Synthesis and properties of phosphorus containing copoly(bismaleimide)

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Abstract

In this article, a phosphorus containing bismaleimide **(V)** based on 2-(6-oxido-6H-dibenz ⟨c,e⟩ ⟨1,2⟩6-yl)-1,4-dihydroxy phenylene **(I)** was synthesized and copolymerized with 4,4′-bismaleimidodiphenylmethane **(BMDM)** in various weight ratio (0–33 phr). DSC scans show that the introduction of **V** into **BMDM** has increased the processing window for the resulted copoly(bismaleimide). DMA scans show these cured BMIs exhibit good modulus (~ 2 GPa) up to 400°C. There is no tangent peak for these cured BMIs implying that there is no relaxation below 400°C. TMA scans show introduction of **V** into **BMDM** increase the coefficient of thermal expansion (CTE). However, CTE of these cured BMIs are less than 50 ppm, which is much less than common epoxy. There is no second transition during TMA heating scans up to 440°C, so T_gs of these cured BMIs are higher than 440°C, which is consistent with the DMA measurement. TGA heating scans also indicate that they have high thermal stability and their char yields increase with the content of **V**. Char yields at 800°C shift from 48 to 63 in nitrogen and from 0 to 18 in air when 25 phr of **V** was introduced into **BMDM**. TGA isothermal experiments show that these cured BMIs are thermally more stable in air than in nitrogen below 450°C. Char yields also increase with the content of **V**. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Bismaleimide; 2-(6-oxido-6H-dibenz ⟨c,e⟩ ⟨1,2⟩ oxaphosphorin-6-yl)-1,4-dihydroxy phenylene; 4,4′-bismaleimidodiphenylmethane

1. Introduction

Owing to its high performance-to-cost ratio, excellent processability, balance of thermal, electrical and mechanical properties, bismaleimides (BMIs) have become one of the important high performance thermosetting engineering plastic in various applications such as, multilayer printed circuit boards for large scale computers, advanced composite for aerospace industries, structural adhesives, potting resin, etc. They have epoxy like processing in that they can be cured at low temperature and low pressure. In addition, their composite can be fabricated using traditional autoclave, filament winding, or resin transfer molding techniques. As a result, a wide variety of BMIs had been studied and introduced into the marketplace.

Recently, Sava et al. [1] have reported that the introduction of the ester groups into the backbone of the bismaleimides would benefit solubility and flexibility with little effect on reactivity or thermal stability to the resulted BMIs. Varma et al. [2–4], Mikroyannidis [5–6] and Kumar et. al. [7] had introduced phosphorus group into BMIs and proved their flame retardancy and high thermal stability. Our objective was to incorporate both phosphorus and ester group into BMI hoping to develop a novel fire and heat resistant resin with high char yields and high flame retardancy. Thus, a novel bismaleimide **(V)** with ester and phosphorus group was synthesized and copolymerized with 4,4′-bismaleimidodiphenylmethane **(BMDM)** in various weight ratios (0–33 phr of **V**). The thermal properties of cured BMIs were evaluated by DSC, DMA, TMA and TGA.

2. Experimental section

2.1. Materials

4-Amino benzoic acid (from Acros), maleic anhydride (from Acros), sodium acetate (from TCI), acetic anhydride (from TCI), thionyl chloride (from TCI), chloroform (from Acros) and acetone (from Tedia) were used without further purification. 2-(6-oxido-6H-dibenz ⟨c,e⟩ ⟨1,2⟩ oxaphosphorin-6-yl)-1,4-dihydroxy phenylene **(I)** was synthesized according to the published procedure [8–9]. N, N-dimethylacetamide (from Acros) were purified by distillation under reduced pressure over calcium hydride (from Acros) and stored over molecular sieves. Triethylamine (from Ferak) was distilled before use.

2.2. Synthesis of 4-maleimido benzoic acid (III)

To a well stirred solution of 4-amino benzoic acid

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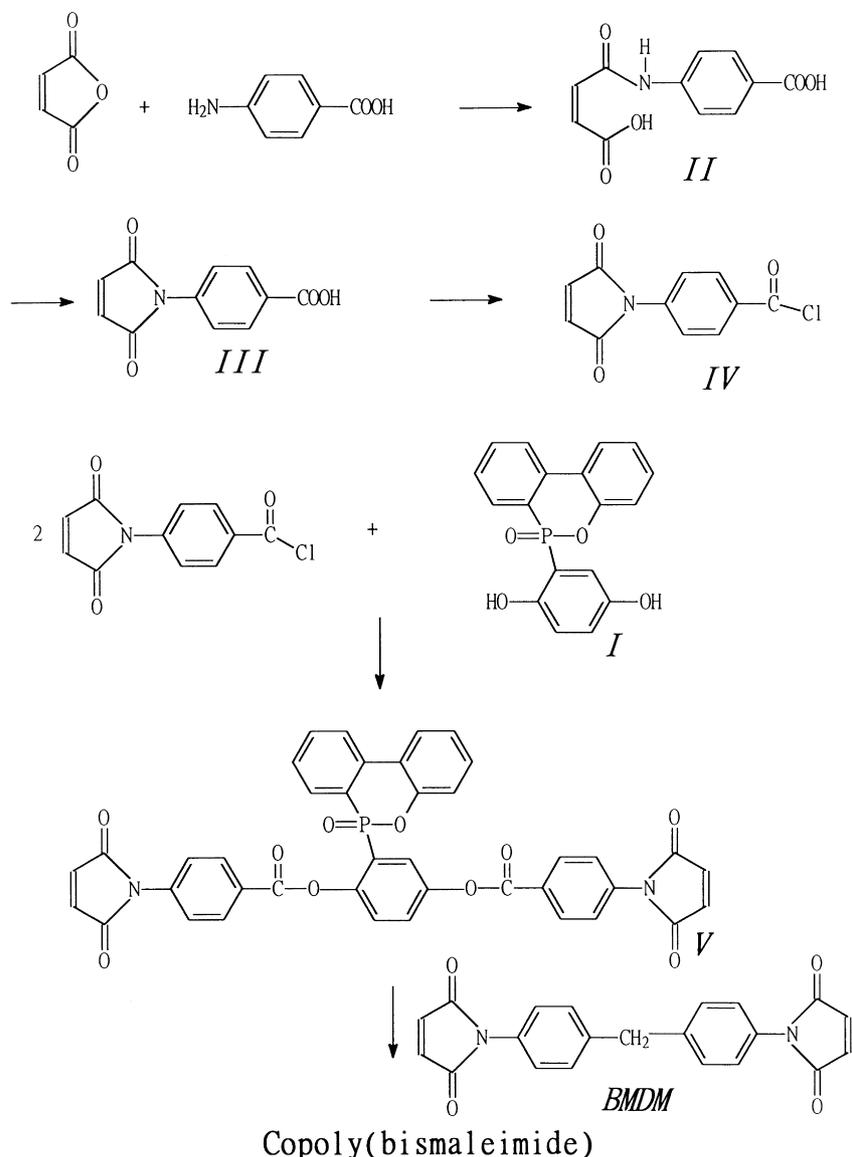
Scheme 1.

(0.3 mol) in 150 ml acetone under nitrogen, maleic anhydride (0.32 mol) in 100 ml acetone was gradually added to the above mixture. An exothermic reaction and product precipitation was observed immediately. The mixture was stirred for 4h at room temperature. The yellow precipitate was collected, washed with fresh acetone to remove excess maleic anhydride, and then dried in vacuum. The yellowish precipitates were purified by recrystallization from DMF/ Ethanol (1/1 wt/wt) solution. Yield: 90%, mp: 244–246°C. Elemental analysis: Calc. %: C, 56.17; H, 3.83; N, 5.96 Found. %: C, 56.07; H, 3.87; N, 5.97. Cyclodehydration of the amic acid (0.1 mol) intermediate to maleimide was carries out by treating with sodium acetate (2.7 g) and acetic anyhydride (30 ml) in DMF (120 ml) for 4 h at a temperature of 65°C. A light yellow precipitate of 4-maleimido benzoic acid was obtained by adding this solution to distilled water. The precipitate was washed several times

with water and then dried at 60°C in vacuum oven. Yield: 81%, mp: 234–236°C. Elemental analysis: Calc. %: C, 60.83; H, 3.23; N, 6.45 Found. %: C, 61.15; H, 3.29; N, 6.55.

2.3. Synthesis of 4-maleimido benzoic acid chloride (IV)

Acid chloride of 4-maleimido benzoic acid was prepared as follows: In a 500 mL round bottom flask, 4-maleimido benzoic acid (0.1 mol) was suspended in 150 ml of toluene under nitrogen with stirring. Five drops of DMF was added as catalyst followed by 200 ml of thionyl chloride then the reaction mixture was heated slowly to 80°C and maintained at 80°C for 3 h. After the reaction was completed, excess thionyl chloride was removed by vacuum distillation. The mixtures were cooled and the yellow products collected by suction filtration.Yield: 60%, mp: 166–169°C. Elemental
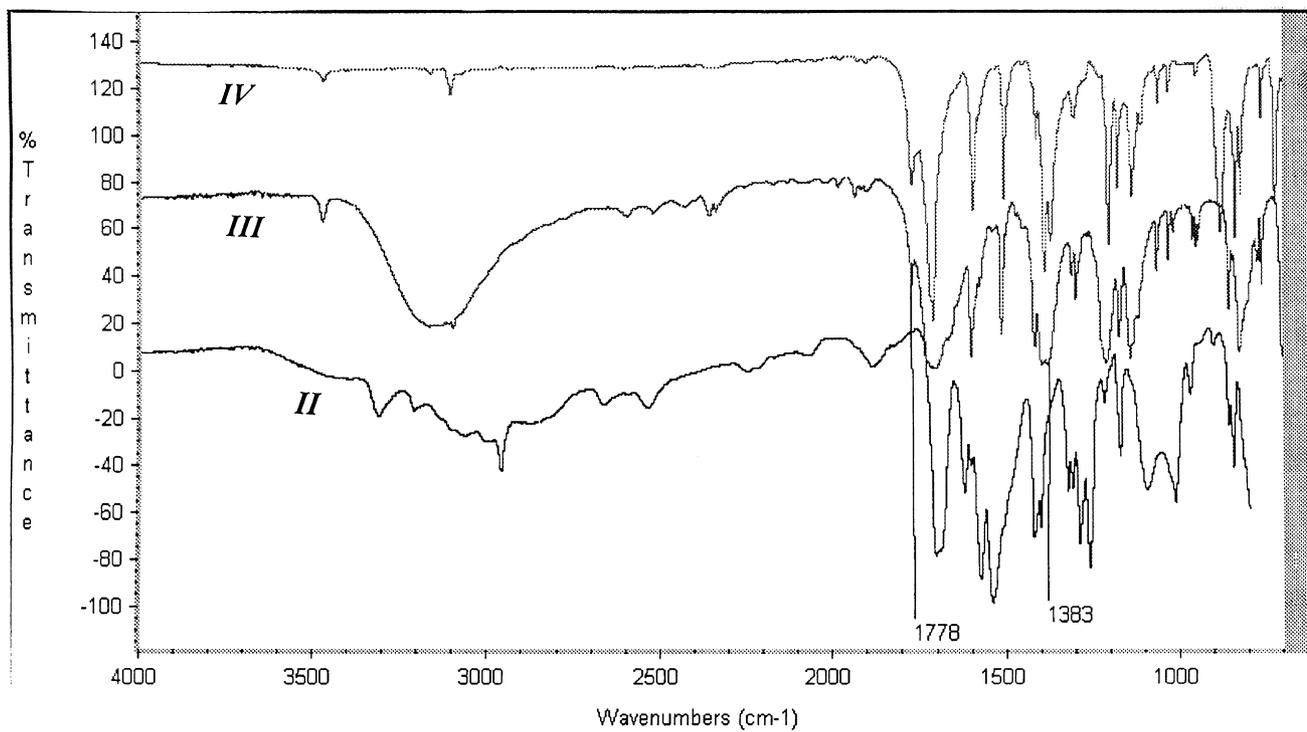
Fig. 1. IR spectra of **II**, **III** and **IV**.

analysis: Calc. %: C, 56.05; H, 2.55; N, 5.94 Found. %: C, 56.37; H, 2.60; N, 5.98.

2.4. Synthesis of bismaleimide (V)

To a 250 ml round bottom flask cooled in an ice bath was added 2-(6-oxido-6H-dibenz ⟨c,e⟩ ⟨1,2⟩ oxaphosphorin-6-yl)-1,4-dihydroxy phenylene (**I**) (0.04 mol), N, N-dimethylacetamide 150 ml and triethylamine (0.084 mol) as an acid acceptor. 4-maleimido benzoic acid chloride (0.082 mol) in 90 ml N, N-dimethylacetamide was added dropwise over 30 min. After stirring for 2 h, the mixture was poured into 400 ml water and the precipitate was filtered and washed with methanol then and dried in a vacuum oven at 80°C for 2 day. Yield: 80%, mp: 281–283°C. Elemental analysis: Calc. %: C, 66.48; H, 3.19; N, 3.88 Found. %: C, 65.97; H, 3.27; N, 3.89.

2.5. Preparation of copoly(bismaleimides)

Various weight of V (0–33 phr to total mixture) was mixed separately with **BMDM** in aluminum pans. The mixtures (about 3 g) each were heated to 180°C with continuous stirring until homogeneous melts were obtained. They were cured at 200°C 4 h, 250°C 2 h and 280°C for 0.5 h in an oven.

2.6. Measurements

The IR spectra were measured with a Nicolet 520 spectrometer. DSC scans were obtained with 5 mg (well mixed powder) sample in a nitrogen or an air atmosphere at a 20°C/min heating rate using a Perkin-Elmer DSC 7. Thermal gravimetric analyses were employed with a Perkin-Elmer TGA 7 at a heating rate of 20°C/min in a nitrogen atmosphere from 30°C to 850°C. Dynamic mechanical analysis was carried out by Perkin-Elmer DMA 7 with a 10°C/min heating rate at a frequency of 1 HZ. Specimen 10 mm in length, 10 mm in width, and approximately 1.2 mm in thickness was used for a tension-amplitude mode, and the amplitude is 10 um.

3. Results and discussion

3.1. IR analysis

Monomer **II, III** and **IV** were synthesized according to the method described by Mikroyannidis [10] with some modification. Their structures were shown in Scheme 1. Fig. 1 shows IR spectrum of **II, III**, and **IV**. Monomer **II** show the characteristic absorption bands around 3313 cm^{-1} (N–H) and a broad absorption at 2500–3500 owing to two acid group (O=C–OH). Cyclodehydration of **II** can be monitored by the appearance of band 1778 cm^{-1} and 1383 cm^{-1}, which result from the imide structure. The disappearance of acid group (3200 cm^{-1} board) in **IV** implies that the acid group was converted to acid chloride group. Phosphorus containing BMI **V** was synthesized by a simple condensation of 4-maleimido benzoic acid chloride (**IV**) with a phosphorus containing diol (**I**). The reaction
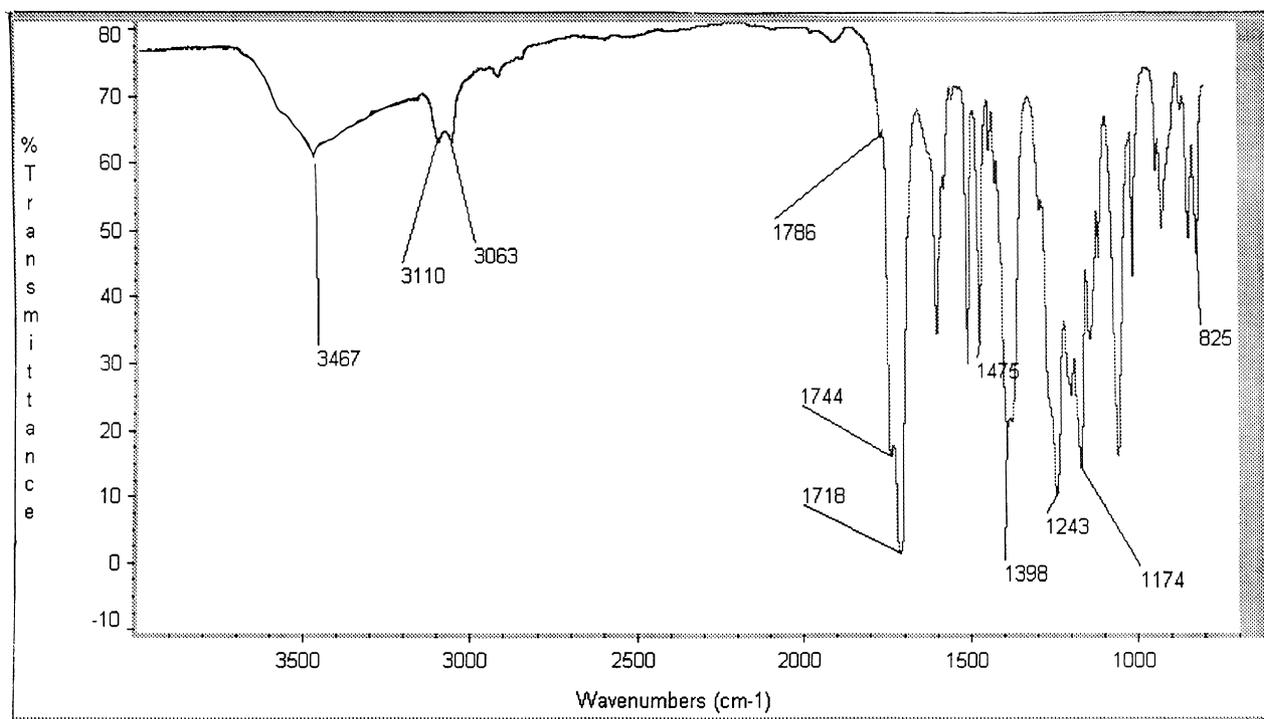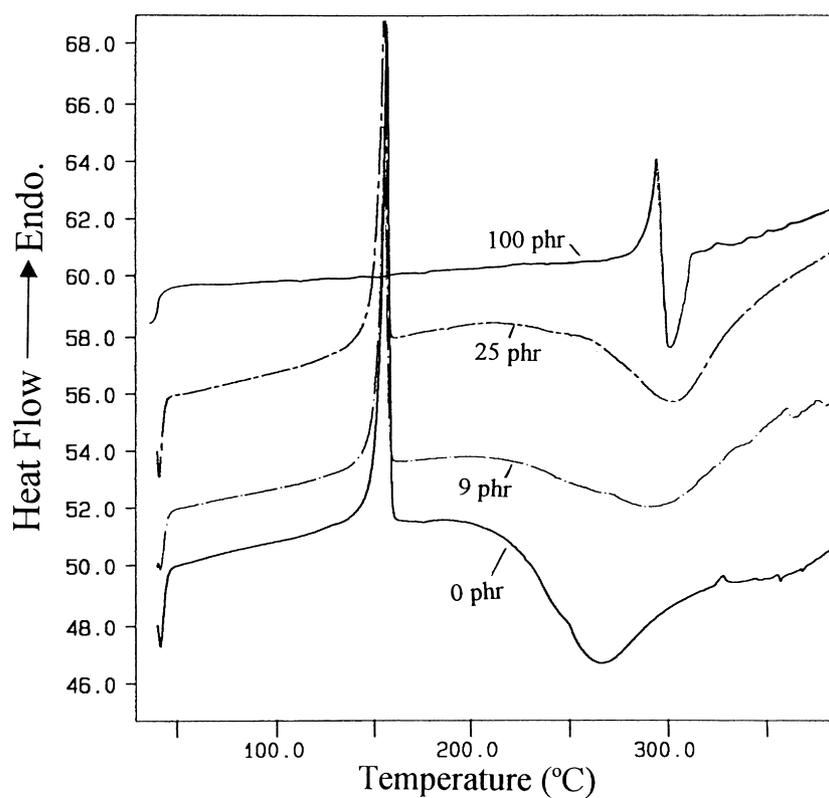
Fig. 2. IR spectrum of **V**.

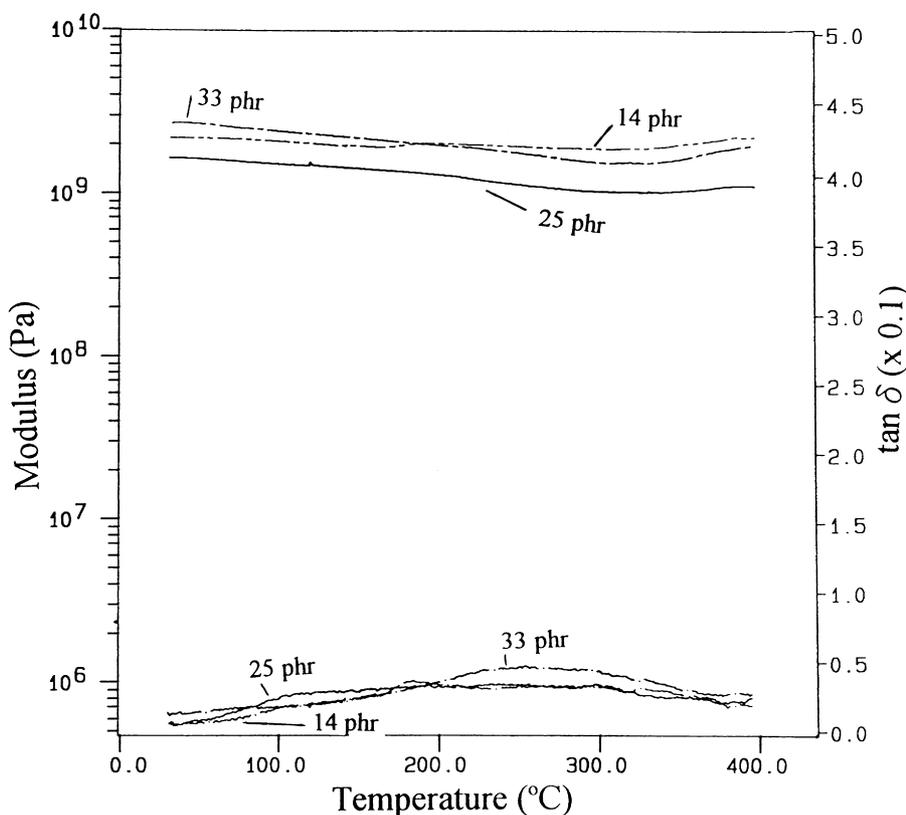Fig. 3. DSC traces of some BMIs (0, 9, 25 and 100 phr of **V**).

Fig. 4. DMA traces of some BMIs (14, 25 and 33 phr of **V**).

occurred immediately after **IV** was added dropwise at 0°C because ET_3NHCl derived from HCl and triethylamine was observed. IR spectrum of **V** is shown in Fig. 2. The characteristic peaks are at $3467\ cm^{-1}$ (C=O overtone) [11], $3110\ cm^{-1}$ (C–H maleimide), $3063\ cm^{-1}$ (aromatic H), $1786\ cm^{-1}$ (C=O, out of phase), $1744\ cm^{-1}$ (C=O, aromatic ester), $1718\ cm^{-1}$ (C=O, inphase), $1475\ cm^{-1}$ (P–Ph), $1398\ cm^{-1}$ (C–N–C), $1243\ cm^{-1}$ (P=O) and $1174\ cm^{-1}$ (P–O–Ar). A strong band at $825\ cm^{-1}$ owing to the out-of-plane hydrogen deformation of a *cis*-disubstituted double bond of the maleimide group conjugated with the carbonyl group is observed. These characteristic peaks were consistent with the structure of **V**.

3.2. DSC analysis

DSC traces of some BMIs (0, 9, 25 and 100 phr of *V*) are given in Fig. 3. For **BMDM,** a sharp endothermic melting peak (T_m) at 152°C is owing to the melting of **BMDM,** an exothermic transition (T_i) starts at 198°C is because of the curing reaction with a maximum reaction rate temperature (T_{max}) at about 270°C. The processing window ($T_i - T_m$) is about 46°C. However, **V** is polymerized immediately after being melted, because of the small difference between the melting point (T_m) and the onset temperature for the curing reaction (T_i). As a result, it is difficult to maintain the uncured resins in a fluid state. During the polymerization process, the viscosity of the resin quickly increases which

traps air bubbles easily and lead to processing difficulties. Owing to its high melting point and rapid curing reaction, **V** will be difficult to use alone for practical applications. Thus, **V** was blend with **BMDM** in this study. The introduction of **V** into **BMDM** has made the melting point of **BMDM** lower slightly and has shifted T_i and T_{max} to higher temperatures and results in an increase of the processing window ($T_i - T_m$). Mellissaris and Mikroyannidis [12] has been reported that the exotherm was shifted to a higher temperature as the length and the formula weight of the bridge between the maleimide group was increased. Since **V** has a longer length between two maleimide group than that of **BMDM**, it is reasonable that the introduction of **V** into **BMDM** will shift the curing exotherms to higher temperatures.

3.3. DMA analysis

T_gs of the crosslinked resins could not be detected by DSC, this could be attributed to the fact that the resin was highly crosslink and the change in C_p was very small, so we detect T_g of these BMIs by DMA. Generally, in a DMA measurement, the peak of tan δ is identified as the glass transition temperature because a large decrease in G' occurs at this point. However, as shown in Fig. 4, there are no tangent peaks for these cured BMIs implying that there are no relaxations below 400°C, that is, T_gs of these cured BMIs are higher than 400°C. These cured BMIs exhibit good modulus (~ 2 GPa) up to 400°C, therefore, these
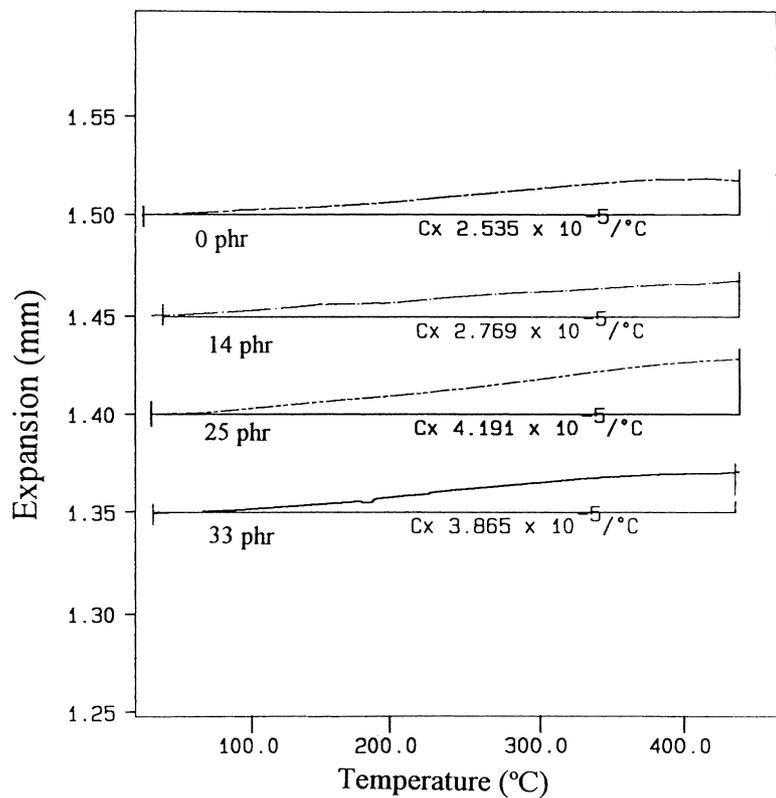
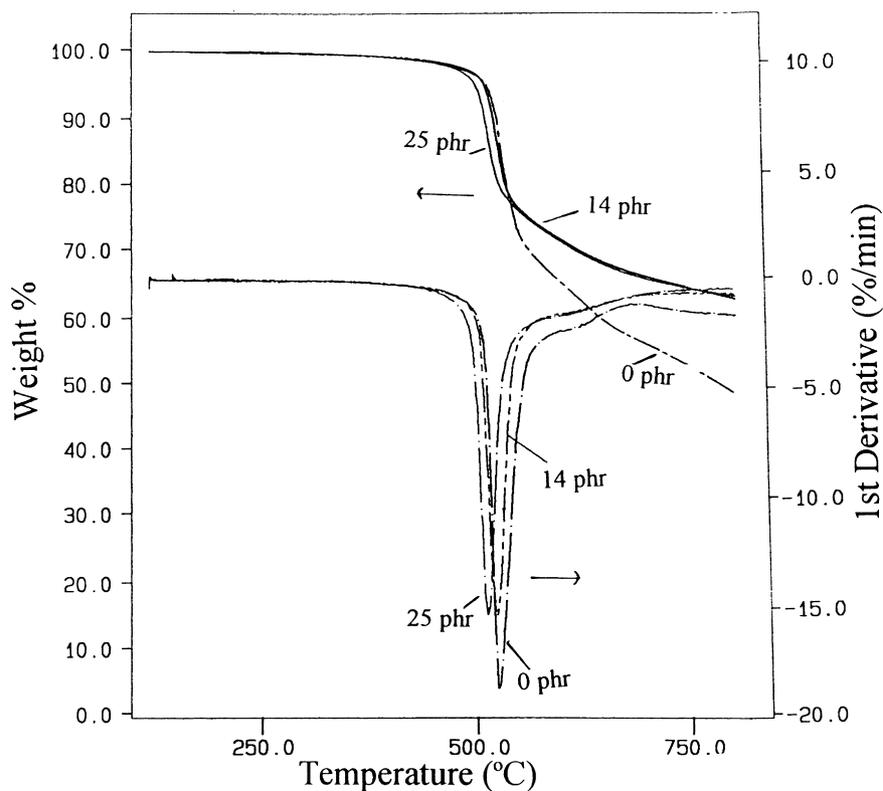Fig. 5. TMA traces of some BMIs (0, 14, 25 and 33 phr of **V**).

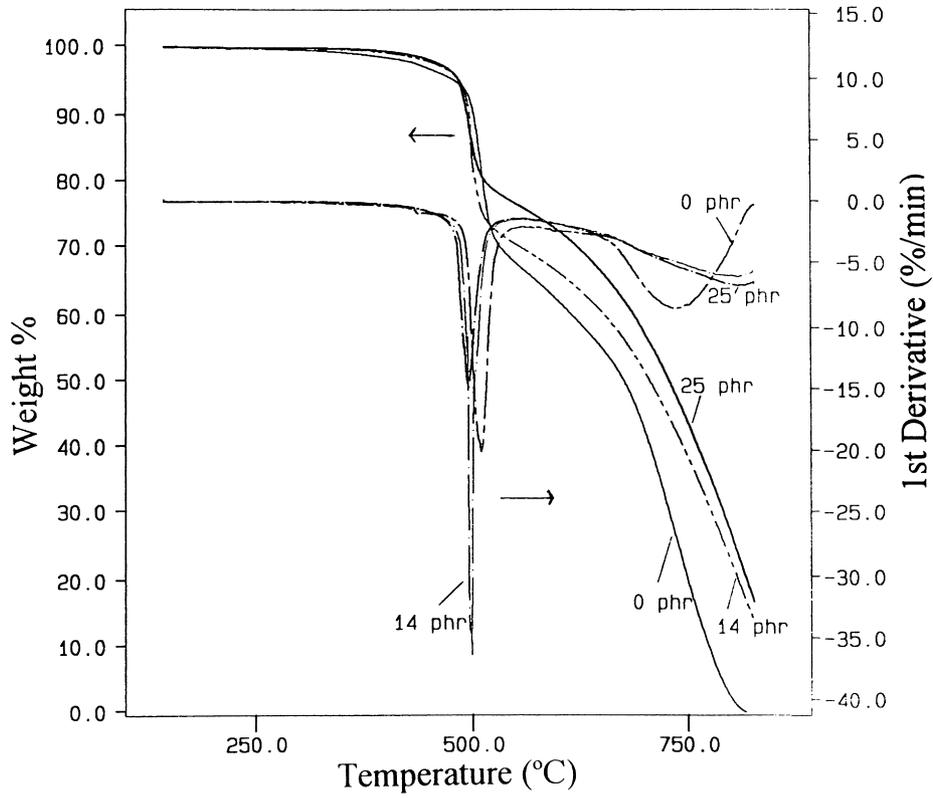Fig. 6. Thermal degradation (under nitrogen) curves of some BMIs (0, 14 and 25 phr of **V**).

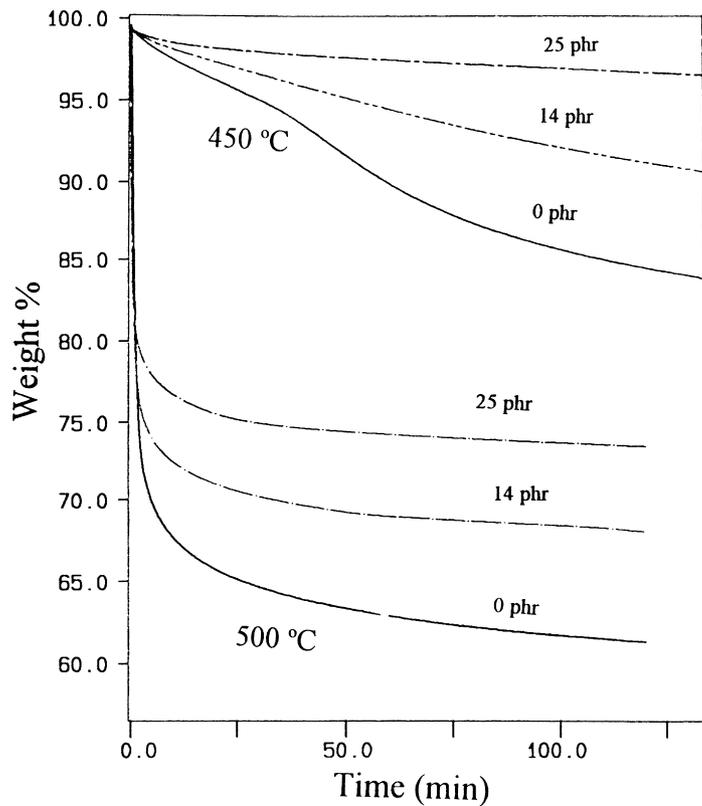Fig. 7. Thermooxidative degradation (under air) curves of some BMIs (0, 14 and 25 phr of **V**).

Fig. 8. TGA isothermal traces of some BMIs (0, 14 and 25 phr of **V**) at 450 and 550°C under nitrogen.
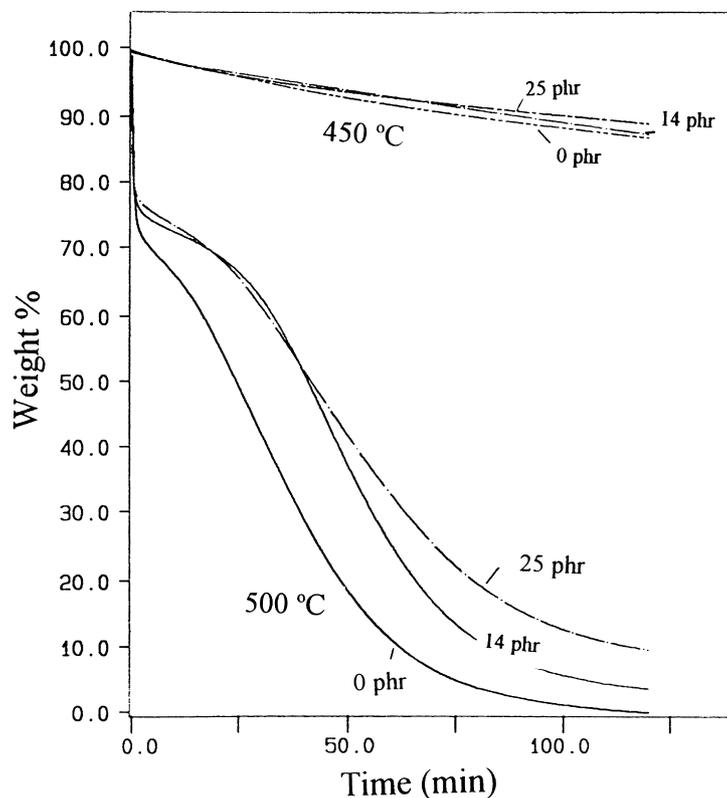
Fig. 9. TGA isothermal traces of some BMIs (0, 14 and 25 phr of **V**) at 450 and 550°C under air.

cured BMIs have use temperature up to 400°C without loss in their mechanical properties.

3.4. TMA analysis

Thermally induced dimensional change of these cured BMIs was investigated by a thermomechanical analyzer. TMA traces of some cured BMIs are shown in Fig. 5. Thermal expansion coefficients of these cured BMIs are about 25–50 ppm and increase with the amount of **V**. This may be because of the introduction of **V** into **BMDM** has decreased its crosslink density. Since **V** has longer length between two maleimide group than that of **BMDM**, it is reasonable that the introduction of **V** into **BMDM** will decrease its cross-link-density and increase free volume of resins, thus increase the thermal expansion coefficient. However, CTEs of these cured BMIs are less than 50 ppm, which is much less than that of common epoxy. Since there is no second transition during TMA heating scans, T_gs of these cured BMIs are higher than 440°C, which is consistent with the DMA measurement.

3.5. TGA analysis

TGA is the most favored technique for the rapid evaluation of the thermal stability of polymeric materials. It is especially useful in comparing and ranking the thermal stabilities of various polymers. Thermogravimetric analyses of the cured samples were carried out in nitrogen and air,

respectively. Fig. 6 and 7 show the thermal degradation (under nitrogen atmosphere) and thermooxidative degradation (under air atmosphere) curves of some cured BMIs. From Fig. 6 and 7, one can see the decomposition temperatures of these cured BMIs are about 500°C. The decomposition temperatures of these BMIs under air or nitrogen are very close, which implies that these cured BMIs are quit resistant to thermooxidative degradation. From 1st derivative curves shown in Fig. 7, cured **BMDM** has a decomposition peak at about 750°C while the decomposition peaks become broad and shift to higher temperatures (about 850°C) for phosphorus-containing cured BMIs. Char yields at 800°C in nitrogen shift from 48 to 63 in nitrogen and from 0 to ∼ 18 in air when 25 phr of **V** was introduced into **BMDM**. Fig. 8 and 9 show TGA isothermal traces of some cured BMIs at 450 and 550°C under nitrogen and air, respectively. As shown in Fig. 8 and 9, when isothermally at 450°C, these cured BMIs show similar degradation behavior in air, while in nitrogen, phosphorus containing cured BMIs show better thermal resistance. When isothermally at 550°C, thermal oxidation occurs, which causes further degradation of these cured BMIs. However, phosphorus-containing cured BMIs still have higher char yields than cured **BMDM** itself. An important phenomenon is observed when they are isothermal at 450°C: these cured BMIs are more thermally stable in air than in nitrogen. Torrecillas et al. [13] had reported similar results and attributed this phenomenon to the formation of an oxidized

protective layers at the surface of these cured BMIs, which act as a barrier against oxygen diffusion. Van Krevelen [14] had proposed that the char residue on pyrolysis is linearly proportional to the oxygen index of halogen-free polymers. Increasing char formation can limit the production of combustible gases, decrease the exothermicity of the pyrolysis reaction and the thermal conductivity of the burning materials, and consequently limit the flammability of the materials. Thus, the incorporation of **V** into **BMDM** is beneficial to the flame retardancy.

4. Conclusion

A phosphorus containing bismaleimide based on 2-(6-oxido-6H-dibenz ⟨c,e⟩ ⟨1,2⟩ oxaphosphorin-6-yl)-1,4-dihydroxy phenylene (**I**) was synthesized and copolymerized with **BMDM**. IR and elemental analyses confirm these monomers. DSC scans show introduction of **V** into **BMDM** increases the processing window. DMA scans show these cured BMIs exhibit good modulus (∼ 2 GPa) up to 400°C. There is no tangent peak for these cured BMIs in DMA implying that there is no relaxation below 400°C. TMA scans show introduction of **V** into **BMDM** increases the CTE. Since **V** has longer length between two maleimide group than that of **BMDM**, the introduction of **V** into **BMDM** will decrease its crosslink-density and increase

free volume of resins, thus increase the thermal expansion coefficient of these cured BMIs. TGA heating scans show that these cured BMIs have high thermal stability and their char yields increase with the content of **V**. These properties should make these cured BMIs attractive for practical applications.

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