3.1 Introduction

Modification of one polymer with other outstanding polymers is an old and successful technique to obtain polymers with diverse properties. It is ‘property-oriented’ moulding of micro- and macrostructures of polymers. Non-reactive and reactive blends, polymer alloys and copolymers are produced to meet the demands of industry. This includes features such as low cost, high temperature resistance, light weight and also to the daily needs of the general population such as polymeric bottles and carrier bags. A ‘multi-component polymeric material’ refers to the combination of two or more polymers, including polymer alloys, blends and composites in all forms. Such materials have been widely investigated through a huge number of polymers in the scientific and engineering fields. Polybenzoxazines (PBZ) have been investigated for their blends, alloys and copolymers with linear polymers and other crosslinking polymers. This chapter unravels the preparation and properties of tailored systems derived from PBZ and their micro- and nano-composites.

3.2 PBZ–Epoxy Blends

Incorporation of epoxy resin into the PBZ network structure resulted in a copolymer that had a higher crosslink density and glass transition temperature \( (T_g) \) than its homopolymers. The copolymerisation reaction between benzoxazine (BZ) monomer and epoxy occurs via the opening of the epoxide ring by the phenolic hydroxyl functionalities present in the PBZ (Scheme 3.1). In the BZ–epoxy copolymers investigated, with epoxy content >45\%, the copolymers experience a sharp decrease in \( T_g \), and the copolymers containing equal amounts of BZ and epoxy exhibited a \( T_g \) lower than that of the pure PBZ. The epoxy-rich samples (those with >45\% epoxy) showed poor mechanical properties because phenolic groups generated by the oxazine ring-opening reaction not only serve to catalyse the copolymerisation, but also participate as reactants and are therefore consumed by the reaction. Thus, as the stoichiometric ratio of components is approached, non-reacted or small-molecular-weight epoxy molecules may remain and interfere with network formation or act as plasticisers.
Increasing molecular weight between epoxy groups by chain extension has afforded copolymers with reduced crosslink density, improved storage modulus, and reduced $T_g$ [1]. Copolymerisation with epoxy reduced char yields compared with pure PBZ, but chain-extended epoxy slightly increased the char yield. The addition of epoxy as a reactive diluent in the BZ matrix reduced the viscosity of the resin, but the curing was shifted to a higher temperature [2].

On the contrary, addition of phenolic novolac into the BZ resin resulted in a mixture that could be cured at a lower temperature. Phenolic novolac resin acts mainly as an initiator for these ternary systems, whereas the low melt viscosity, flexibility and improved crosslink density of the materials are attributed to the epoxy fraction. PBZ imparts thermal stability and mechanical properties, as well as low water-uptake, to the ternary systems [3]. The properties of a high-performance thermosetting resin can be improved by tightening its network structure. Hence, the modified novolac resins with BZ rings were prepared and cured with isobutyl bis(glycidylpropylether) phosphine oxide as the crosslinking agent [4].

The maleimide-functionalised BZ was copolymerised with diglycidyl ether bisphenol A (DGEBA) in various compositions in which three polymerisation reactions involving
an epoxy ring, a BZ ring, and a vinyl group were observed [5]. For copolymers with a high content of epoxy, the polymerisation of the maleimide group was incomplete, whereas polymerisations of epoxy and BZ were less affected. The resulting polymer achieved a high $T_g$ of 278 °C at 10 mol% DGEBA, and was higher than that of the homopolymer ($T_g = 253$ °C). Meanwhile, flexural strain at breakage increased with the increase in epoxy content. The flexural modulus was ~5.0 GPa for 10 mol% DGEBA and decreased to 4.2 GPa with 50 mol% DGEBA. The toughness of PBZ can effectively be improved by alloying with isophorone diisocyanate-based urethane prepolymer (PU) or with flexible epoxy [6].

### 3.3 PBZ–Poly(ε-Caprolactone) Blends

Hydrogen bonding is adequate to induce rigidity and constrain the mobility in the glassy state for thermosetting resins. Polymer blends of bisphenol A and an aniline-based benzoxazine (BA-a), and poly(ε-caprolactone) (PCL) indicated that hydrogen-bonding interactions occur between the carbonyl groups of PCL and the hydroxyl groups of PBA-a upon curing [7]. The most pronounced effect of the addition of PCL was to broaden the glass-transition region, and a decrease in the value of the loss tangent ($\tan \delta$) in the transition region upon increasing the PCL content. Before curing, the benzoxazine BA-a/PCL blends were miscible, but the phase separation induced by polymerisation was observed after curing at elevated temperature [8]. The $T_g$ of the PCL/BZ monomer blend exhibited a continuous increase as the PCL composition increased from 0 wt% to 33 wt% [9]. The intermolecular hydrogen bonding between PBZ and polycarbonate (PC) is illustrated in Scheme 3.2 [10].

![Scheme 3.2](image-url)  
3.4 PBZ–Polyimide Blends

Benzoxazine monomer (BA-a) was blended with soluble polyimide-siloxanes (PDMS) with and without pendant phenolic groups [11]. The onset and maximum of the exotherm due to the ring-opening polymerisation for the pristine BA-a appeared on differential scanning calorimetry (DSC) curves at ~200 °C and 240 °C, respectively. In the presence of poly(imide-siloxane)s, the exothermic temperatures were lowered: the onset to 130–140 °C and the maximum to 210–220 °C. The cured blends containing poly(imide-siloxane) with -OH functionality showed two \( T_g \) values, at a low temperature ~255 °C and at a high temperature ~250–300 °C, displaying phase separation between PDMS and the combined phase consisting of polyimide and PBZ (PBA-a) components due to the formation of AB-crosslinked polymers. For the blends containing poly(imide-siloxane) without OH functionalities, in addition to the \( T_g \) due to PDMS, two \( T_g \) values were observed in high-temperature ranges at 230–260 °C and 300–350 °C. This indicated further phase separation between the polyimide and PBZ components due to the formation of semi-interpenetrating networks (IPN). In both cases, the \( T_g \) increased with increasing poly(imide-siloxane) content. Tensile measurements showed that the toughness of PBA-a was enhanced by the addition of poly(imide-siloxane). Thermogravimetric analysis (TGA) revealed that the thermal stability of PBA-a was also enhanced by the addition of poly(imide-siloxane).

Polymer alloys of PBZ (BA-a) and soluble polyimide (PI) or its precursor, poly(amide acid) (PAA) were prepared and characterised [12]. The BA-a/PI formed a IPN structure. The ring-opening polymerisation of BA-a occurred \textit{in situ} with the imidisation of PAA, accordingly causing a complicated reaction. It was proposed that, in addition to the imidisation of PAA, the reaction between the phenolic OH of polyBA-a and the carboxylic acid of PAA could occur, affording an AB-crosslinked structure (Scheme 3.3).

The polymer alloy films from PI/BA-a and PAA/BA-a showed only one \( T_g \). The \( T_g \) values and thermal stabilities were increased remarkably as the content of PI increased. As the content of BA-a increased, the modulus of the polymer alloy films was also enhanced.
Polysiloxane-block-polyimide (SPI) has several attractive characteristics such as low moisture absorption and excellent thermal stability. Hence, this flexible material was incorporated into a PBZ matrix (PBA-a). The $T_g$ of blends with different SPI content showed a slight increase from the neat matrix, i.e., 160 °C to 169 °C, and the system exhibited partial miscibility as evidenced from an opaque appearance of cured blends. A noted advantage of blending is that the flexibility of PBZ is improved by SPI. In addition, the temperature at 5% weight loss ($T_{10\%}$) increased from 360 °C to 450 °C (75% weight of SPI) and the char yield increased from 30% (PBA-a) to 45% at 5% weight of SPI [13].
3.5 Other Blend Systems

Any chemical modification or additive to enhance toughness (with a minimum sacrifice of the original mechanical and physical properties of the PBZ) is attractive. Sequential IPN, based on PU and PBZ, was synthesised. The kinetics indicated the presence of physical bonding only in the resulting IPN. Morphological investigations revealed slight phase separation behaviour in all of the IPN studied [14]. In the blend of PBZ/PC, the ring-opening reaction and subsequent polymerisation reaction of the BZ were significantly inhibited by the presence of PC [15]. The hydrogen-bonding interaction in the blends occurs between the hydroxyl groups of the PBZ and the carbonyl groups of the PC. This is the ‘driving force’ that results in the miscibility of the PC/BZ blend in the entire composition range along with possible copolymer formation. The $T_g$ of the resulting blends decreased as the concentration of PC increased and deviated markedly from the Fox equation. In addition, an earlier degradation event appeared in the blend with 11 wt% and 33 wt% of PC. The possibility of the exchange reaction (which can occur in the blends containing PBZ and PC) was also confirmed [16]. The rubber-modified system of this PBZ-PCL matrix showed poorer thermal properties [17].

Study of thermosetting blends composed of BA-a and polyethylene oxide indicated that the phenolic hydroxyl groups could not form favourable intermolecular hydrogen-bonding interactions at elevated temperatures (e.g., the curing temperatures), i.e., the phenolic hydroxyl groups existed mainly in the non-associated form in the system [18]. Therefore, the phase separation is ascribed to the decrease of the entropic contribution to mixing energy due to the increase in molecular weight. The occurrence of the trans esterification replaced the original hydroxyl groups from the BZ main chain to the phenolic chain ends of the PC, and ‘scissored’ the long chain of PC into short segments. The result of the former can facilitate the ring-opening polymerisation, whereas the latter sacrificed the thermal properties of the blends. Polybenzoxazine/poly(N-vinyl-2-pyrrolidone) exhibited strong hydrogen-bonding interactions between PBA-a and polyvinyl pyrrolidone segments [19].

Ortho-, meta-, and para-phenylnitrile functional BZ were polymerised at different compositions with phthalonitrile-functional monomers (structures given in Scheme 2.12 in Chapter 2) and which produced copolybenzoxazines of high thermal stability and easy processability [20]. The $T_g$ also dramatically increased from 180 °C for neat ortho-phenylnitrile polymer to 294 °C for the copolymer with 30 mol% of phthalonitrile-functional monomer. Additionally, the high melt viscosity of phthalonitrile-functional BZ decreases upon blending with phenylnitrile-functional monomer. It has been demonstrated that only 30 mol% of phthalonitrile-functional BZ added to the ortho-phenylnitrile-substituted monomer significantly improves the
char yield from 59 wt% to 77 wt%, which is the value of the neat phthalonitrile-based PBZ.

Amine-terminated butadiene–acrylonitrile copolymer (ATBN) and carboxyl-terminated butadiene acrylonitrile rubber (CTBN) were introduced to PBZ. On a comparative scale, ATBN was more effective than CTBN in improving the fracture toughness of PBA-a. This was attributed to the better distribution of rubber particles in an ATBN-modified matrix than for the CTBN-modified matrix. Dynamic mechanical analysis (DMA) showed the existence of two networks in the ATBN-modified matrix [21].

Poly(urethane-benzoxazine) films as novel PU/phenolic resin composites were prepared by blending a BZ monomer (BA-a) and PU prepolymer [22]. All the films had only one \( T_g \) from viscoelastic measurements, indicating no phase separation in poly(urethane-benzoxazine) due to in-situ polymerisation. The films containing <15% of BA-a had elasticity characteristics with good elongation and excellent recovering behaviour, whereas those containing >20% of BA-a had plastic characteristics.

Polymer alloys composed of epoxy-terminated polyurethane and high-molecular-weight PBZ (derived from bisphenol A and methylenedianiline) showed good electrical and mechanical properties. These blends have excellent solvent resistance and a moisture uptake of 1.21–1.61%. However, the blends exhibited two alpha transitions in dynamic mechanical thermal analysis (DMTA) related to each of the components, which showed the phase-separated nature of the blends. The tensile strength of blends was of 24.0–30.5 MPa, which was lower than that of PBZ (30–40 MPa) [23].

A blend of bisphenol A-based BZ (BA-a) and a bismaleimide (2,2-bis[4(4-maleimidophenoxy) phenyl] propane (BMI) was thermally polymerised in varying proportions, and the cure and thermal characteristics investigated. The DSC analysis, supplemented by rheology, confirmed lowering of the cure temperature of BMI in the blend, implying catalysis of the maleimide polymerisation by BZ. The peak cure temperature \( (T_p) \) of the blend decreased to 211 °C in comparison with those of BMI (270 °C) and BA-a (218 °C). Moreover, the final cure temperature \( (T_f) \) of the blend was 284 °C, compared with 339 °C for BMI. Hence, from the viewpoint of BMI, the processing characteristics of the blend are improved. A wide cure regimen between 142 °C and 284 °C was observed for the blend (Table 3.1). Hence, by realising a blend of these resins, the initial and peak curing temperatures are lowered in comparison with those of the component resins, i.e., the processing is facilitated [24].
Table 3.1 DSC results of BA-a/BMI blends

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_i$ (°C)</th>
<th>$T_p$ (°C)</th>
<th>$T_f$ (°C)</th>
<th>CCW (°C)</th>
<th>Cure window (°C)</th>
<th>Heat of reaction (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Experimental</td>
</tr>
<tr>
<td>BA-a</td>
<td>156</td>
<td>218</td>
<td>270</td>
<td>62</td>
<td>114</td>
<td>257</td>
</tr>
<tr>
<td>BMI</td>
<td>195</td>
<td>270</td>
<td>339</td>
<td>75</td>
<td>144</td>
<td>130</td>
</tr>
<tr>
<td>BA-a/BMI (1/0.5)</td>
<td>128</td>
<td>212</td>
<td>293</td>
<td>81</td>
<td>165</td>
<td>225</td>
</tr>
<tr>
<td>BA-a/BMI (1/1)</td>
<td>142</td>
<td>211</td>
<td>284</td>
<td>69</td>
<td>142</td>
<td>180</td>
</tr>
<tr>
<td>BA-a/BMI (1/3)</td>
<td>130</td>
<td>224</td>
<td>342</td>
<td>118</td>
<td>212</td>
<td>174</td>
</tr>
</tbody>
</table>

$T_i$: Initial curing temperature
$T_p$: Peak curing temperature
$T_f$: Final curing temperature
CCW: Cure-controllable window ($T_p - T_i$)
Cure window: $T_f - T_i$

Fourier-transform infrared (FTIR) studies provided evidence for the hydrogen bonding between the carbonyl group of BMI and the –OH group of PBZ in the cured matrix. In the BA-a/BMI blend, there are two areas of interest in the FTIR spectra of the blends. One is the carbonyl region (1800–1650 cm$^{-1}$) and the other is the hydroxyl region (3600–3000 cm$^{-1}$). In the cured blend, the characteristic carbonyl band was observed at 1714 cm$^{-1}$. In addition, two relatively weak bands were observed at 1702 cm$^{-1}$ and 1687 cm$^{-1}$. These two bands are assigned to the hydrogen-bonded carbonyl groups generated in different environments in the blend. The two possibilities are depicted in Scheme 3.4. The hydroxyl group may be hydrogen-bonded with the carbonyl moiety of the bismaleimides, and hydroxyl groups which are already hydrogen-bonded (intermolecular hydrogen bonding) may be bonded to the carbonyl moiety of another bismaleimide group. Hydrogen bonding is expected to facilitate a homogeneous phase in the IPN or co-reacted matrices.
The cured matrix manifested dual-phase behaviour in scanning electron microscopy (SEM) and DMTA with the minor phase constituted by PBZ dispersed in an IPN of PBZ and cured BMI. The DMTA of the monomers and their blends implied a mutual catalysis of the two monomers. The maleimide groups are electron deficient whereas BZ groups possess electron-rich centres. The likely nπ– pπ interaction between the amine group of the BZ and the unsaturated group of maleimide may render the O-CH$_2$-N bond weaker and facilitate its cleavage. The π bond in maleimide becomes electron-rich and susceptible to addition polymerisation (Scheme 3.5) [25]. Similar situations have been encountered for maleimide mixed with electron-rich monomers (e.g., copolymerisation with styrene).
Scheme 3.5 Weakening of the –C-O bond of the oxazine group by nπ–pπ interaction in the BA-a/BMI blend

The DMTA of the cured resins is shown in Figure 3.1. Two distinct peaks in tan δ at 145 °C and 267 °C are seen for the BA-a/BMI system. This is due to some micro-level phase separation as also seen in SEM analysis. The BA-a/BMI IPN resulted in a higher \( T_g \). The lower \( T_g \) is attributed to the phase-separated PBZ segments.

Figure 3.1 Tan-δ behaviour of cured BA-a/BMI (1/1) in comparison with BA-a and BMI
The curing of allyl containing BZ–bismaleimide blends (BA-allyl/BMI) was also studied. In the 1/0.5 (BA-allyl/BMI) blend, two exotherms were observed, at 228 °C and 269 °C, respectively. The first exotherm is the co-curing of allyl-bismaleimide and the second exotherm corresponds to the ring-opening of BZ. Further addition of bismaleimide to BZ resulted in a decrease in the overall curing temperature. As the BMI concentration was enhanced from a molar ratio of 0.5 to 1, a broad exotherm was observed, predominantly due to the reaction between the allyl groups in BZ and the maleimide groups. The $T_p$ was lowered to 229 °C from 273 °C. Beyond this composition, bismaleimide did not significantly influence the cure because the $T_p$ and heat of reaction remained constant. The heat of reaction for independent curing of BA-allyl is 40 J/g and is 130 J/g for BMI. The heat of reaction in the 1/1 blend was found to be 190 J/g, indicating a change in the mechanism of cure. A proposed mechanism is shown in Scheme 3.6, involving the Alder-Ene reaction and ring opening of BA-allyl.
Scheme 3.6 Cure reaction in BA-allyl and BMI blends
Blends and Composites of Polybenzoxazines

BA-allyl/BMI blend formed predominantly a co-reacted network, so a homogeneous morphology was observed in SEM analysis. The $T_g$ of cured BMI and cured BA-allyl are 307 °C and 298 °C, respectively, (Figure 3.2). The BA-allyl/BMI system demonstrated a single $T_g$ at 274 °C owing to the formation of co-reacted networks. The thermal stability of BA-a/BMI and BA-allyl/BMI blends was improved compared with PBZ (Table 3.2).

![Figure 3.2 DMTA of BA-allyl/BMI, BA-allyl and BMI](image)

However, polymer alloys were reported by blending 1,1′-(methylenedi-4,1-phenylene)-bismaleimide (BMI) and BA-a. The obtained alloy films had improved toughness which increased with increase in BMI content. The authors proposed a thermal reaction between the double bond of BMI and the hydroxyl groups of BA-a. They suggested
that the reactions of the double bond and ring opening of BA-a occurs simultaneously, leading to a AB-co-crosslinked structure. The $T_g$ of alloys also increased from 154 °C to 268 °C at 76% of BMI content [26].

As described in Chapter 1, cyanate ester (CE) resins have good thermal and hygrothermal properties for use in the electronics, aerospace and adhesive arenas. To incorporate the properties of CE into PBZ, thermosetting polymer blends composed of benzoxazine (BA-a) and bisphenol A cyanate ester (BACY; structure is shown in the inset of Figure 3.3) was investigated [27].

The blend was prepared by powder mixing of two monomers in a mortar and by using a solvent method (AR acetone). The DSC of the powder-blended system was conducted immediately after mixing. Four distinct exotherms were observed in the DSC analysis. The exothermic heat for curing of BA-a and BACY are 262 J/g and 760 J/g, respectively, but the exothermicity of the (1/1) blend was reduced by as much as 210 J/g (powder blend).