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Examining The Thermal Behaviour of Novel Aromatic Polybenzoxazines Blends Containing Organophosphorus Compounds and POSS Reagents

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Abstract: 2,2-Bis(3,4-dihydro-3-phenyl-2H-1,3-benzoxazine)propane (BA-a) is blended with different commercial polyhedral oligomeric silsesquioxane (POSS) reagents and an organophosphorous compound bis(4-hydroxyphenyl)phenylphosphine oxide (BPPO), at a range of loadings (1 – 10 wt %). The influence of the additives on the onset and a rate of polymerisation of the BA-a is examined using differential scanning calorimetry. An initial screen of blends containing various additives (5 wt%) shows that a combination of aminoethylaminopropyl isobutyl POSS (AEAP) and BPPO has the greatest effect on reactivity with a reduction in reaction onset of some 65 K and an increase in T_g of 18 K when compared with the BA-a homopolymer. The activation energy for the polymerization of BA-a containing 5 wt% AEAP was determined to be 84-88 kJ/mol (using Kissinger and Ozawa kinetic models), with a first order rate constant of $1.9 \times 10^8 \text{ s}^{-1}$. The thermal stability of the cured blends containing 5 wt% flame retardant were examined using thermogravimetric analysis (TGA) and both onset of degradation and char yield are increased by 15 K and 5 % respectively when compared with the BA-a homopolymer.

Keywords: Polybenzoxazines, flame retardants, POSS reagents, organophosphorous compounds, polymerisation kinetics, thermal stability, nanocomposites.

INTRODUCTION

Polymers and their composites are being applied increasingly in the aerospace industry in recent years [1], more recently composites have been used in commercial airliners, most notably in the case of the Airbus A350 and Boeing 787 which comprise up to 50 % composite by volume [2,3]. Composites are now being applied in the primary structure of aircraft so their integrity is very important, developing methods to improve toughness of neat resins and trying to understand how

the toughening agent works is the first step in developing robust composites. Polybenzoxazines (PBZs) show promising thermal and mechanical performance for these applications, but improvements in toughness are required before this can be a reality. The potential for the use of oligomers based on engineering thermoplastics have been examined for some years as modifiers in aerospace composite matrices [4,5], due to their inherent toughness and the ability to blend them more easily than high molecular weight species without incurring the penalty of high melt viscosity. The high aromatic content and potential to produce high yields of char during combustion make PBZs particularly attractive in an environment in which the polymer industry has moved away from the extensive use that was made of halogenated polymers or halogenated additives [6].

Another considerable drawback of BZ monomers is that they are typically slow to react, requiring curing temperatures in the range of 200 °C [7,8]. High curing temperatures are a major limitation for the adoption of PBZs in advanced industrial applications, when compared to other competitor resins; for instance, epoxies may be cured at comparatively modest temperatures (60 °C and 120 °C), yet still achieve relatively high values of glass transition temperature (dry T_g = 150 °C). Compounds containing an active hydrogen atom, such as carboxylic acids and phenols have been widely established as effective catalysts for the ring-opening polymerisation of BZ monomers [9], which as already mentioned proceeds *via* a cationic mechanism. However, from the viewpoint of practical applications, the use of strong catalysts may severely compromise the shelf life of one-pot formulations [9, 10]. Other compounds that have been investigated as initiators include Lewis acids [11], bi-functional catalysts [12], phosphonic and sulfonic acids as well as basic compounds such as imidazoles and amines [13], and the latter are examined in this work.

Polyhedral oligomeric silsesquioxane (POSS) reagents have attracted considerable interest in the area of polymer nanocomposites, since they demonstrate excellent properties as nano-phase additives or nano-scale modifiers [14], including high thermal stability and good mechanical properties [15,16,17]. Thus, they are an active and important part of the system. POSS reagents are inorganic ceramic-like nanocages that comprise a silicon-oxygen framework. A typical POSS molecule possesses a rigid cubic structure, represented by the formula $R_8Si_8O_{12}$, where the central inorganic core (Si_8O_{12}) is functionalised with organic moieties (R) at up to eight corners [15], although more typically mono- or difunctional species are used. This class of hybrid materials has the ability to improve the mechanical properties of polymer nanocomposites, as the incorporation of small amounts into the polymer matrix can have a positive impact on various features, such as the modulus, T_g and fracture toughness. Ormasil nanoparticles can lead to changes in toughness, but also mechanism [18]. In addition, POSS fillers have been proven to enhance significantly the

thermal stability of polymer blends, a property that arises from the thermally stable inorganic Si-O core [17].

The preparation of PBZs incorporating functionalised POSS reagents dates from 2004 [19] and, in common with other families of high performance polymers, there has been a steady growth in interest in the use of both mono- and poly-functional POSS reagents with PBZs with several research groups concentrating on their exploration. Common approaches have utilised appropriately functionalised POSS reagents to effect co-reaction with the oxazine ring, thus vinyl groups [20,21] and glycidyl ethers [22]. Alongside the more numerous studies to examine the effects of blending POSS with PBZ and its blends or copolymers such as bisoxazolines [23] or epoxies [24], is the use of benzoxazines as pendant groups within more flexible fluoropolymer films [25]. Less common is the use of more sophisticated synthetic methodologies such as the use of click chemistry [26] to introduce benzoxazine functionality into the POSS reagent, but a model POSS reagent with mixed functionality, allowing the potential for the formation of an A-B copolymer has been reported [27]. The favourable influence of POSS/PBZ nanocomposites on dielectric behaviour is well established with several studies [28,29,30] in this field, but there has been particular emphasis on the production of ultra low κ polymers [31] for use as interconnects in the semi-conductor applications. In the present paper, the focus is on the action of POSS reagents on the thermal behaviour of a common, commercial difunctional benzoxazine monomer. We have recently completed a study on the thermal degradation behaviour of organophosphorous compounds on a commercial PBZ [32] and in the present work we have taken the best performing of these, bis(4-hydroxyphenyl)phenylphosphine oxide (BPPO), and combined it with POSS. The influence of different POSS reagents on the kinetics of polymerisation and the properties of the final polybenzoxazine will be discussed.

EXPERIMENTAL SECTION

Materials. 2,2-Bis(3,4-dihydro-3-phenyl-2H-1,3-benzoxazine)propane (BA-a) was supplied by Huntsman Advanced Materials (Basel, Switzerland) as Araldite MT35600. Three POSS reagents, epoxycyclohexyl isobutyl POSS (EPC), aminopropyl isobutyl POSS (AP) and aminoethylaminopropyl isobutyl POSS (AEAP), were obtained from Hybrid Plastics (Hattiesburg, USA). Bis(4-hydroxyphenyl)phenylphosphine oxide (BPPO) was obtained from Carbosynth Ltd. Following characterization using ^1H NMR, Fourier transform infrared spectroscopy and elemental analysis to determine identity, all reagents (Scheme 1) were used as received without further purification.

Scheme 1. Reagents used in this study (R = isobutyl)

Blending of small-scale polymer samples for miscibility studies. All the POSS reagents were provided in white powder form. A small portion of the neat resin, BA-a, remained in crystalline form and was used in the preparation of the BA-a/POSS blends. Since both components were in powder form, the corresponding blends were easily prepared by grinding, using mortar and pestle. Initially, blends containing 5 wt % of the respective POSS species were prepared (Table 1). Note as BA-a is present in all blends this is omitted from the sample designation. No measurements were made to determine whether aggregation had occurred on the nano/microscale, but there was no evidence of any significant aggregates being present; the samples were apparently homogeneous.

Table 1. Blends examined during the course of this study

Instrumentation and test methods. Fourier Transform Infrared (FT-IR) spectra were recorded (at a resolution of 4 cm^{-1}) using a Perkin Elmer (System 2000) FT-IR spectrometer using an attenuated total reflectance attachment with a Specac Golden GateTM diamond anvil single reflection (45° angle of incidence) attenuated total reflectance (ATR) accessory.

Differential scanning calorimetry (DSC) was undertaken using a TA Instruments Q1000 running TA Q Series Advantage software on samples ($4.0 \pm 0.5\text{ mg}$) in hermetically sealed aluminium pans. Experiments were conducted under flowing nitrogen ($50\text{ cm}^3/\text{min.}$) at heating rates of 5, 10, 15, and 20 K/min. from room temperature to $300\text{ }^\circ\text{C}$, cooled to room temperature at 20 K/min, then rescanned to $250\text{ }^\circ\text{C}$ at 10 K/min (to determine the glass transition temperature, T_g). In order to gauge the reactivity of the monomer in the bulk, dynamic DSC analysis was performed on all of the systems.

Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 (operating TA Q Series Advantage) on the previously cured DSC samples ($3.0 \pm 0.5\text{ mg}$), which had a well-defined thermal history. Samples were placed in a platinum crucible and were heated from room temperature to $800\text{ }^\circ\text{C}$ at 10 K/min in nitrogen ($60\text{ cm}^3/\text{min.}$).

RESULTS AND DISCUSSION

Exploring the effects of the additives on polymerisation behaviour. In this work, three different mono-functionalised POSS reagents were examined as potential initiators for the ring-opening polymerisation of the BA-a monomer. The R group in all cases is isobutyl, which can be regarded as chemically inert, as it has no effect on reactivity, but does impart a degree of hydrophobicity.

Differential scanning calorimetry (DSC) was carried out to observe how the addition of POSS and BPPO affect the curing behaviour and T_g of the resulting BA-a blends. In addition to examining whether the POSS reagents would enhance the reactivity of the monomer, the influence on glass transition temperature (T_g) and thermal stability were also explored. Preliminary scans of the three-separately introduced POSS reagents was undertaken at a concentration of 5 wt %. The preliminary results obtained from DSC (Table 2), indicate that the epoxide functional group does not influence the reactivity of the benzoxazine ring, as the lone pair of the oxygen atom is only weakly nucleophilic.

Table 2. DSC Data for selected BA-a blends (10 K/min, under nitrogen, 50 cm³/min.)

The DSC data for the blends of BA-a containing 5 wt% of each additive (Fig. 1, see supplementary Fig. S1 for coloured figure) demonstrate that the AP and EPC have little influence on the reactivity of the monomer. The behaviour of the EPC is quite surprising since the opening of the strained epoxy ring should occur comparatively easily under these conditions, leading to the production of a hydroxyl group with a labile hydrogen atom.

Fig. 1 DSC data for BA-a blends (10 K/min under nitrogen).

Wang *et al.* [33] studied the application of POSS reagents as latent curing agents, and investigated the effect of octa(*p*-toluenesulfonic acid ammonium salt) (OPAAS) POSS on the polymerisation of a binary polybenzoxazine/polybenzoxazole (PBZ/PBO) blend. The addition of OPAAS (3 wt %) resulted in the reduction of the T_{op} from 193 °C (for the pristine system) to 178 °C, accompanied by a simultaneous decrease in the peak curing temperature (T_{max}) from 234 °C to 218 °C. Increasing the incorporation of OPAAS to 4 wt % displayed the highest storage modulus (E') of 2.00 GPa (at 100 °C), corresponding to a net increase of 0.75 GPa [33]. Nonetheless, the introduction of OPAAS in the range between 3 and 5 wt % resulted in slight reductions in both T_g and char yield, and was attributed by the authors to the existence of minor aggregation in the matrix.

The introduction of active hydrogen donor species, more specifically 3,3'-thiodiphenol (TDP) and 3,3'-thiodipropionic acid (TDA), have been found to significantly affect the polymerisation kinetics of the BA-a monomer. In this case, the diacid has been shown to be more effective at reducing the temperature of onset polymerisation (T_{op}) and generally, resulted in the formation of more densely cross-linked networks, with higher T_g values [34]. In particular, the addition of 15 wt % TDA achieved a significant reduction in the T_{op} from 203 °C for the neat resin to 145 °C, coupled with a

significant increase in the T_g (27 °K) [34]. Sulfonic acids, sulfonates and sulfonic salts have also been demonstrated to be effective initiators [10,35]. *p*-Toluenesulfonic acid (TsOH) and methyl *p*-toluenesulfonate (TsOMe) were both found to be very effective initiators for the ring-opening polymerisation of BZs [10], as they induced polymerisation at 60 °C and 80 °C respectively, in the presence of only 1 mol %. The catalytic effect of salts of *p*-toluenesulfonic acid (TsOH) and various aliphatic amines have been studied on the polymerisation of the BA-a/ bisoxazoline system and the salts of TsOH and isopropanolamine as well as TsOH and methylamine were found to have the greatest effect on reactivity. These were found to reduce the T_{op} of the pristine system from 180 °C to 74 °C and 77 °C respectively; at concentrations of 10 wt %, this is an impressive reduction in processing temperature [35]. The addition of BPPO to the BA-a has a similar effect, reducing the onset temperature by some 30 K at higher loadings, but it is telling that the end of the polymerization process (T_{ep}) remains unmoved at 298 °C.

Surprisingly, the presence of the amino functionality on the other two POSS reagents produces results, which are quite contradictory. It is evident that the aminopropyl (AP) group does not initiate the ring opening of the BA-a monomer at a lower temperature, but in contrast the bifunctional aminoethylaminopropyl (AEAP) group has a significant effect on reactivity, as the onset temperature of polymerisation (T_{op}) is reduced from 204 to 180 °C. One reason that could explain the reduced reactivity of the AP-POSS, is the potential interaction of the nucleophilic N atom of the primary amine with the electron-deficient Si atoms of the POSS nanocage, which results in the lone pair becoming less readily available. Nonetheless, the presence of the two amino functionalities in AEAP has an observable effect in the reactivity of the BA-a monomer as already pointed out, which most likely arises from the greater nucleophilicity of the N atoms. Moreover, the addition of 5 % AEAP not only achieved an improvement in T_{op} , but also decreased the peak curing temperature (T_{max}) from 244 to 233 °C (Fig. 2, see supplementary Fig. S2 for coloured figure). Once again, the incorporation of the POSS reagents produced no effect on the observed end point of the polymerisation (T_{ep}).

Fig. 2 DSC data for BA-a-AEAP_{5%} blends; Cycle 1 at different heating rates (10 K/min).

Following the preliminary DSC results, it was apparent that from the POSS initiators under examination, AEAP-POSS had the greatest impact on reactivity. Hence it was decided to run another DSC analysis, under identical conditions, in order to determine the effect of varying initiator concentration on reactivity. The results (Table 3) show that increasing the content of AEAP

above 5 wt % has only a marginal effect on reactivity. Another important observation was the fact that T_g showed no dependency on varying POSS concentration. Hence in terms of a formulated system, 5 wt % of the POSS catalyst would be the concentration of choice.

Table 3. DSC Data for selected BA-a/AEAP blends (10 K/min, under nitrogen, 50 cm³/min.)

The T_g values were obtained from rescan experiments and of the POSS reagents, only EPC-POSS had an appreciable effect on T_g , corresponding to a net increase of 9 K (Fig. 3, see supplementary Fig. S3 for coloured figure). In contrast, Wang *et al.* found that increasing the incorporation of OPAAS to 4 wt % displayed the highest storage (E') modulus of 2.00 GPa (at 100 °C), corresponding to a net increase of 0.75 GPa [33]. Nonetheless, the introduction of OPAAS in the range between 3 and 5 wt % resulted in slight reductions in both T_g and char yield, which might be consistent with the existence of minor aggregation in the matrix.

Fig. 3 DSC data (second scan showing T_g values) for BA-a blends.

Determination of cure kinetics using DSC. A number of DSC experiments were performed on a blend of BA-a and AEAP (5 wt %) at different heating rates (Fig. 4, see supplementary Fig. S4 for coloured figure). This particular blend was selected as it gave a significant reduction in the temperature of the onset of polymerisation, yet still afforded a comparatively high T_g for the cured polymer.

Fig. 4 DSC data for BA-a-AEAP_{5%} blend; Cycle 1 at different heating rates.

Kinetic analysis of the dynamic cure of the monomers was based on the rate equation given in Equation 1 where the rate constant ($k(T)$) is temperature dependent according to Arrhenius' law [36] shown in Equation 2.

$$\frac{d\alpha}{dt} \equiv \beta \frac{d\alpha}{dT} = k(T)f(\alpha) \dots \text{Equation 1}$$

where $k(T)$ is a temperature-dependent rate constant, $f(\alpha)$ the differential conversion function and $\beta = dT/dt$ is a constant heating rate.

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \dots \text{Equation 2}$$

where A is the pre-exponential factor, E_a is activation energy and T is the absolute temperature.

Two different methods of kinetic analysis (proposed independently by Kissinger [37] and Ozawa [38]) were used. The Kissinger method relates the exothermic peak maximum temperature ($T_{\max}$) to the activation energy (E_a) for data obtained at various heating rates (β) through Equation 3.

$$\ln\left(\frac{\beta}{T_{\max}^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_{\max}^2} \dots \text{Equation 3}$$

The Ozawa method is similar to the Kissinger method, where the inverse relationship between the logarithm of heating rate to exothermic peak temperature in Equation 4 (Fig. 5) allows graphical determination of activation from the slope of the resulting line.

$$\ln\beta = \ln\left(\frac{AE_a}{R}\right) - \ln F(\alpha) - 5.331 - 1.052 \left(\frac{E_a}{RT_{\max}}\right) \dots \text{Equation 4}$$

where $F(\alpha)$ is a constant function.

All analyses using both of the aforementioned methods showed a good linear relationship (with $r^2 > 0.98$) yielding an activation energy of 84-88 kJ/mol (using both Kissinger and Ozawa kinetic models) for the polymerization of BA-a containing 5 wt% AEAP with a first order rate constant of $1.9 \times 10^8 \text{ s}^{-1}$. This compares with values of 81-88 kJ/mol obtained for the homopolymerisation of BA-a using a similar method [39].

Fig. 5 (a) Kissinger and (b) Ozawa plots for polymerisation of BA-a-AEAP_{5%} blend

Influence of organophosphorous compounds on polymerisation behaviour. DSC also indicates that BPPO has an apparent effect on reactivity, resulting in an approximate reduction of 40 K in the onset temperature of polymerisation. This observation is by no means surprising as BPPO comprises two phenol groups bonded to the central P atom, and phenols have been previously reported as good catalysts for the polymerisation of BZs [10]. Generally, it was observed that a reduction in the value of onset polymerisation was accompanied by an increase in the enthalpy of polymerisation (ΔH_p), which broadly indicates a higher degree of conversion. Not only did the addition of BPPO at 5 wt % in the BZ/POSS blends enhance the reactivity and degree of conversion, but it also had a significant effect on the measured T_g , with a maximum increase of 18 K being achieved in the case of the 5% AEAP + 5% BPPO blend. The DSC thermogram for cycle 1 of the aforementioned blend is illustrated in Fig. 6 (see supplementary Fig. S5 for coloured figure).

Fig. 6 DSC data for BA-a-AEAP_{5%}-BPPO_{5%} blend; Cycle 1 shown with annotations.

Determining thermal stability of selected POSS/organophosphorous blends.

Thermogravimetric analysis (TGA) was conducted to evaluate the mass loss as a function of temperature for the poly(BA-a) and in cured blends containing various concentrations of POSS and or BPPO (Table 4). Previous studies [40,41] conducted on poly(BA-a) have shown that the initial mass loss occurs at around 260-280 °C, with the loss of amine species accounting for the majority of the loss. The bulk of the mass loss occurs between 300-450 °C, associated with the degradation of phenolic moieties [42,43]. Finally, the formation of char tends to occur at temperatures above 500 °C and the typical yield for poly(BA-a) resin has been identified [44] to be around 30 % at 800 °C, which is in close agreement with the present work. The incorporation of the POSS reagents alone (at 5 wt %) was found to provide little enhancement in the thermal stability (Fig. 7, see supplementary Fig. S6 for coloured figure)), although a slightly higher char yield was obtained in all cases compared to the unmodified resin.

Fig. 7 TGA data for poly(BA-a) blends at 10 K/min under nitrogen.

The effect of blending BPPO on the thermal stability of the poly(BA-a) is more noticeable, even at 5 wt %, coupled with an increase in char yield. Initially, the temperature for 10 % mass loss is elevated in the presence of BPPO, with a maximum difference of 15 K observed between the pristine resin and the BA-a blend containing 5 wt % AEAP + 5% BPPO. The same is true of the corresponding temperature for 50 % mass loss, with a maximum improvement of 20 K achieved.

Table 4. TGA data for selected BA-a blends containing different additives (wt%) acquired at 10 K/min (nitrogen)

More importantly, the char yield (Y_c) is significantly higher for the BPPO-containing blends than for the neat poly(BA-a), with char yield of 35.4 % obtained for the BA-a blend containing 5 wt % AEAP + 5 wt % BPPO, compared with 30.4 % for poly(BA-a). The enhanced char yield observed for the cured blends containing BPPO and AEAP arises from the incorporation of the phosphorus and silicon atoms within the Poly(BA-a) network. Despite the improvement in thermal stability provided by BPPO (in another study, the incorporation of 6 wt % BPPO alone in the same polymer led to a value of 33 for Y_c [32]), it appears that the derivative of maximum weight loss occurs at a lower temperature, approximately 15 K lower than for the pristine poly(BA-a). An example of a TGA thermogram is provided in Fig. 8 (see supplementary Fig. S7 for coloured figure), for the 5% AEAP + 5% BPPO blend. The addition of BPPO has been observed to reduce the temperature at

which the first 5-10% of mass loss is measured in the PBZ, whereas the temperature at which 20% mass loss is recorded is in line with the cured, unmodified PBZ. BPPO is a well known flame retardant, which degrades thermally and acts in the gas phase to disrupts the flame chemistry (and reduces the heat evolution). The early degradation accounts for the lowering in the derivative of the maximum weight loss and this is discussed in greater depth elsewhere [6].

Fig. 8 TGA data for poly(BA-a) containing AEAP (5 wt %) + BPPO (5 wt %) at 10 K/min under nitrogen.

CONCLUSIONS

The blending of the bisphenol A and aniline based benzoxazine monomer and three POSS reagents and an organophosphorous dopant bis(4-hydroxyphenyl)phenylphosphine oxide is reported. Incorporation of all dopants resulted in a reduction in the temperature of the initiation of the curing mechanism, but the BPPO has the most marked effect, leading to a reduction of some 30-50 K in the onset temperature and 15 K in the peak maximum. Unfortunately, none of the additives had any influence on the crosslinking reaction taking place at higher temperatures, meaning that there was no reduction in the end temperature. The BPPO also yields a slightly more highly crosslinked network with both a higher polymerization enthalpy and T_g (up to 10 K higher than the homopolymer). The incorporation of 5 wt% the organophosphorous compound BPPO leads to a 5% increase in char yield. The next phase of this work will involve conducting flame testing on the best performing of these materials in glass fibre reinforced composites.

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Scheme 1. Reagents used in this study (R = isobutyl)

Fig. 1 DSC data for BA-a blends (10 K/min under nitrogen).

Fig. 2 DSC data for BA-a-AEAP blends; Cycle 1 at different heating rates (10 K/min).

Fig. 3 DSC data (second scan showing T_g values) for BA-a blends.

Fig. 4 DSC data for BA-a-AEAP_{5%} blend; Cycle 1 at different heating rates.

Fig. 5 (a) Kissinger and (b) Ozawa plots for polymerisation of BA-a-AEAP_{5%} blend

Fig. 6 DSC data for BA-a-AEAP₅%-BPPO₅% blend; Cycle 1 shown with annotations.

Fig. 7 TGA data for poly(BA-a) blends at 10 K/min under nitrogen.

Fig. 8 TGA data for poly(BA-a) containing AEAP (5 wt %) + BPPO (5 wt %) at 10 K/min under nitrogen.

Table 1. Blends examined during the course of this study

Sample	BA-a (g)	BPPO (g)	POSS (g)
BA-a	1	-	-
EPC _{5%}	0.95	-	0.05 (EPC)
AP _{5%}	0.95	-	0.05 (AP)
AEAP _{5%}	0.95	-	0.05 (AEAP)
EPC _{5%} BPPO _{5%}	0.90	0.05	0.05 (EPC)
AP _{5%} BPPO _{5%}	0.90	0.05	0.05 (AP)
AEAP _{5%} BPPO _{5%}	0.90	0.05	0.05 (AEAP)

Table 2. DSC Data for selected BA-a blends (10 K/min, under nitrogen, 50 cm³/min.)

Sample	T _m (°C)	T _{op} (°C)	T _{max} (°C)	T _{ep} (°C)	ΔH _p , J/g	T _g (°C) ^a
BA-a	42	204	244	298	294.7	156
EPC _{5%}	42	210	245	298	292.9	165
AP _{5%}	42	210	243	298	281.0	156
AEAP _{5%}	42	180	233	297	302.2	153
EPC _{5%} BPPO _{5%}	41	161	228	298	316.7	165
AP _{5%} BPPO _{5%}	42	161	226	298	319.8	170
AEAP _{5%} BPPO _{5%}	42	159	226	296	304.2	174

Key:

T_m = melting temperature, T_{op} = onset of polymerisation exotherm, T_{max} = Peak maximum of exotherm, T_{ep} = endpoint of polymerisation exotherm, T_g = glass transition temperature, ΔH_p = polymerisation enthalpy.

^a Recorded following cycle 1: 27-300 °C at 10 K/min, cycle 2: cool 10 K/min to 27 °C and cycle 3: 27-300 °C at 10 K/min.

Table 3. DSC Data for selected BA-a/AEAP blends (10 K/min, under nitrogen, 50 cm³/min.)

Additive (wt %)	T _m (°C)	T _{op} (°C)	T _{max} (°C)	T _{ep} (°C)	T _g (°C) ^a	ΔH _p (J/g)
0	39-42	182-204	235-244	298	156-157	295-341
BPPO						
1	42	175	235	298	140	358
2	41	171	233	298	160	347
4	42	165	232	298	161	357
6	41	158	226	298	165	362
8	41	155	223	298	166	356
10	39	150	218	298	166	355
AEAP						
1	43	192	240	298	157	319
2.5	43	196	239	298	155	326
5	42	180	233	297	153	302
7.5	42	181	236	298	155	272
10	42	177	233	298	155	326

Key:

T_m = melting temperature, T_{op} = onset of polymerisation exotherm, T_{max} = Peak maximum of exotherm, T_{ep} = endpoint of polymerisation exotherm, T_g = glass transition temperature, ΔH_p = polymerisation enthalpy.

^a Recorded following cycle 1: 27-300 °C at 10 K/min, cycle 2: cool 10 K/min to 27 °C and cycle 3: 27-300 °C at 10 K/min.

Table 4. TGA data for selected BA-a blends containing different additives (wt%) acquired at 10 K/min (nitrogen)

Additive (wt %)	Temperature (°C) at which weight loss (%) recorded						T _{max} (°C)	Y _c (%)
	5 %	10 %	20 %	30 %	40 %	50 %		
-	279	320	354	378	402	435	374	30
EPC _{5%}	276	321	356	376	400	433	372	31
AP _{5%}	276	321	354	377	401	435	372	33
AEAP _{5%}	273	316	349	375	401	440	372	33
EPC _{5%} BPPO _{5%}	284	319	349	374	402	444	359	34
AP _{5%} BPPO _{5%}	284	318	350	375	405	449	358	34
AEAP _{5%} BPPO _{5%}	249	320	350	376	407	455	358	35

Key:

T_{max} = Temperature at which maximum rate of mass loss recorded, Y_c = Residual mass recorded at 800 °C