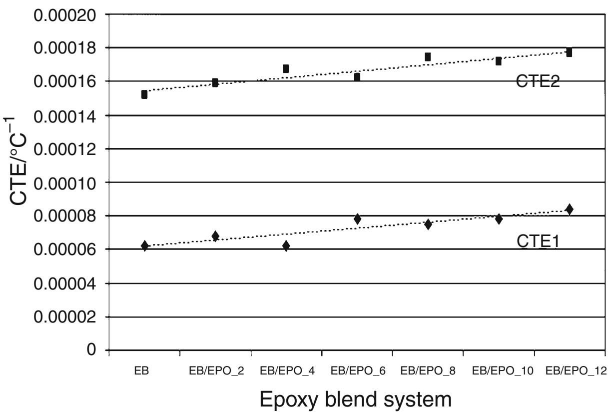

Fig. 6 Effects of EPO loading on the coefficient of thermal expansion (CTE) of epoxy blends

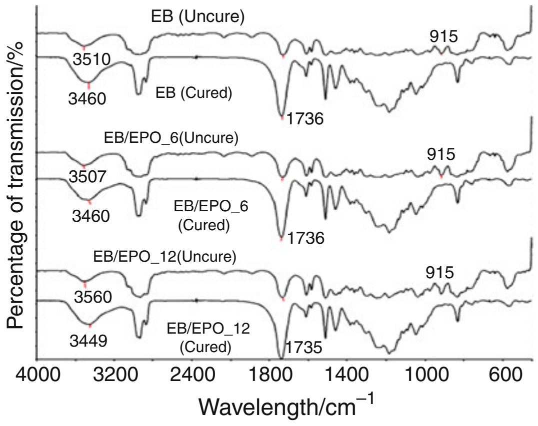

Fig. 7 FTIR spectra of the epoxy blends before and after curing process

in Fig. 7, it is found that the 915 cm^{-1} peak in the FTIR spectrum for uncured epoxy system disappears after the thermal curing process. According to Morita [36] and Park et al. [14], this absorption assignable to C–O stretching of the epoxides at the 915 cm^{-1} is totally reduced upon thermal curing process. The disappearance of epoxy group at 915 cm^{-1} provides evidence for the oxirane cleavage reaction of anhydride to initiate thermal curing process [38]. Figure 7 also shows the emergence of the 1736 and 3460 cm^{-1} peak on the FTIR spectrum for cured epoxy system. The appearance of broad peak at 3460 and 1736 cm^{-1} represent the present of hydroxyl groups and carbonyl groups in the epoxy blends, respectively [14, 36]. According to Garima and Deepak [39], the generation of hydroxyl groups on epoxy blends indicates the initiation of the curing process of epoxy system with the anhydride curing agent. The intensity of the absorption band corresponding to carbonyl group in the epoxy blends increases after the thermal curing process as shown in Fig. 7. The increment of the intensity of the carbonyl absorption band after curing is an indication of the ring opening of the anhydride group.

Internal stress determination

Both the DMT and TM techniques were used to determine the theoretical internal stress developed in the thermal curable epoxy blends. Figure 8 shows the theoretical internal stress of the thermal curable epoxy system. As mentioned by Callister [40], the theoretical internal stress can be calculated using Eq. 1 with the assumptions that the shrinkage of the resin in the glassy region is completely converted to internal stress [41].

$$\sigma = \int_{RT}^{T_g} E\beta_l (T_0 - T_f) = \int_{RT}^{T_g} E\beta_l \, \mathrm{d}T \tag{1}$$

where σ is theoretical internal stress, E is modulus of elasticity, β_l is linear coefficient of thermal expansion, T_0 is initial temperature and T_f is the final temperature.

As can be seen from Fig. 8, increasing of the EPO loading causes the reduction of the internal thermal stresses in the epoxy blends (i.e., reduction of the area under the graph). This finding is mainly due to the decrease in crosslink density, modulus of elasticity and T_g in the epoxy blends by the addition of EPO. Socrates et al. [42] reported that greater internal thermal stress tends to be developed in the epoxy blend because the highly cross-linked network in this system greatly reduces the time for the polymer relaxation to take place and the ability for the system to shrink. As the result of the internal thermal stress in the molecular segments of the amorphous region fails to be dispersed [43], internal stress will be built up in the epoxy blends. Owing to polymers with high cross-link density will have high T_g [31], Brahateeswaran and Gupta [41] and Graham et al. [44] mentioned that T_g plays a crucial role in influencing the magnitude of the internal stress; the greater the T_g, the higher the internal stress. Graham et al. [44] reported that reduction in elastic modulus of the polymer system will minimize the internal thermal stress of the system. This is because Eq. 1 shows that there is a direct relationship between the magnitude of the internal thermal stress developed and the elastic modulus of the system. It is believed that epoxy blends with high EPO content possesses low magnitude of internal thermal stress because increasing the EPO loading in thermal curable epoxy blend system will gradually increase the numbers of triglycerides or fatty acid chains which will impart flexibility and plasticizing effect to the system. Similar result was reported by Ricardo et al. [45].

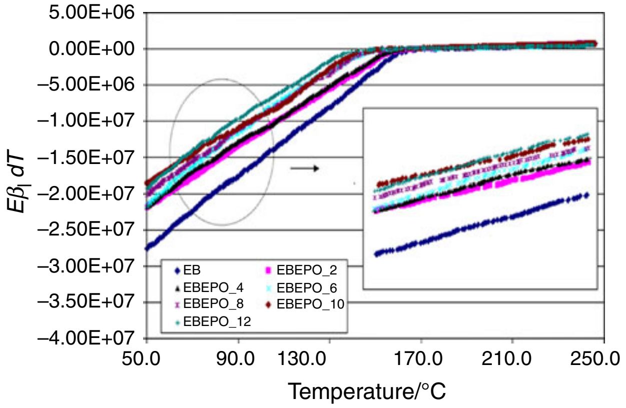

Fig. 8 Effect of EPO loading on the internal stress of the epoxy blends

Comparison of T_g value obtained from DSC, TM, and DMT

The T_g can be considered as one of the important parameters used in polymer characterization to determine the end-use temperature of the polymeric material. However, different thermal techniques provide different T_g value of the materials analyzed [46, 47]. Thus, it is important to compare the T_g value obtained using different techniques to obtain a more precise and accurate T_g value [48]. Again, Fig. 4 shows the T_g values of the EB/EPO blends obtained from DSC, TM and DMT. Figure 4 showed that T_g (detected by DMT) is the highest followed by the T_g (detected by DSC). The T_g value obtained from TM is the lowest. This observation is in agreement with the finding reported by Clyde [46] and Chartoff et al. [49]. On account of the T_g value obtained is highly relied on the mode of the techniques used to measure the glass transition, there will be a relatively different between the T_g value determined from DSC, DMT, and TM as shown in Fig. 4. For example, DMT measures the modulus of the material against temperature changes rather than the dimensional changes and heat flow measured by TM and DSC, respectively [46]. Furthermore, owing to DMT signal strength is much more higher compared to that of DSC to detect T_g [49] and the T_g profiles from TM are usually broad due to the volume relaxation effects which usually takes place near the T_g value [11], the T_g value obtained from each technique tends to deviate from each other as shown in Fig. 4. Apart from that, Witold et al. [50] reported that the different experimental techniques give rise to different T_g due to the side- and main-chain polar groups in the system which possesses different time response of motions. In addition, the difference of T_g value detected by DSC, TM, and DMT can be attributed to the different heating rate during the thermal characterization [51].

Conclusions

The epoxy blends [diglycidyl ether of bisphenol-A (DGEBA)/cycloaliphatic epoxide resin/epoxy novolac resin]/epoxidized palm oil systems can be thermal cured by methylhexahydrophthalic anhydride (MHHPA) crosslinking agent. The effects of the EPO on the thermal behaviors of the epoxy blends have been characterized using DSC, TM, and DMT. From the DSC, it was found that the glass transition temperature, cold crystallization temperature, melting temperature and crystallization temperature of the EPO is −18, 1.7, 27.3, and −0.97 °C, respectively. TG curves revealed that EPO is relatively stable at 250 °C, it experiences 5% mass loss at 325 °C and begins to decompose at 357 °C. The thermal behaviors (glass transition temperature, storage modulus, tanδ, CTE, and internal thermal stress) of the epoxy blends were greatly influenced by the addition of EPO.

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