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Thermal and Flame Retardation Properties of Melamine Phosphate-Modified Epoxy Resins

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Abstract

We have synthesized a series of epoxy resins containing melamine phosphate (MP) and investigated their thermal and flame retardation properties. MP functions as a hardener and a flame retardant or as an additive of the cured epoxy resin to enhance flame retardation properties of epoxy resins. The reactions of DGEBA cured in the presence of MP were monitored by NMR and FTIR. Our results show that in both reactive and additive modes, MP is effective in increasing limiting oxide index (LOI) and the char yields of epoxy resins at lower phosphorous content. We observed that flame retardation by MP in its reactive mode is better than in its additive mode; the same phenomenon was found also for the glass-transition temperature (T_g). Thermogravimetric analysis (TGA) demonstrated that epoxy resins containing MP decompose at relatively lower temperatures than those lacking MP; this decomposition results in a protective layer forming that prevents the epoxy resins from decomposing further by combustion.

Introduction

Epoxy resins are used widely in coatings, adhesives, insulating materials, and composites [1–3]. Like most organic polymeric materials, epoxy resins have rather poor flame retardation properties, what limits their applicability in some areas.

Many different approaches have been reported for improving the flame retardation of epoxy resins [4–17]. Halogen-containing compounds in conjunction with antimony oxide [14–16] are reported to be effective flame-retardant agents for various epoxy resins. The main drawbacks of using these halogen-containing epoxy systems are the release of highly toxic and corrosive products during combustion [10, 17]. Therefore, the preparation of non-halogen flame retardants is the subject of extensive investigations [5–8]. Phosphorylated compounds blended with epoxy resins result in relatively poorer flame retardancy, thermal and mechanical properties [18, 19]. Flame retardants formed by linking phosphorus units covalently into the main chains of the epoxy or the hardener have better physical and mechanical properties than those formed by simple blending [13].

Melamine phosphate (Scheme 1(A)) can be prepared by reacting melamine with phosphoric acid [20]. Melamine phosphate has been used for some time for coating the surfaces of metals. In 1970's, the melamine phosphate was blended into many polymers as an additive-type flame retardant [21–24], but, to the best of our knowledge, it has not been used as a reactive-type flame retardant for epoxy resin. In this paper, we report that melamine phosphate functions as a curing agent and a flame retardant of cured epoxy resins.

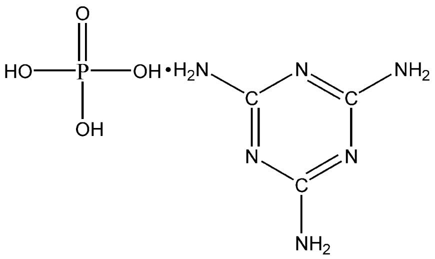
Experimental

Materials

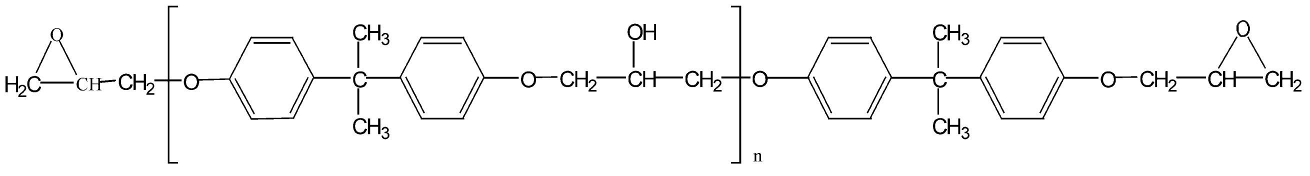
The liquid epoxy resin employed in this study is a diglycidyl ether of bisphenol A (DGEBA, BE-188), obtained from Chang Chun Chemical Plastics of Taiwan with an epoxide equivalent weight of 188 g/eq. The flame retardant used is the melamine phosphate (MP, $C_3N_6H_6 \cdot H_3PO_4$) was obtained from the Chung-Shan Institute of Science and Technology of Taiwan; 4,4′-diaminodiphenylmethane (DDM) was purchased from the Aldrich Chemical Company, USA. Scheme 1 presents their chemical structures.

Sample Preparation

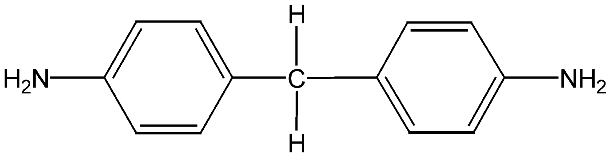
Table 1 shows the codes and compositions used in this study. Mixtures of DGEBA having varying contents of MP were cured first at 190 °C for 180 min (precuring) and then at 220 °C for 120 min (postcuring). DGEBA mixed with DDM and containing various amounts of MP were cured initially at 100 °C for 120 min (precuring) and then at 120 °C for 60 min (postcuring).



(A) Melamine Phosphate



(B) DGEBA



(C) 4,4’-diaminodiphenylmethane

Scheme 1. Chemical structures of compounds used in this study.

Table 1. Codes and compositions of materials prepared in this study

Codes	Components
Neat epoxy	DGEBA : DDM = 100 : 26 (phr)
R5	DGEBA : MP = 100 : 5 (phr)
R10	DGEBA : MP = 100 : 10 (phr)
R20	DGEBA : MP = 100 : 20 (phr)
R30	DGEBA : MP = 100 : 30 (phr)
A5	DGEBA : DDM : MP = 100 : 26 : 5 (phr)
A10	DGEBA : DDM : MP = 100 : 26 : 10 (phr)
A20	DGEBA : DDM : MP = 100 : 26 : 20 (phr)
A30	DGEBA : DDM : MP = 100 : 26 : 30 (phr)

Fourier Transform Infrared (FT-IR)

The sample was placed on a KBr pellet and FTIR spectra were obtained at 220 °C using a Nicolet AVATAR 320 FT-IR (Madison, Wisconsin, USA), to analyze the epoxide content of the system at a resolution of 2 cm^{-1}.

Solid-State NMR

High-resolution solid-state ^{13}C-NMR experiments were carried out at room temperature using a Bruker DSX-400 spectrometer operated at resonance frequencies of 100.47 MHz for ^{13}C. The ^{13}C CP/MAS spectra were measured with a 3.9 μs 90° pulse, with 3 s pulse delay time, acquisition time of 30 ms and 2048 scans. All NMR spectra were taken at 300 K using broadband proton decoupling and normal cross-polarization pulse sequencing. A magic angle sample-spinning (MAS) rate of 5.4 kHz was used to eliminate resonance broadening due to the anisotropy of the chemical shift tensors.

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical measurements were carried out on a DuPont dynamic mechanical analyzer (DMA 2980). The clamp model was a single cantilever with frequency of 1 Hz and the heating rate was 3 °C/min from 40 to 250 °C. The specimen dimensions are ca. 17.5 mm × 11.5 mm × 2.8 mm.

Thermogravimetric Analysis (TGA)

Thermal stability studies were carried out using a DuPont thermo-gravimetric analyzer (TGA 2050) operating under a nitrogen or air atmosphere. The cured sample (ca. 7 mg) was placed in a Pt cell and heated at a rate of 20 °C min from 30 to 750 °C with a nitrogen or air flow of 90 mL/min, respectively.

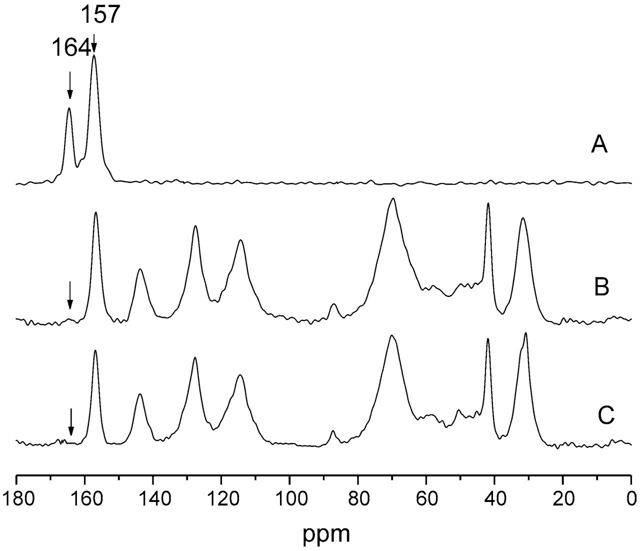


Figure 1. Solid-state ^{13}C NMR spectra of: (A) melamine phosphate and (B) DGEBA cured with melamine phosphate; (C) DGEBA cured with melamine.

Limiting Oxygen Index (LOI)

The value of the limiting oxygen index (LOI) was measured on a Stanton Redcroft flame meter using a modification of a method reported in the literature [25]. The percentage of O_2 in an O_2-N_2 mixture that was barely sufficient to sustain a flame was taken as the value of the LOI.

Elemental Analysis

Elemental analyses were performed using a Heraeus CHN–O rapid elemental analyzer with 4-nitroaniline as the standard. The phosphorus content of the synthesized compound was determined by phosphorus analysis with a microdigestion apparatus equipped with a spectrophotometer.

Morphology

To investigate the morphology of DGEBA-DDM-MP, the specimen was fractured under the cryogenic conditions by using liquid nitrogen. A scanning electron microscope (SEM, HITACHI-S2500) was used to observe the fracture surface after it was coated with a thin layer of gold.

Results and Discussion

Synthesis of Sample of the DGEBA-MP System

The curing mechanism of the epoxy-amine system has been characterized by NMR and FT-IR spectroscopes. Figure 1A displays the solid-state ^{13}C NMR spectrum of melamine phosphate. The chemical shift of the free and hydrogen bonding are located at 164 and 157 ppm, respectively. The hydrogen bonds are between PO_4 group and melamine molecules, intra and inter of PO_4 group and different melamine molecules, respectively [26]. Figure 1B, which displays the solid-state ^{13}C NMR spectrum of DGEBA cured with melamine phosphate at 220 °C for 100 min, indicated that the peak at 164 ppm has nearly disappeared, implying that almost amine group of the melamine phosphate has reacted with DGEBA. Therefore, the melamine phosphate had nearly decomposed to melamine and phosphoric acid and less amine groups without reaction with DGEBA. The chemical shift of 157 ppm overlapped with chemical shift of phenyl group of DGEBA at 158 ppm. Figure 1C shows the ^{13}C solid-state NMR spectrum of DGEBA cured with melamine at 220 °C for 100 min. These peaks are almost same as the DGEBA cured with melamine phosphate and Figures 1C and 1B are different for peak at 164 ppm. Therefore, the epoxide-amine reaction of the DGEBA/MP system takes place between melamine and the epoxy.

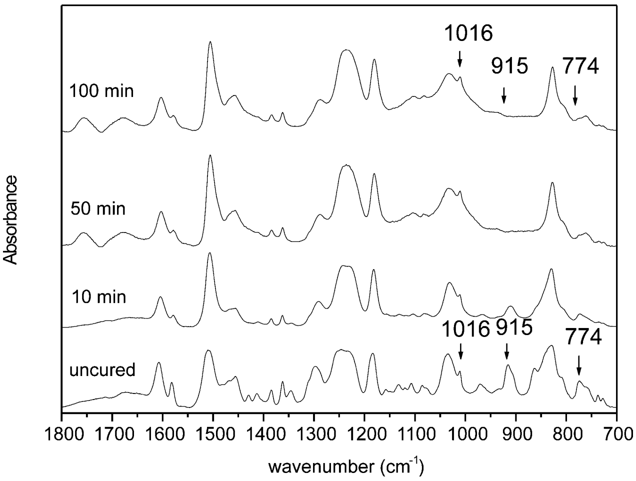


Figure 2. FTIR spectra recorded various time of DGEBA-MP at 220 °C.

Figure 2 displays the FTIR absorption spectra obtained before (uncured) and after heat treatment of amine/epoxide system at 220 °C over various periods of time. A comparison of these spectra reveals that upon curing at 220 °C the stretching vibration band of the epoxy ring at 915 cm^{-1} decreases in intensity and shifts downward. At the same time, the absorption peak of the NH_2 group at 774 cm^{-1} also decreases in intensity. These observations relate to the degree of reaction between the epoxide and amine. The absorption peak of the –P–O–C– group at 1016 cm^{-1} increases with curing time as a result of etherification.

Thermal Properties

Glass Transition Temperature (T_g)

Dynamic mechanical analysis (DMA) can obtain accurate values of T_g as well as giving information on the microstructure of the cured epoxy resin. The curve plotted from the values of tan δ *versus* temperature for a control network exhibits a major relaxation that is often observed in a cured epoxy resin [27]. This transition corresponds to the major value of T_g of the cured epoxy resin, above which temperature significant chain motion takes place. The thermal properties are summarized in Table 2. The value of T_g of the neat epoxy is 156.8 °C and those of the DGEBA-MP and DGEBA-DDM-MP systems range from 145.6 to 172.9 °C and 123.4 to 156.8 °C, respectively. Thus, the observed value of T_g

Table 2. Thermal properties of the DGEBA-MP and the DGEBA-DDM-MP systems

Code	T_g	5% weight-loss temperature (°C)		10% weight-loss temperature (°C)		DTG value (%/min)		Char yield at 700°C (%)	
		N_2	Air	N_2	Air	N_2	Air	N_2	Air
Neat epoxy	156.8	372.84	362.13	378.92	375.57	47.2	41.8	7.25	0
R5	145.6	305.8	303.6	324.1	323.7	16.5	18.9	24.9	3.0
R10	152.8	304.5	293.7	316.9	317.8	13.7	15.9	26.1	3.4
R20	160.3	294.3	287.7	315.3	313.9	11.3	10.6	28.1	8.6
R30	172.9	292.7	284.3	312.6	310.9	10.3	9.0	30.0	11.3
A5	137.1	351.3	348.7	364.1	362.3	26.9	24.0	9.6	1.0
A10	134.6	343.5	343.6	358.4	357.8	23.2	21.1	15.6	2.7
A20	129.9	334.5	330.8	350.1	351.6	20.4	20.2	19.8	5.1
A30	123.4	328.6	319.4	348.7	345.7	16.5	16.5	24.8	7.8

Char yield: residuary wt% of sample.
DTG : differential thermo-gravimetry.

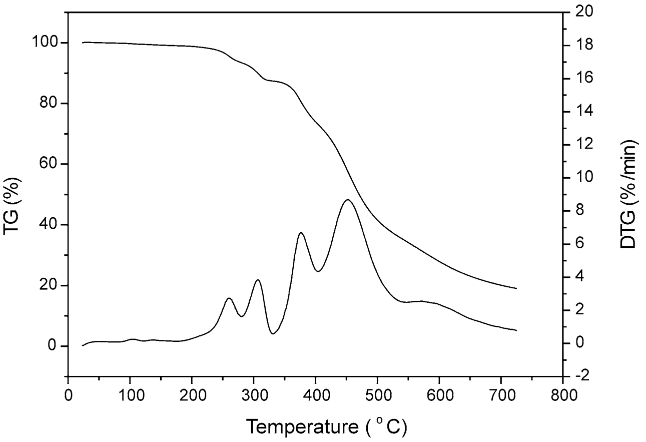


Figure 3. TGA thermograms of MP under an N_2 atmosphere.

increase in the order DGEBA-MP > neat epoxy > DGEBA-DDM-MP. For the DGEBA-DDM-MP system, the value of T_g decreases upon increasing the content of melamine phosphate. The MP units are well dispersed in the epoxy resin matrix and its bulky and rigid structure tends to decrease the crosslinking density of the cured DGEBA-DDM-MP and the decrease in T_g of the DGEBA-DDM-MP system is due to the plastic effect [28, 29]. In contrast, the value of T_g increases with upon increasing the melamine phosphate content of the DGEBA-MP system. This phenomenon suggests that MP acts as a curing agent having more reactive sites than does DDM. Hence, the DGEBA-MP system has a higher crosslinking density than does the DGEBA-DDM-MP system and it has high glass-transition temperatures than the neat epoxy and the DGEBA-DDM-MP system.

Thermal Stability

The TGA thermogram of melamine phosphate under a N_2 atmosphere is shown in Figure 3; the 5% and 10% weight-loss temperatures are 264.1 and 306.7 °C, respectively. Figures 4 and 5 display the TGA thermograms of the DGEBA-MP and DGEBA-DDM-MP systems under N_2 atmosphere; their results are summarized in Table 2. The 5% and 10% weight-loss temperatures of the neat epoxy (372.4, 378.9 °C) are higher than those of systems containing MP. Both the reactive and additive types of MP-containing epoxies have lower temperatures for 5% and 10% weight loss relative to those of the neat epoxy because the phosphorus group of melamine phosphate degrades at a relatively low temperature. This phenomenon was also observed for other phosphorylated epoxy resins [30–33]. The reactive type DGEBA-MP shows the lowest degradation temperatures because the phosphorus-containing functional groups incorporated into the network's backbone reduce the thermal stability of the cured epoxy through low temperature decomposition of the weak P–O–C bond [30, 34]. This observed phenomenon indicates that MP plays an important role in improving the flame retardation of epoxy resins by forming a protective layer on the epoxy surface. Consequently, the weight loss of phosphorus-containing epoxies at high temperature is less than that of the phosphorus-free ones. Upon heating, the phosphorous group of the MP-containing epoxy decomposes firstly to produce a phosphorus-rich residue [35, 37], which is able to protect and retard the matrix beneath it from further decomposition and thus, higher char yield are the result. As shown in Figures 4 and 5, both DGEBA-MP and DGEBA-DDM-MP systems have higher char yield than does neat epoxy at 700 °C in either N_2 or air and their char yields increases with the increasing MP content. In addition, the DGEBA-MP system has higher char yields than does the DGEBA-DDM-MP system. Figures 6 and 7 indicated that the TGA thermograms of the DGEBA-MP and DGEBA-DDM-MP systems in air display a similar trend as they do in N_2.

Differentiated TGA (DTG) curves indicate the rate of degradation. The DTG values or degradation rates of DGEBA-MP and DGEBA-DDM-MP systems are significantly lower than that of the neat epoxy both in air and in N_2 (Table 2). Such degradation retardation has also been observed for other phosphorylated polymer systems [30–38]. The reflection of a sample's flame retardancy [42]; this feature has been widely established in studies of polymer flame retardancy [37, 39–43]. Increasing char formation means reduction in concentration of combustible gases,

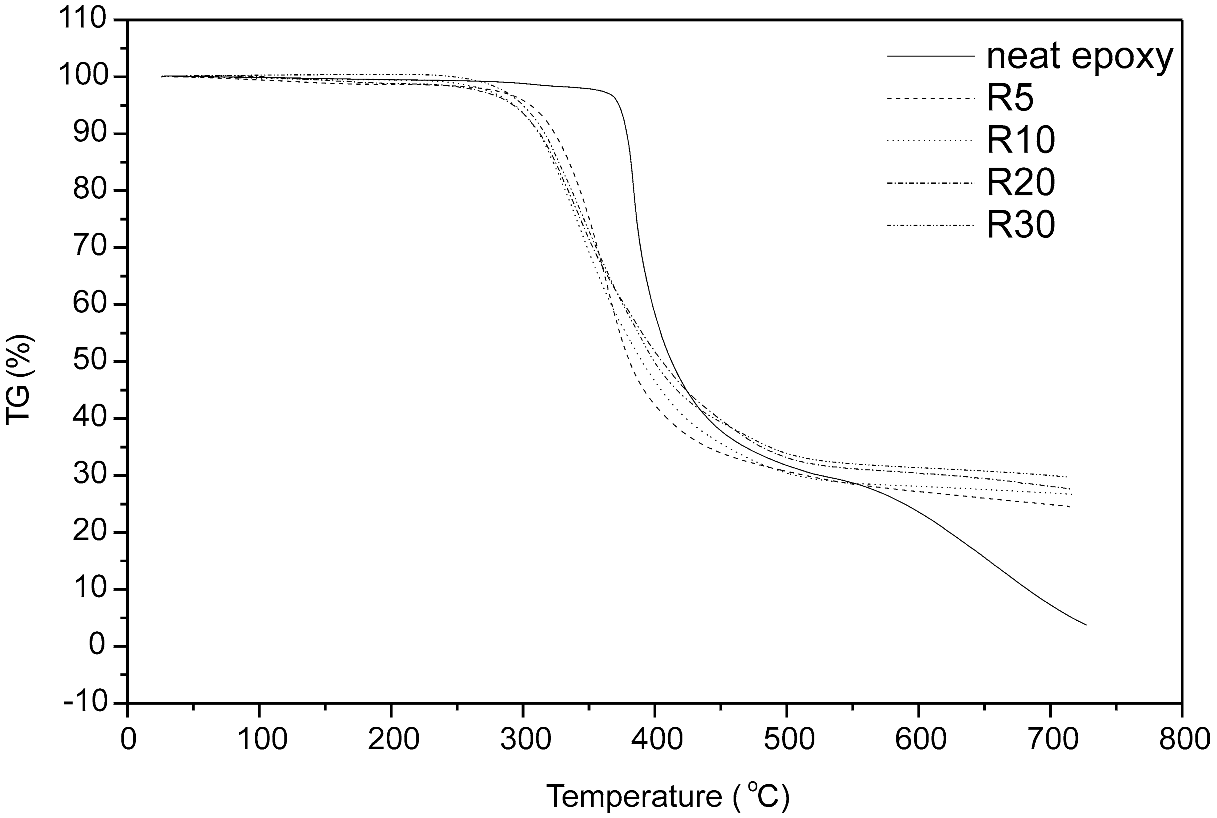


Figure 4. TGA thermograms of DGEBA-MP system under an N_2 atmosphere.

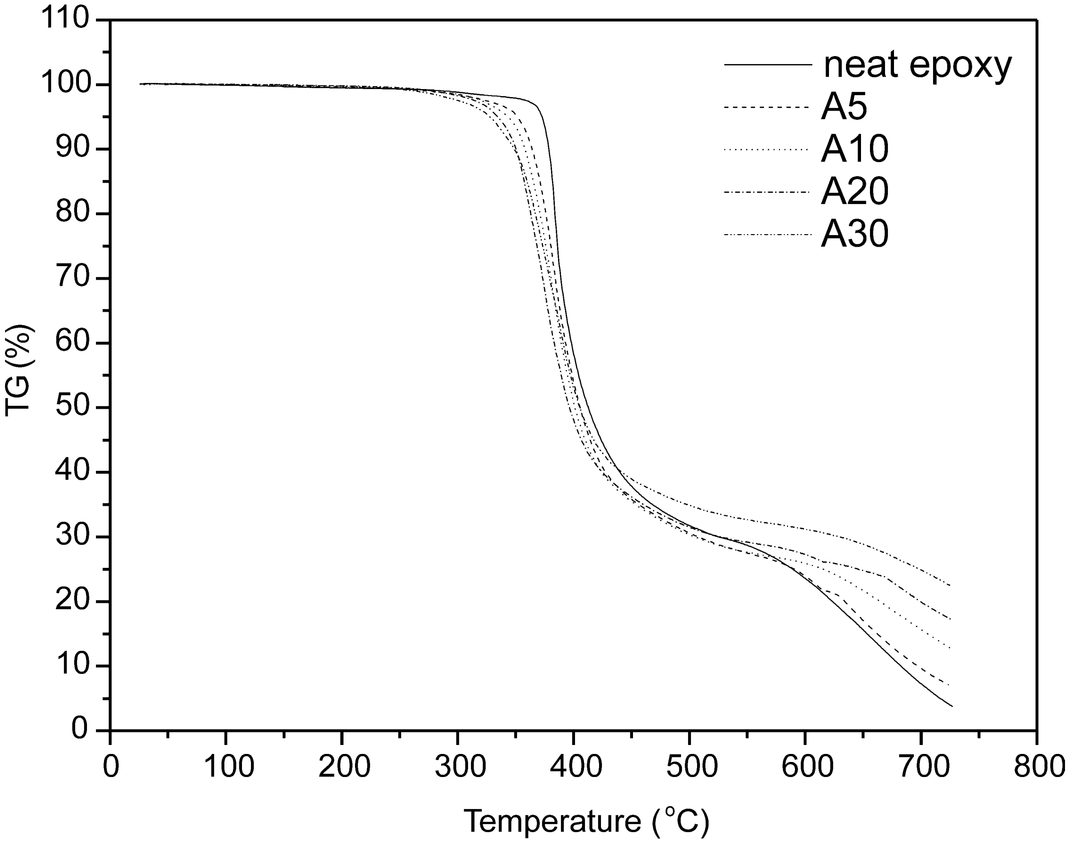


Figure 5. TGA thermograms of DGEBA-DDM-MP system under an N_2 atmosphere.

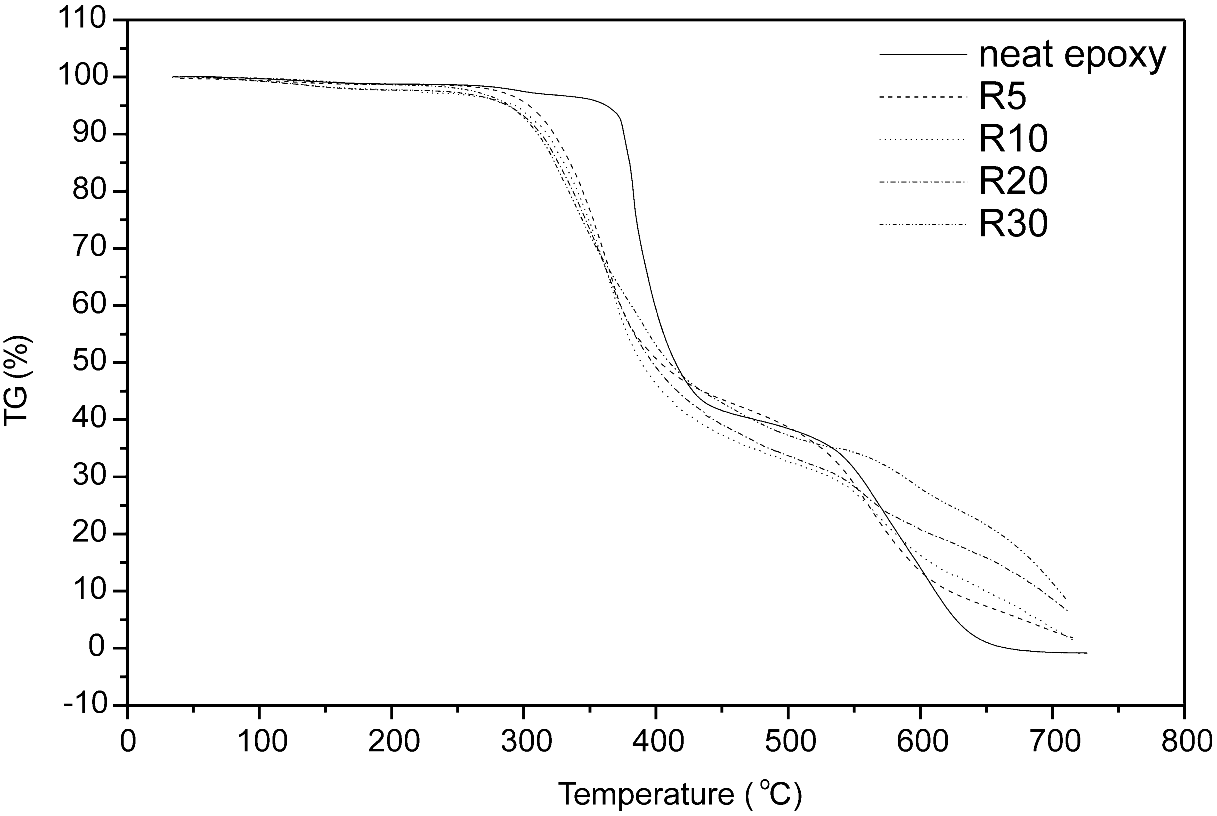


Figure 6. TGA thermograms of DGEBA-MP system under an air atmosphere.

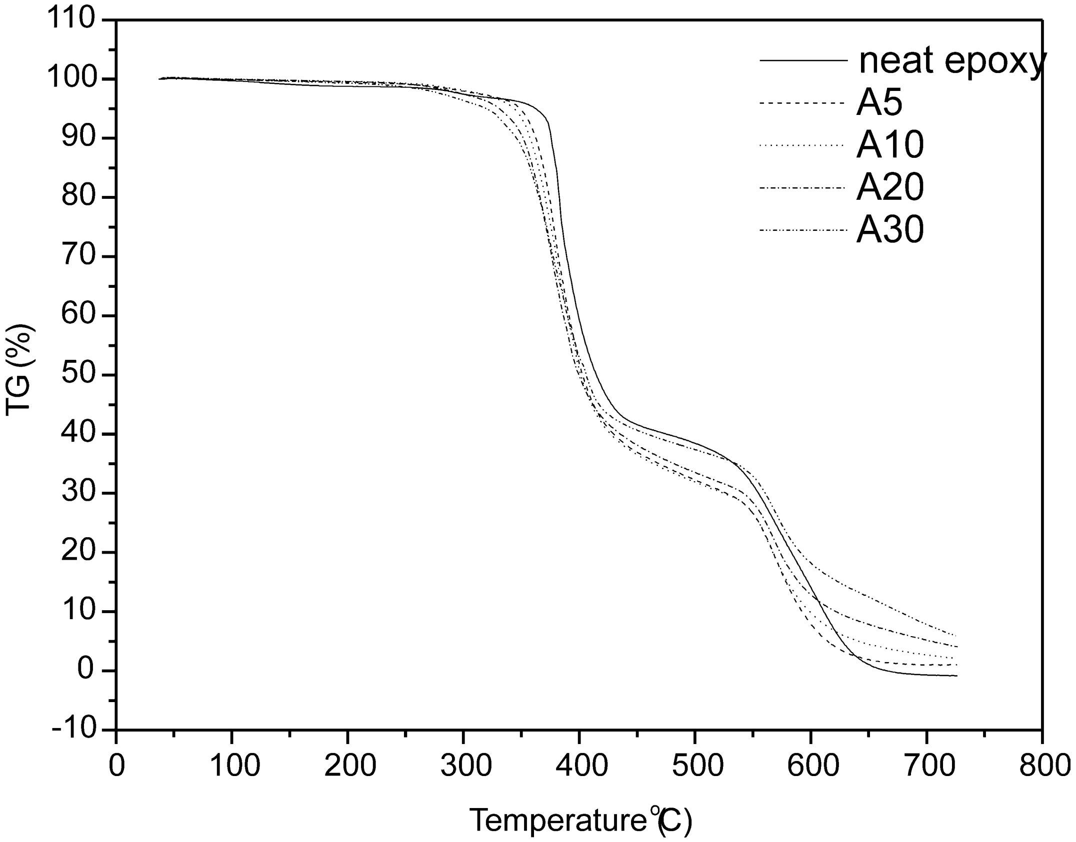


Figure 7. TGA thermograms of DGEBA-DDM-MP system under an air atmosphere.

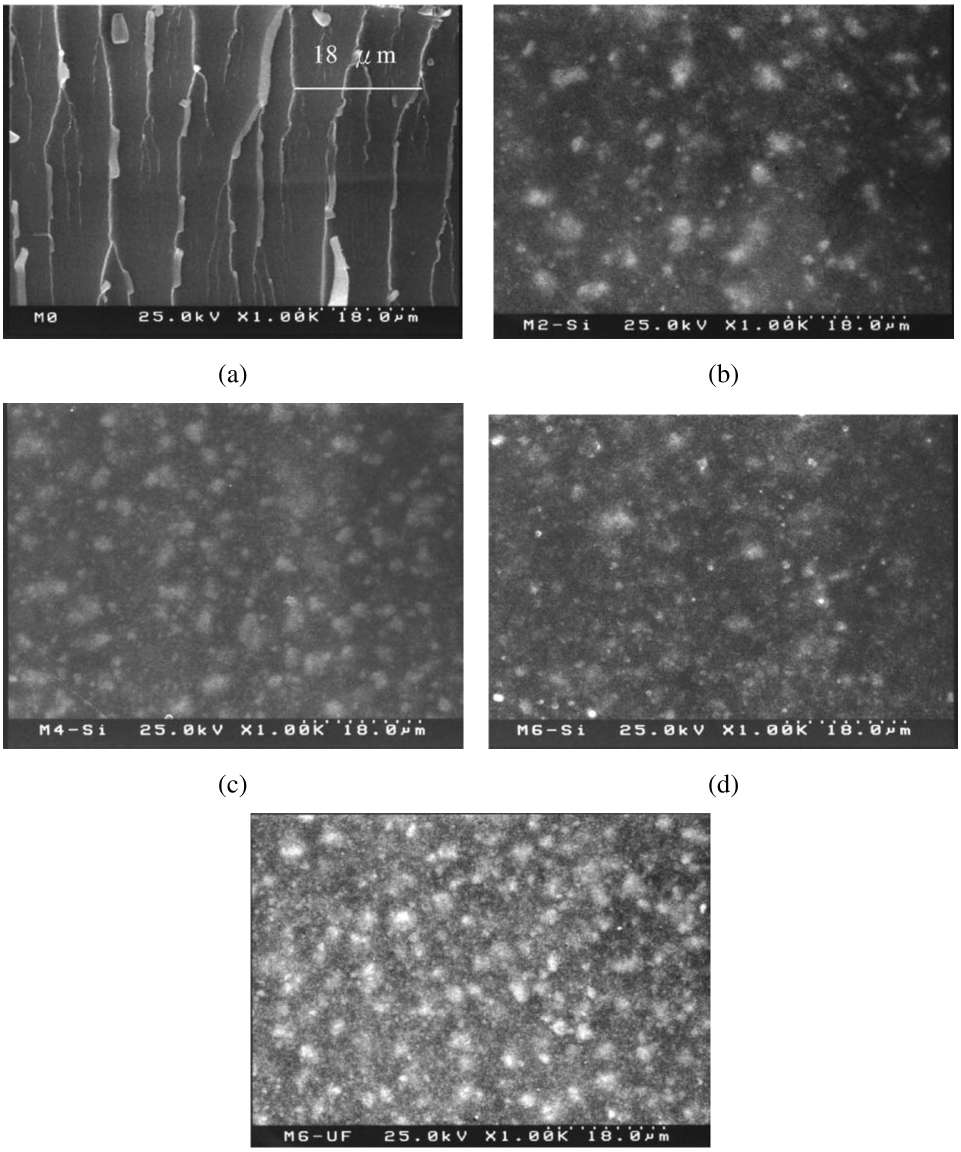
Table 3. LOI values and phosphorus contents of the DGEBA-MP and the DGEBA-DDM-MP systems

Code	Phosphorous content (%)	LOI
Neat epoxy (DGEBA-DDM)	0	19
R5	1.1	29
R10	2.1	30
R20	3.9	33
R30	5.5	34
A5	0.65	22
A10	1.95	24
A20	3.02	26
A30	4.13	29

lower exothermicity of the pyrolysis reaction, and lower thermal conductivity of the burning material.

Flame Retardation

The flame retardant properties of the obtained epoxy resin were determined by measuring the LOI of the resin. Table 3 shows the effect that phosphorus content (%) has on the value of the LOI. The LOI range of the DGEBA-MP system is from 29 to 34 even at a low phosphorus-content while the LOI range of the DGEBA-DDM-MP system is from 22 to 29. In DGEBA-DDM-MP system, the value of LOI of the DGEBA-DDM-MP increases upon this increase of MP content. Since melamine pyrophosphate (1/2 melamine $H_4P_2O_7$, MPP) was formed from melamine phosphate at high temperatures [21] and phosphoric acid is a strong acid that promotes the char formation [43]. MPP reacts with oxygen to produce carbon dioxide, steam, NO_2



(a) (b)

(c) (d)

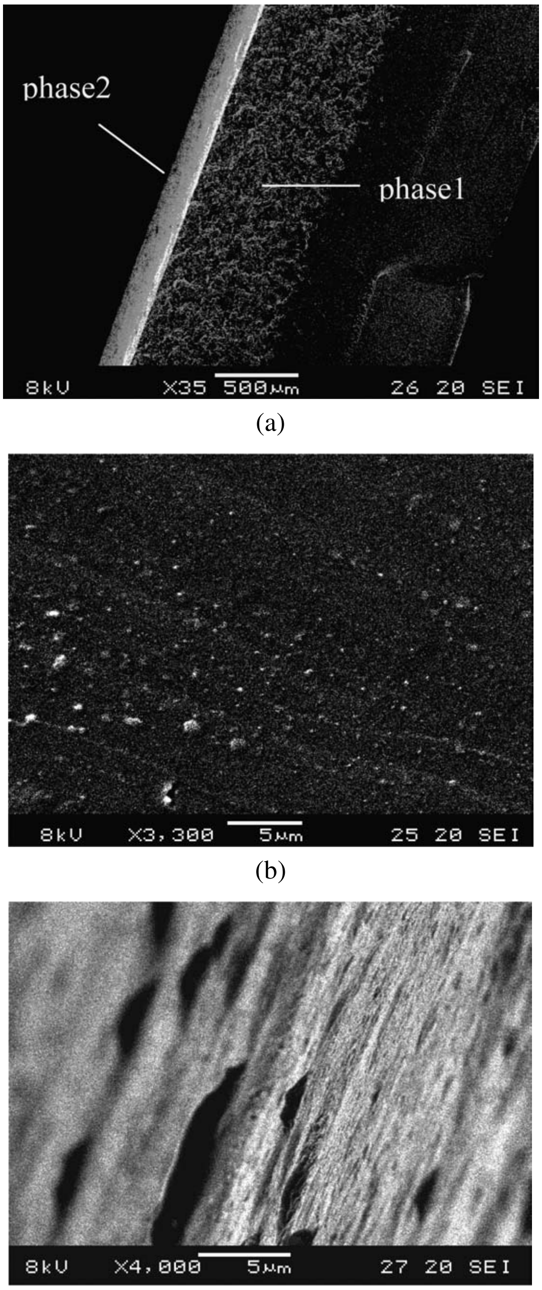
(e)

Figure 8. SEM micrograph of the fracture of: (a) A0; (b) A5; (c) A10; (d) A20; (e) A30.

and P_2O_5. Since the carbon dioxide is a non-flammable gas, the evolved CO_2 tends to dilute the oxygen concentration of the surrounding air above the burning surface, and the steam is able to lower the temperature of fire field. The high density and vitric thin film from the reaction between P_2O_5 and NO_2 results in a P–N synergism effect [21] and yields an intumescent film to protect the matrix from further combustion. In other way, MPP had higher phosphorus content than MP and gave a proportionately larger yield of the $(PNO)_x$ and the $(PNO)_x$ was a very thermal stable crosslinked polymer containing both phosphorus and nitrogen compounds to cover on substrate then protect the matrix from further combustion [35, 36]. In DGEBA-MP system, the weak –P–O–C bond decomposed at lower temperature than DGEBA-DDM-MP system (TGA results) to form thermal stable phosphorus-rich compounds to cover on matrix and the melamine decomposed to yield nitrogen at higher temperature. Both phosphorus-rich compounds and nitrogen were combined to yield the intumescent film to protect the matrix from further combustion. Therefore, the value of LOI of DGEBA-MP system is better than DGEBA-DDM-MP system. In this present investigation, we have obtained a higher value of LOI than some other phosphorus-containing epoxy resins [37, 45–47]. Thus, the melamine phosphate is an excellent reactive-type flame retardant for epoxy resins.

Morphology

The morphology of the DGEBA-DDM-MP system was investigated by a scanning electron microscopy (SEM). Figure 8 presents SEM images of the fracture surface of specimens created by freezing in liquid nitrogen. Figure 8(a) shows that a smooth fracture surface is formed from the neat epoxy that lacks any melamine phosphate. Figures 8(b) to 8(e) are SEM micrographs of fracture surfaces of the DGEBA-DDM-MP system where the particle size of the melamine phosphate domain is ca. 1 μm in dimension. The melamine phosphate particles occasionally agglomerate and form large particles that may affect the fracture process by initiating cracks and this phenomenon is increased with increasing the melamine phosphate content. Figure 9 presents SEM images of the fracture surface of specimens of DGEBA-MP system created by freezing in liquid nitrogen. Figure 9(a) is SEM micrographs of fracture surfaces of R5 where two phases revealing. Due to ratio of epoxy ring and amine is less low than stoichiometric ratio of epoxy to amine. Therefore, it presented two phases of R5. Figure 9(b) is SEM micrographs of fracture surface of phase 1 and it shows that a fracture surface is formed from the DGEBA. Figure 9(c) shows that a fracture surface of DGEBA reacted with MP (phase 2) and it presented one phase in SEM micrograph.



(a)

(b)

(c)

Figure 9. SEM micrograph of the fracture of: (a) R5; (b) phase 1; (c) phase 2.

Conclusions

In this investigation, MP was incorporated into epoxy resins and functions as a hardener and flame retardant or additive of the cured epoxy resin. The flame retardation and char yields of the cured epoxy resins containing MP are increasing; the DTG of epoxy resin is reduced at lower phosphorous content. These MP-containing systems demonstrate that the melamine phosphate is an excellent flame retardant for epoxy resin.

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