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Phosphorus-containing diamine for flame retardancy of high functionality epoxy resins. Part II. The thermal and mechanical properties of mixed amine systems

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Abstract

Bis(4-aminophenoxy)phenyl phosphonate (BAPP) was used in various ratios in combination with diethyltoluenediamine (DETDA) to investigate the effect of increasing phosphorous addition upon the thermal and mechanical properties of diglycidyl ether of bisphenol A (DGEBA) and tetra glycidyl dimethylenedianiline (TGDDM) based epoxy networks. Increasing phosphorous content was shown to decrease the temperature of the initial onset of degradation, while the char yield at 540 °C increased in both the nitrogen and air atmosphere. At 700 °C, however, the char formation was shown to be dependent upon the atmosphere with an oxidative environment promoting further chain scission, while a non-oxidative environment promoted char formation through crosslinking reactions. Increasing phosphorous content was found to produce only modest decreases in the glass transition temperatures, while no significant deleterious effects upon the mechanical and physical properties such as flexural properties and CTE were observed.

Keywords: Epoxy resin; Phosphorous; Flammability

1. Introduction

In the modern polymer industry, epoxy resins are widely used as encapsulating materials in the electronic/electrical industries and advanced composite matrices for structural laminates, owing to their high tensile strength and modulus, good chemical and corrosion resistance and excellent dimensional stability [1,2]. The main drawback of epoxy resins, like other organic polymer materials, is their flammability. Although brominated compounds can be blended into epoxy resins to improve their flame retardancy, the generation of toxic, corrosive gases produced during combustion is increasingly an area of concern to environmental legislators. As a result of this there is a need to develop more environmentally benign, halogen-free fire retardants [3,4]. As an alternative to simply adding or blending high levels of a non-reactive fire retardant to a polymer, lower levels of fire retardant can be used by incorporating them into the polymer backbone if they have reactive species, which allow this to occur. This enables lower levels of fire retardant to be used, which generally will have less of a deleterious effect upon the physical and mechanical properties of epoxy resins [5,6]. Of this class of additive, reactive organo-phosphorus compounds have been shown to have a powerful flame retardant effect and, in the case of epoxy resins, can be incorporated into the backbone of the network either through being part of the amine hardener or the epoxy itself [7–18].

When compared to phosphorus-free epoxy resins, phosphorus-containing epoxy resins show a lower thermal stability, with a reduced initial decomposition temperature, but exhibit a multi-step degradation with a higher final char yield. During the first degradation step, a thermally stable char is formed and serves as an outer layer to prevent the further degradation of the bulk and thus improve the flame retardancy. Recent work in the literature for systems where the phosphorous species was incorporated into the network via a pre-reaction step with a commercial epoxy resin, substantial decreases in T_g compared to the non-phosphorous species were observed [7–11,16] due to an inevitable decrease in crosslink density as a result of attaching the phosphorous species to a reactive epoxide functional group. Other systems which reported the use of

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bulky phosphorous containing groups in curing agents derived from phenol novolac [12–14], also tended to show a decrease in T_g. When phosphorus-containing diamines have also been used as curing agents for epoxy resins [15–18], they have also tended to report low T_gs. While most of the work reported in the literature to date has focused on the thermal and flame retardant properties of phosphorus-containing epoxy resins, reports upon the effects on the physical and mechanical properties of the network are less common. Bis(4-aminophenoxy)phenyl phosphonate (BAPP) is an example of one such amine that has been synthesized and used as a curing agent for commercial, high-functionality epoxy resins [17–19]. While BAPP is a more reactive hardener in comparison to the commercially important hardeners used in the aerospace industry, diamino diphenyl sulphone (DDS) and diethyl toluene diamine (DETDA), its predominantly aromatic structure provides potential for physical and mechanical properties to be comparable to those systems. The use of BAPP as a hardener gives rise, therefore, to the possibility of producing materials with improvement in fire performance while having properties suitable for aerospace applications.

This paper seeks to investigate the effect of varying the blend ratio of the hardener systems BAPP and DETDA, to determine whether an optimum balance of properties can be achieved which maximizes processability and properties. Further to this providing information concerning the likely impact upon fire performance through understanding the degradation process is also a priority in this paper. In this work, BAPP was used in combination with DETDA as the curing agents for two resins, diglycidyl ether of bisphenol A (DGEBA) and tetra glycidyl dimethylenedianiline (TGDDM). The thermal degradative properties were studied by using thermogravimetric analysis (TGA), molecular relaxations (glass transition) were studied using dynamic mechanical thermal analysis (DMTA), coefficients of thermal expansions (CTE) were determined using thermomechanical analysis (TMA) and mechanical properties were determined using a three-point bend test.

2. Experimental

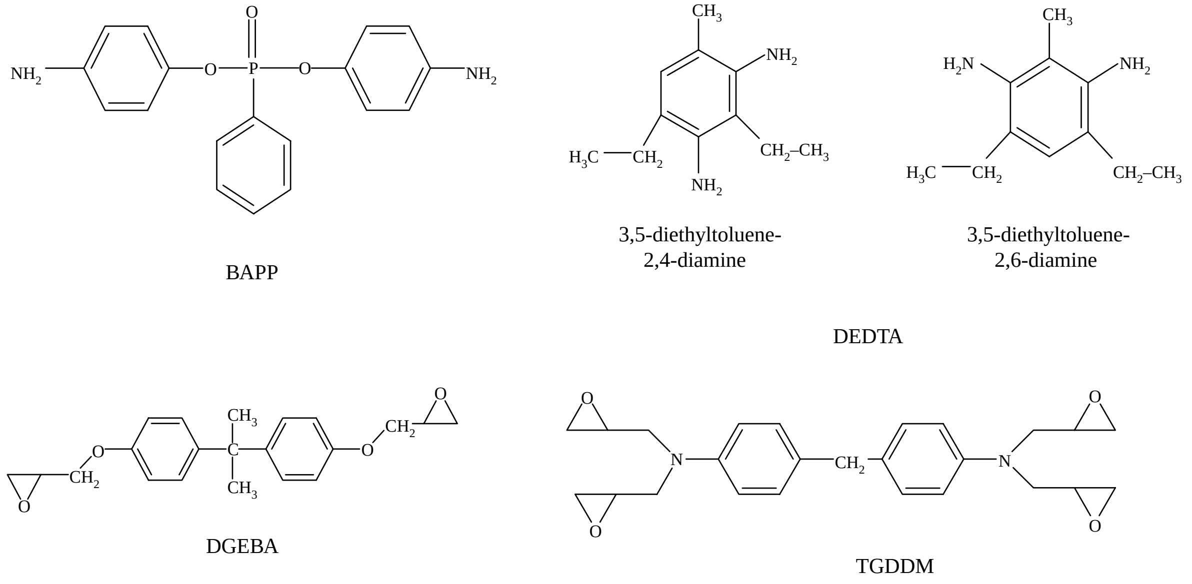
2.1. Materials

Two epoxide products, DGEBA and TGDDM, were obtained from Vantico, Australia, the epoxide equivalent weights (EEW) being 189.7 and 105.5 g/epoxide, respectively. BAPP was synthesized and purified according to the method previously reported [19]. The other amine used, diethyltoluenediamine (DETDA), is a mixture of two isomers of 3,5-diethyltoluene-2,4-diamine (75–81%) and 3,5-diethyltoluene-2,6-diamine (18–20%). and purchased from Albemarle Co. (USA) and used without further purification. The structures of BAPP, DETDA, DGEBA and TGDDM are shown in Scheme 1.

2.2. Characterization

Thermogravimetric analysis (TGA) was carried out with a Mettler Toledo TGA/SDTA 851E in both the air and nitrogen atmosphere, respectively. A sample of approximately 15 mg was sent for the measurement under the flow rate at 50 ml/min and a heating rate of 10 °C/min.

Dynamic mechanical thermal analysis (DMTA) was undertaken using a Rheometric Scientific DMTA MkIV. A sample of 40 mm in length, 10 mm in width and approximately 2 mm in thickness was used. The test method was performed using the dual cantilever bend mode, with strains set at 0.1%. The storage modulus G', loss modulus G'' and tan δ were determined as the solid sample was subjected to temperature scan mode at a ramping rate of 2 °C/min from 25 to 280 °C, at a frequency of 1 Hz. The glass transition (T_g) was determined as the peak temperature of the tan δ plot.



Scheme 1. Chemical structure of the materials used in this work.

Thermomechanical (thermal expansion) analysis (TMA) was carried out with a Perkin–Elmer DMA7 with a heating rate of 5 °C/min from 40 to 250 °C, in a helium environment, with a flow rate of 40 ml/min. A cubic sample approximately 5 mm in length was used. The coefficients of linear thermal expansion (CTE) in both the glassy and rubbery state were calculated from the slope of the thermal expansion curve before and after glass transition, respectively.

Flexural mechanical testing was carried out using a Miniature Materials Tester MiniMat 2000. A three-point loading mode was used, with a support span of 18 mm. A sample of 32 mm in length, 9 mm in width and approximately 1.5 mm in thickness was placed in the device, and deformed by a crosshead at a rate of 0.3 mm/min.

2.3. Preparation of epoxy resins

The curing agents BAPP and DETDA were combined in various equivalent ratios to determine the effect of phosphorus-containing structures on the thermal and mechanical properties. The epoxide products were mixed with the stoichiometric concentrations curing agents at 80 °C and the curing cycle set at 100 °C 2 h, 120 °C 2 h and 175 °C 4 h. A postcure procedure was carried out at 200 °C for 2 h. From previous kinetics studies on these systems, using near infra-red spectroscopy [20] and differential scanning calorimetry [19], the BAPP hardener was known to promote faster cure (through a strongly autocatalytic reaction mechanism), than other aromatic amine hardeners such as diamino diphenyl sulphone or diethyl toluene diamine. As a result of this, and to avoid the possibility of an uncontrolled exotherm, the cure profile was deliberately chosen to being at a low temperature and gradually increases to a temperature typical of high performance systems. The abbreviated sample name and used for all of the samples prepared, for example, DGEBA-70-30, indicates that DGEBA was the epoxy resin used, and the molar ratio between DETDA and BAPP was 70:30. Table 1 lists the formulations prepared and the level of phosphorous that was present in each of the formulations.

3. Results and discussion

3.1. TGA analysis of cured epoxy resins

The manner in which a sample loses mass with increasing temperature as measured using TGA provides direct information about the thermal stability and the degradation mechanism. Depending upon the fire retardancy mechanism that is operating, (in this case largely related to the formation of a char layer) it also provides indirect information about the potential flame retardancy of the cured epoxy resin system. The TGA curves of the DGEBA series performed under both a nitrogen and in an air atmosphere are, therefore, shown in Figs. 1 and 2, respectively.

The TGA traces for the DGEBA series in the non-oxidative nitrogen environment exhibited a mass loss via a single large decrease from 400 to 500 °C, after which the rate of mass loss decreases substantially. The effect of increasing phosphorous content in the cured resin system is shown through (1) a decrease in the onset temperature, (2) increasing evidence of a bimodal process and (3) an increasing char yield at 700 °C. The two degradation steps for the phosphorous containing systems occurred from about 320 to 380 °C, and then from about 380 to 500 °C. In the case of the DGEBA series, degradation in air/oxidative environment shows a more complicated behaviour. The thermogram shown in Fig. 2, again shows a decrease in the onset temperature of degradation with increasing phosphorous content, although a multi-step process is clearly evident, similar to the 3–4 step process as reported by Bellenger et al. [21] for the oxidative degradation of epoxy resins. Following initial degradation resulting in an approximately 50% decrease in mass, there is a region from around 400 to 550 °C where the mass continues to decrease, but at a reduced rate. This region of intermediate thermal stability reflects the thermal stability of the char layer formed during oxidative degradation. The increased rate of mass loss beyond 550 °C illustrates the continued degradation of the char layer and the variations in rate and final yields point to the effect of increased phosphorous addition upon the network.

The char yields for the DGEBA series in nitrogen at 700 °C and in air at 540 and 700 °C are, therefore, shown in Fig. 3,

Table 1
Parameters derived from dynamic mechanical and thermomechanical measurements on the TGDDM and DGEBA cured network series

Sample ID	P (%)	T_g (°C)	Height of tan δ	CTE$_g$ ($\times10^{-6}$) (°C^{-1})	CTE$_r$ ($\times10^{-6}$) (°C^{-1})	CTE$_f$ ($\times10^{-6}$) (°C^{-1})
DGEBA-100-0	0	203	0.654	79.99	166.85	86.85
DGEBA-90-10	0.33	197	0.518	74.45	167.78	93.33
DGEBA-70-30	0.94	186	0.609	72.76	170.72	97.97
DGEBA-50-50	1.52	176	0.640	69.44	168.20	98.76
DGEBA-30-70	2.07	176	0.689	67.62	172.86	105.24
DGEBA-0-100	2.82	176	0.754	65.12	156.79	91.67
TGDDM-100-0	0	239	0.481	66.89	153.18	86.29
TGDDM-90-10	0.5	232	0.425	61.08	173.50	112.42
TGDDM-70-30	1.43	237	0.456	60.04	170.23	110.19
TGDDM-50-50	2.27	240	0.441	59.71	178.44	118.72
TGDDM-30-70	3.04	237	0.403	55.30	157.78	102.48
TGDDM-0-100	4.06	232	0.362	56.66	164.02	107.36

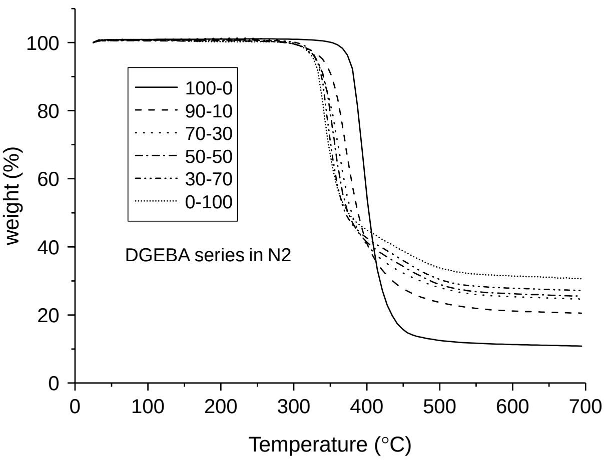


Fig. 1. Thermogravimetric analysis of the DGEBA series showing the effect of increasing phosphorous content in a nitrogen atmosphere on the decomposition mechanism.

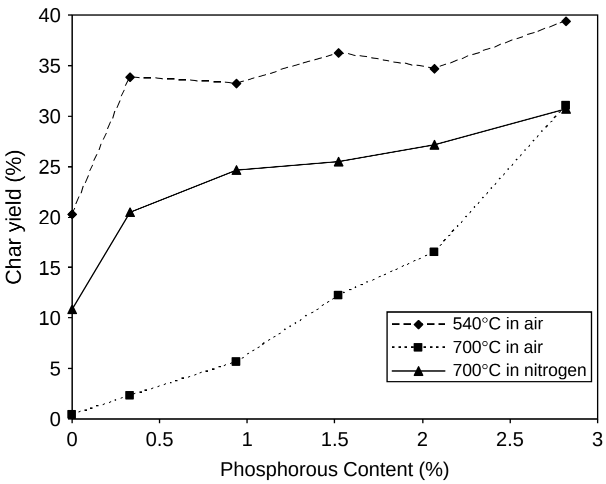


Fig. 3. Effect of increasing phosphorous content on the char yield in nitrogen and air atmospheres as determined using TGA for the DGEBA series of resin systems.

which shows clearly the effect of increasing phosphorous content. In the nitrogen atmosphere at 700 °C, the char yield increased sharply from 10.8 to 30.6%, as the phosphorus content increases from 0 to 2.82%. In an air or oxidative environment after the initial degradation (or char formation) step at 540 °C, the char yield was quite constant at around 35%. Also, at 700 °C in an oxidative environment, the char yield increased gradually to 31% as the phosphorus content increased to 2.82%. As can be seen, at 540 °C, the char yield in air is significantly higher than the char yield in nitrogen at 700 °C (or 540 °C), while conversely at 700 °C in air, the char yield is well below that of the char yield at 700 °C. This phenomenon is known, to be related to the differences in degradation mechanism occurring in an oxidative and non-oxidative environment. The initial degradation step of the epoxy network occurs through a dehydration process to form an unsaturated alkene species and water, which is essentially independent of the oxidative or non-oxidative nature of the atmosphere [21]. Beyond this point, further degradation can be considered to be a competition between crosslinking of the unsaturated species with radical species being formed (to form the char) or continued chain scission processes occurring, which evolve flammable, combustible materials which continue until there is nothing left. Rose et al. [22] used ESR to highlight this competition by showing that at elevated temperature the concentration of radical species remained constant, implying a competition between a condensation (or crosslinking process) or chain breaking, (i.e. volatilization). In the case of degradation under a nitrogen atmosphere (in this case shown at 700 °C), this balance is tipped in favour of crosslinking or char formation so that the carbonaceous product is structurally ‘fixed’ in the solid or condensed phase. However, in the case of degradation occurring in the oxidative atmosphere, the situation is more complex due to the thermo-oxidative process being an autocatalytic free radical process. It appears from the results here, that the oxidation process, (after the initial dehydration process), at first results in an increased level of crosslinking of the unsaturated species as evidenced by the higher intermediate char yield at 540 °C, compared to the non-oxidative environment. This process, however, also introduces oxygenated species into the network, ensuring that the network is vulnerable to further chain scission as the temperature increases (at 700 °C). This allows further degradation through volatilization and explains the observed substantial decrease in char yield in air is compared to that in a non-oxidative environment.

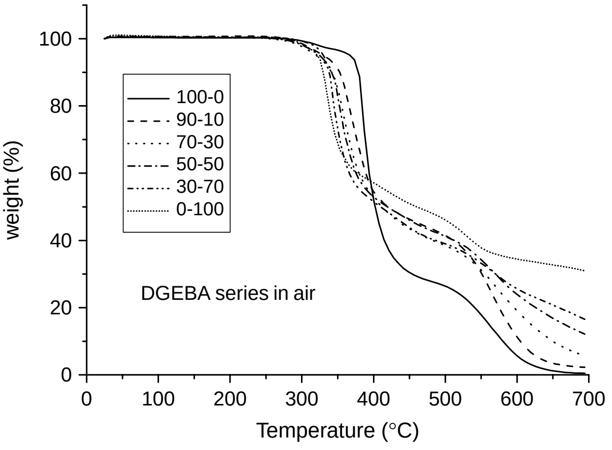


Fig. 2. Thermogravimetric analysis of the DGEBA series showing the effect of increasing phosphorous content in an air atmosphere on the decomposition mechanism.

The effect of phosphorous addition appears to act in a somewhat similar manner to oxidative decomposition at the lower temperatures, by accelerating the crosslinking process, fixing the carbon to the carbonaceous residue. The difference between the action of phosphorous and the oxidative process is that the char layer formed through this process is more thermally resistant to further chain scission. The crosslinking process is promoted because the phosphorous species, or more specifically in this case, the P–O–C linkage, is less stable than the –C–C– group and, therefore, decomposes at a lower temperature. This creates a highly reactive phosphoruous radical species which is able to react with the unsaturated groups formed via dehydration [23] and facilitate the crosslinking. Levchik et al. [24], also discussed the degradation mechanism and char formation being promoted by an increasing concentration of radicals in the solid phase, despite not measuring any increase in free radical concentration using EPR absorption. This was explained to be due to the high reactivity of the phosphorous radical due and the ease of hydrogen abstraction promoting char formation.

The TGA curves for the high functionality TGDDM with increasing phosphorous content performed under both nitrogen and air atmosphere are also shown in Figs. 4 and 5, respectively. As can be seen, the traces show similar behaviour to that seen for the DGEBA systems although are clearly further complicated (particularly in the case of oxidative degradation). Again, increasing phosphorous content has the effect of reducing the onset of degradation temperature and increasing the char yield in both air and nitrogen. The addition of phosphorous introduces several multiple and small degradation processes primarily between the initial degradation at 300 °C to the onset of the degradation of the char at about 500 °C indicative of a significant increase in the complexity of the degradation mechanism to form the char layer. This is expected to be a result of the increased crosslink density of the TGDDM network and the corresponding high levels of branching compared to the bifunctional DGEBA. The changes in char yield also exhibit similar trends, with the char yields in nitrogen and air to that of the DGEBA system, exhibiting increases in char yield with increasing phosphorous content as shown in Fig. 6. This plot also shows that the degradation of the char layer, that is, the degradation processes occurring beyond 500 °C continue to be governed by the competition between improved stability of the char layer through carbonization/polymerization and continued chain scission and volatilsation as discussed previously.

The onset of degradation temperature (taken as the temperature at which the weight loss is 10%) is shown in Fig. 7 for the TGDDM and DGEBA systems versus phosphorous content in both nitrogen and air. As can be seen, the DGEBA and TGDDM systems both display a two phase behaviour, consisting of an initial rapid decrease in onset temperature for content up to 1% of P, followed by a more gradual and consistent decrease with increasing P content. The DGEBA systems exhibit a more rapid decrease in the 10% mass loss degradation temperature than TGDDM systems, and from a higher temperature. This decrease in expected to be broadly a result of the more rapid cleavage of the P–O–C bonds in concert with dehydration of the opened epoxy ring. The larger effect for the DGEBA network at lower phosphorous content may be a result of the fact that it has a lower crosslink density and contains more linear chain extended species compared to that of the tetra functional TGDDM network. Cleavage of a phosphorous species in a chain extended component of the network may cause a larger decrease in thermal stability compared to that of a more highly crosslinked TGDDM system. The decreasing influence of this effect at higher phosphorous contents may be a result of the linear chains being exhausted or unavailable and more highly crosslinked components of the network being

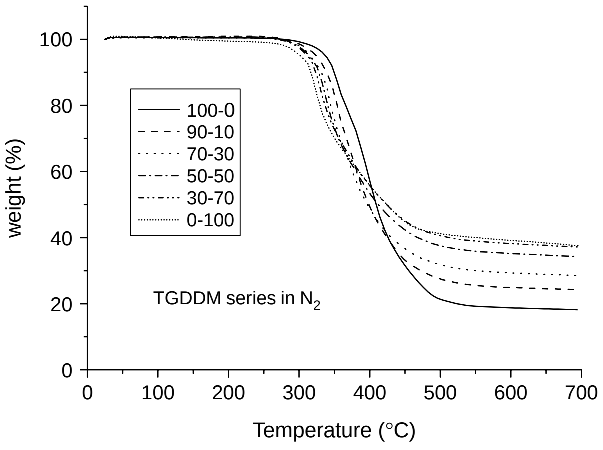


Fig. 4. Thermogravimetric analysis of the TGDDM series showing the effect of increasing phosphorous content in a nitrogen atmosphere on the decomposition mechanism.

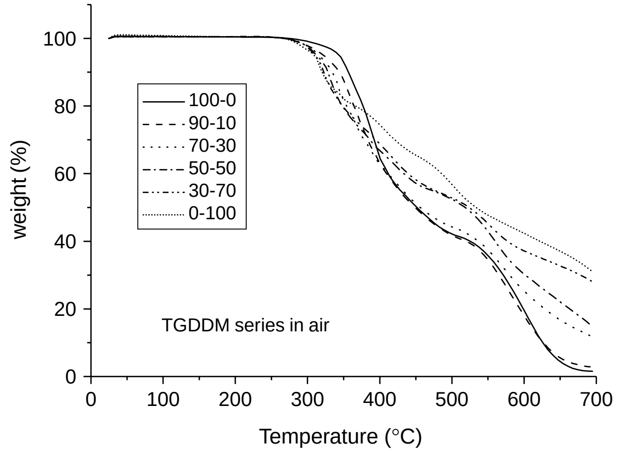


Fig. 5. Thermogravimetric analysis of the TGDDM series showing the effect of increasing phosphorous content in an air atmosphere on the decomposition mechanism.

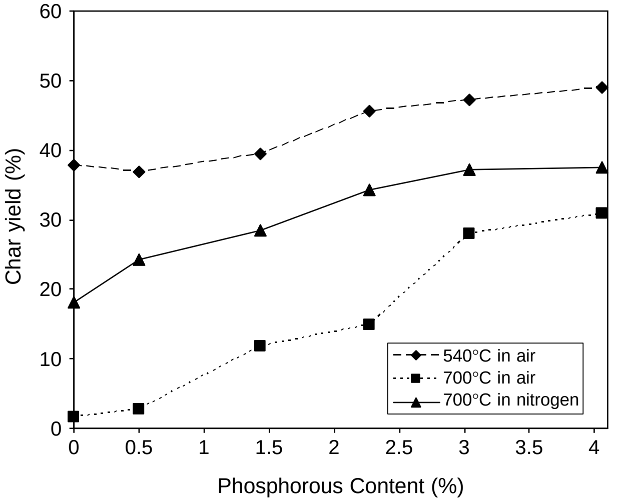


Fig. 6. Effect of increasing phosphorous content on the char yield in nitrogen and air atmospheres as determined using TGA for the TGDDM series of resin systems.

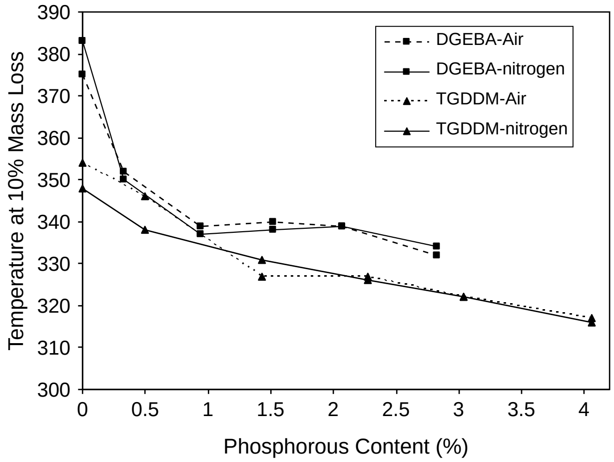


Fig. 7. Temperature at 10% mass loss for the TGDDM and DGEBA systems in both air and nitrogen for varying levels of phosphorous content.

cleaved with smaller reductions in the degradation temperature. Also of importance to note here is that there is little difference in the onset of degradation temperatures in either a nitrogen or air atmosphere because the initial degradation step of dehydration to form the unsaturated species is unaffected by either oxidative or non-oxidative conditions.

3.2. Dynamic mechanical thermal analysis

The glass transition temperatures as determined using dynamic mechanical thermal analysis (DMTA) for the DGEBA and TGDDM series are shown in Table 1. As can be seen, there is a decrease in the glass transition temperature from 203 to 176 °C for the DGEBA series with increasing phosphorus content. The TGDDM system (traces not shown) demonstrated a much smaller decrease in T_g with increasing phosphorous content, from 239 to 232 °C. Such a decrease can be ascribed to the higher molecular weight of BAPP than DETDA and a greater level of flexibility and mobility of the P–O–C bonds. The raw data traces of the tan δ spectra are shown in Fig. 8 where the consistent decrease is evident, as is the uniformity of the tan δ peak indicating the absence of any network heterogeneity (at least on the microscale domain that the DMTA is able to probe). The decreases in the T_g, however, are not large, particularly for the TGDDM system and suggest that BAPP has potential to be used for high performance applications in particular in mixtures with DETDA. An example of this is the fact that the T_g of DGEBA-0-100 is comparable to that of the widely used DGEBA/diaminodiphenylmethane (DDM) system [25].

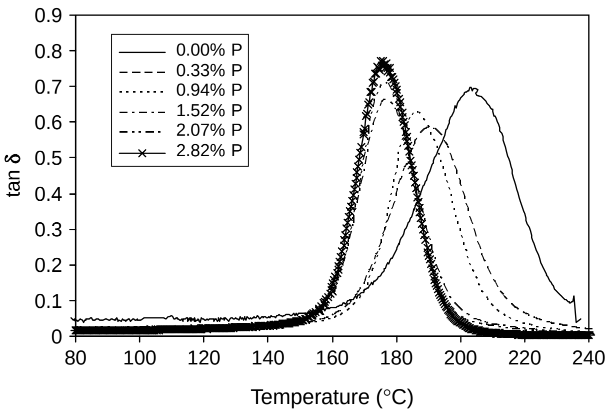


Fig. 8. Raw tan δ traces showing the effect of increasing phosphorous content on the glass transition temperature for the DGEBA networks.

3.3. Mechanical and thermal properties

Coefficients of thermal expansion were determined using TMA and are summarised in Table 1. The TMA results showed that in all cases, the CTE below T_g decreased with increasing the phosphorus content. Comparatively, the CTE with DGEBA decreased by 19%, while the CTE of TGDDM decreased by 15%. The CTE below the T_g is attributed mainly the expansion of the chemical bonds, because the expansion of the free volume is negligible due to being in a glassy state. The decrease in CTE can be described in terms of the varying levels of aromaticity compared to aliphatic components of a network [26]. In this case, the higher level of aromaticity of the BAPP compared to the DETDA, which has pendant aliphatic chains with a larger degree of freedom to move in the glassy state contributes to the decrease in CTE for the BAPP. The higher CTE for DGEBA compared to TGDDM series can also be attributed to this concept. According to free volume theory, the difference between the CTE below T_g (CTE$_g$) and the CTE above T_g (CTE$_r$) gives the CTE of the free volume (CTE$_f$). This has been calculated and is shown in Table 1. According to the differences in crosslink density, the CTE$_f$ of TGDDM would not be expected to be larger than those of DGEBA series. However, the TMA traces always contain the sum of at least two effects: thermal expansion and time-dependent creep. The typical TMA curves of DGEBA and TGDDM series are shown in Fig. 9 for the DGEBA-and TGDDM 50-50 samples. The DGEBA-50-50 trace shows that time dependent creep contributes to CTE determination, whilst the similar phenomenon was not observed in the TGDDM-50-50 sample. This is likely because of the higher level of packing density caused by

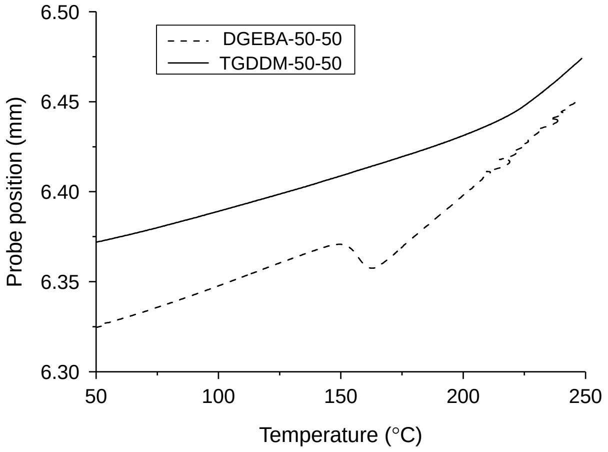


Fig. 9. Raw thermomechanical analysis traces obtained from the DGEBA-50-50 and TGDDM-50-50 samples.

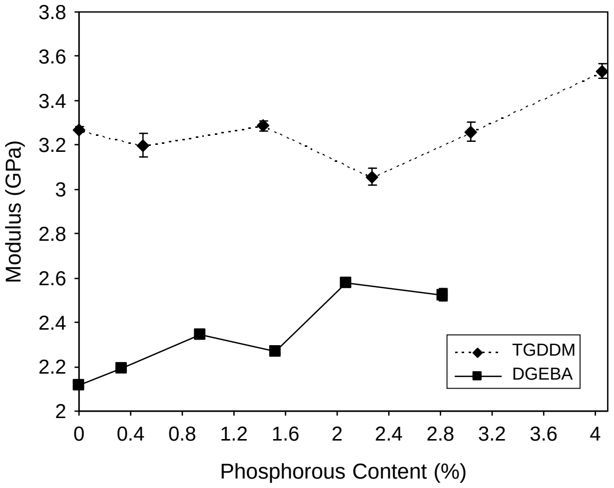


Fig. 10. Plot of bending modulus determined as a function of % phosphorous content for the DGEBA and TGDDM series (error bars denote ±80% confidence level).

the increased level of aromaticity of the TGDDM network compared to the DGEBA network preventing creep at high temperature. It is clear, however, that for all of the systems, the CTE in both the glassy and rubbery state decreases with increasing phosphorous content due to a decreasing level of internal stresses within the cured network.

The flexural properties of the cured epoxy resins were characterized by three-point bending test a Minimat instrument. The effect of increasing phosphorous content on the bending modulus for the DGEBA and TGDDM series is shown in Fig. 10 where it can be seen that increasing phosphorous content does not have a deleterious impact upon the properties. The results tend to indicate that there is a modest increase in modulus for the DGEBA system, while the TGDDM displays little change with increasing phosphorous content. Fig. 11 plots the effect of the strain at failure and the network strength with increasing phosphorous content. As can be seen, the DGEBA network again displays a very modest increase in both the strength and the strain to failure up to a level of about almost 3 wt% phosphorous content. Similarly, the TGDDM network also shows little change in both strength and strain to failure up to a approximately 2.3% phosphorous content, after which there is a significant decrease as the weight percent phosphorous content increases to 4.1 wt%.

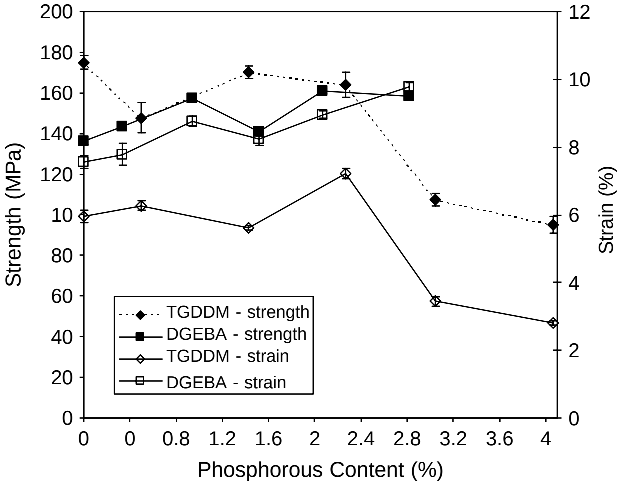


Fig. 11. Plot of the % strain at failure and the strength plotted as a function of % phosphorous content for the DGEBA and TGDDM series (error bars denote ± 80% confidence). Open symbols refer to the strain values while the closed symbols refer to the strength of the network.

4. Conclusion

The aim of the current research was to study the thermal and mechanical properties of DGEBA/DETDA and TGDDM/DETDA resins chemically modified by BAPP. Although the thermal stability of the network decreased with the introduction of the phosphorus-containing hardener, as determined by the decrease of the initial degradation temperature; the char yield at 700 °C increased in both the nitrogen and air atmosphere, implying good flame retardancy is likely to be achieved via the high levels of char formation. The char formation was discussed in terms the inherent competition between continued chain scission and hence volatilisation versus crosslinking of the unsaturated species with available free radicals. A nitrogen atmosphere was shown to promote char formation, while for an oxidative environment it was shown to be dependent upon the temperature.

The glass transition temperature of the DGEBA series decreased gradually with increasing phosphorus content, while the TGDDM series remained relatively constant. The bending moduli for the DGEBA and TGDDM series showed that and the strain at failure showed that mechanical properties of the network were unaffected by increasing levels of phosphorous content. The DGEBA and TGDDM systems also exhibited little change in their flexural strength and strain to failure results up to 2.2% P (in the case of TGDDM) and 2.8% P (in the case of DGEBA). However, at higher levels of phosphorous content the TGDDM system demonstrated significant decreases ion both strength and strain to failure. Coefficient of thermals expansion as measured according to TMA, also demonstrated decreases in the glassy state, for both the TGDDM and DGEBA networks with increasing phosphorous content. In conclusion, therefore, the combination of the good thermal and mechanical properties along with the potential improvement in fire performance (as inferred from the from char yields using TGA) suggest that BAPP is a potential candidate material for aerospace applications where improved fire performance may be a critical parameter.

References

[1] Nakamura Y, Yamaguchi M, Okubo M, Matsumoto T. J Appl Polym Sci 1992;45:1281–9.
[2] Shieh JY, Ho TH, Wang CS. Angew Makromol Chem 1995;224:21–32.
[3] Green J. J Fire Sci 1992;10:470.
[4] Schut JH. Plas World 1995;31.
[5] Mikroyannidis JA, Kourtides DA. J Appl Polym Sci 1984;29:197–209.
[6] Chin WK, Shau MD, Tsai WC. J Polym Sci, Part A: Polym Chem 1995; 33:373–9.
[7] Lin CH, Wang CS. Polymer 2001;42:1869–78.

[8] Chun SW, Ching H, Wang CS, Lin CH. J Polym Sci, Part A: Polym Chem 1999;37:3903–9.
[9] Chun-Shan W, Jeng-Yueh S. Polymer 1998;39:5819–26.
[10] Lin CH, Wu CY, Wang CS. J Appl Polym Sci 2000;78:228–35.
[11] Derouet D, Morvan F, Brosse JC. J Appl Polym Sci 1996;62:1855–68.
[12] Jeng-Yueh S, Chun-Shan W. J Appl Polym Sci 2000;78:1636–44.
[13] Ying Ling L. Polymer 2001;42:3445–54.
[14] Jeng-Yueh S, Chun-Shan W. Polymer 2001;42:7617–25.
[15] Tchatchoua C, Qing J, Srinivasan SA, Ghassemi H, Yoon TH, Martinez-Nunez M, et al. Polym Prepr 1997;38:113–4.
[16] Ru-Jong J, Shi-Min S, Jiang-Jen L, Wen-Chiung S, Yie-Shun C. Eur Polym J 2002;38:683–93.
[17] Liu YL, Hsiue GH, Lee RH, Chiu YS. J Appl Polym Sci 1997;63: 895–901.
[18] Hsiue GH, Liu YL, Tsiao J. J Appl Polym Sci 2000;78:1–7.
[19] Weichang L, Varley RJ, Simon GP. J Appl Polym Sci 2004;92: 2093–3000.
[20] Varley RJ, Liu W, Simon GP. J Appl Polym Sci 2006;99:3288–3299.
[21] Bellenger V, Fontaine E, Fleishmann A, Saporito J, Verdu J. Polym Degrad Stab 1984;9:195–209.
[22] Rose N, LeBras M, Delobel R, Costes B, Henry Y. Polym Degrad Stab 1993;42:307–16.
[23] Troitzsch JH. Prog Org Coat 1983;11:41–69.
[24] Levchik SV, Camino G, Luda MP, Costa L, Costes B, Henry Y, et al. Polym Degrad Stab 1985;48:359–70.
[25] Kamon T, Furukawa H. Adv Polym Sci 1986;80:173–202.
[26] Tobolsky AV. Properties and structure of polymers. New York: Wiley; 1960.