

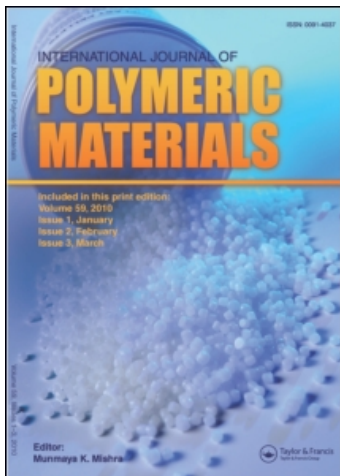
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Preparation and Characterization of Novel Polybenzoxazine–Polyester Resin Blends

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Blends consisting of polybenzoxazine and polyester with various weight ratios have been prepared by using a solution blending method. Thermal properties of the blends have been investigated by using thermogravimetric and differential scanning calorimetric analysis. Formation of hydrogen bonding was detected by using Fourier transformed infrared spectroscopy. Thermal stability of the blends increased with increasing the amount of polybenzoxazine in the composition. The composition having 70 wt% polybenzoxazine and 30 wt% polyester resin possesses the highest hardness and comparatively good thermal stability, with an initial decomposition temperature of 274°C and char yield = 21%.

Keywords blend, polybenzoxazine, thermal analysis, unsaturated polyester

INTRODUCTION

Polybenzoxazine is a recently developed new type of addition polymerized phenolic system, having a wide range of interesting properties and the capability to overcome several shortcomings associated with conventional novolac and resole type phenolic resins [1,2]. These materials exhibit (i) near-zero volumetric change upon curing, (ii) low water absorption, (iii) for some polybenzoxazine T_g is much higher than cure temperature, (iv) high char

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yield, (v) no strong acid catalysts required for curing, and (vi) no toxic by-product release during curing [3]. The molecular structure of polybenzoxazine offers enormous design flexibility, which allows tailoring the properties of the cured materials for a wide range of applications [4]. Although benzoxazine-based materials possess several advantages, they have not yet become very attractive to the industries. Some of the disadvantages associated with pure polybenzoxazine are (i) high curing temperature ($\sim 200^\circ\text{C}$ or higher), (ii) difficulty in processing, and (iii) poor mechanical strength [1,2,5]. To improve the mechanical properties and processibility, several strategies have been reported including (i) synthesis of benzoxazine monomers with additional functionality [3], (ii) preparation of blends of polybenzoxazine by blending it with another polymer or inorganic fillers, which appears to be an easier alternative. Benzoxazine-based blends can be categorized as (i) polybenzoxazine blends with another polymeric resin such as epoxy [5–7], polyurethane [8,9], poly(ϵ -caprolactone) [10,11], polycarbonate [12], and poly(N-vinyl-2-pyrrolidone) [13], (ii) consisting inorganic particles such as silica [14,15], TiO_2 [16] dispersed in a polybenzoxazine matrix, and (iii) fiber-reinforced polybenzoxazine composites [17,18]. We have recently reviewed different synthetic strategies reported for the preparation of benzoxazine monomers and blends, their polymerization reaction mechanisms, and the structure–property relationships and up-to-date development of benzoxazine chemistry and references are cited [1,2]. In this paper, we have reported the preparation of blends consisting of polybenzoxazine and unsaturated polyester. We have chosen unsaturated polyester as one of the components of the blends because (i) it is cheap and commercially available, (ii) it possesses low viscosity, which helps in processing, and (iii) polybenzoxazine can form hydrogen bonding with the carbonyl group of polyester [10–12]. This hydrogen bond can play a critical role in improving the mechanical properties of polybenzoxazine-based blends.

We have prepared the polybenzoxazine–polyester blends with various compositions by using a solution blending method. Thermal stability of the cured blends and cure temperature was investigated by using thermogravimetric (TG-DTA) and differential scanning calorimetric analysis (DSC). FTIR spectroscopy was used to understand the presence of hydrogen bonding between the carbonyl group of polyester with the $-\text{OH}$ group of polybenzoxazine in the blends. Hardness of the cured blend was determined by using Barcol Hardness.

EXPERIMENTAL

Materials

Starting chemicals used were isophthalate unsaturated polyester resin (bis(1-(4-methoxy-4-oxobut-2-enyloxy)propan-2-yl)isophthalate) diluted with

styrene (PER) ($M_w = 1500$) (Mechanco Industries, India), bezoxyl peroxide (BPO) (98% Amrut Chemicals, India), bisphenol-A, paraformaldehyde and aniline (99% Merck, India). The chemical composition of isophthalate unsaturated polyester resin was isophthalic anhydride, maleic anhydride, and propylene glycol. All these materials were used without further purification. Here, bezoxyl peroxide was used as an initiator.

Synthesis of Benzoxazine Monomer

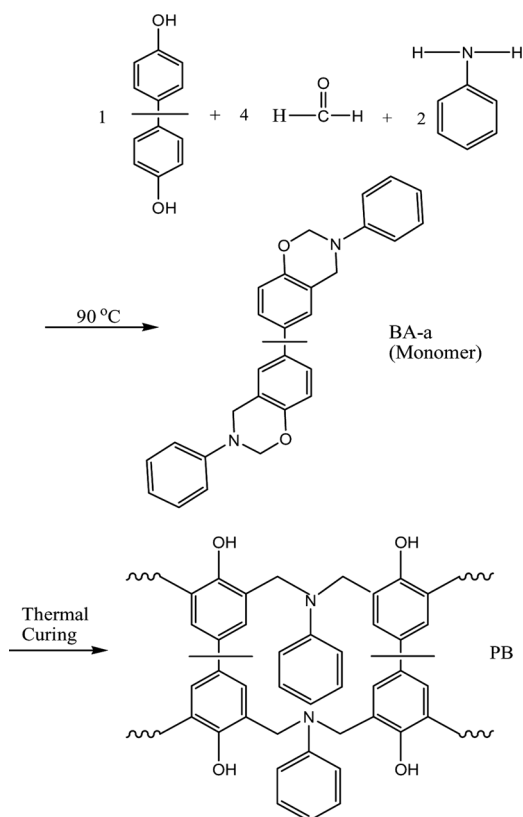
Benzoxazine (bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl)isopropane) (BA-a) was synthesized using a solventless method by reacting bisphenol-A, aniline and paraformaldehyde [19]. In a typical synthesis, 4.48 g of bisphenol-A, 3.68 ml aniline, 2.4 g of paraformaldehyde were mixed in a round-bottom flask and slowly heated at 90°C in an oil bath for 90 min. After cooling the resulting material was dissolved in CHCl_3 and filtered. CHCl_3 was then evaporated to obtain benzoxazine monomer. Synthesized benzoxazine monomer was dried in a vacuum oven for 24 h at 55°C to remove traces of chloroform. The synthesis route and structure of BA-a prior and after curing are shown in Scheme 1.

Preparation of Polybenzoxazine/Polyester Blend

Blends of polybenzoxazine (PB) and polyester (PER) with several compositions were prepared by using a solution blending method, where acetone was used as solvent. Various compositions of blends are listed in Table 1. Preparation of the PB-10/PER-90 blend was as follows: a calculated amount of benzoxazine monomer was dissolved in acetone in a 250 ml beaker and stirred mechanically with the slow addition of an appropriate amount of polyester resin. This mixing results in the formation of a yellowish semi-viscous transparent material. The mixture was further stirred for 45 min to obtain a homogenous mixture. To this yellowish mixture, a solution of bezoxyl peroxides (BPO) in acetone (0.5 wt%), was added and stirred for 1–2 min. The semi-viscous reaction mass was immediately poured into an aluminum mould. The whole process was carried out at room temperature. A solid mass was thus obtained. Acetone was evaporated from the blend slowly at room temperature for about 24 h. The resulting solid was further cured by using a curing profile as shown in Table 2.

Sample Characterization

Differential scanning calorimetric (DSC) analysis was carried out for the uncured samples by using a Shimadzu DSC-60 (Japan) in an air atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$ from 40 to 550°C. Thermogravimetric analysis (TG- DTA) was performed for the cured polymer blends by using a Shimadzu DTG-60 (Japan). The experiments were performed at a heating rate of



Scheme 1: Benzoxazine monomer (BA-a) and polymer (PB) nomenclature and structure used in this study.

Table 1: Different PB/PER blend compositions.

Sample code	Wt% ratio	
	PB	PER
PB-100/PER-0	100	0
PB-90/PER-10	90	10
PB-80/PER-20	80	20
PB-70/PER-30	70	30
PB-60/PER-40	60	40
PB-50/PER-50	50	50
PB-40/PER-60	40	60
PB-30/PER-70	30	70
PB-20/PER-80	20	80
PB-10/PER-90	10	90
PB-0/PER-100	0	100

Table 2: Curing profile for PB/PER blend.

Temperature (°C)	Time (hrs)
100	2
120	1/2
160	1/2
180	2
200	2

10°C min⁻¹ in air and the temperature range was 40 to 700°C. Fourier transform infrared (FTIR) spectra of the samples were acquired using a Shimadzu IR Spectrophotometer (model 840, Japan), equipped with a potassium bromide (KBr) beam-splitter. All spectra were recorded with 50 scans at a resolution of 4 cm⁻¹ and spectral range between 4000–400 cm⁻¹. Hardness of the cured samples was measured using a Barcol Hardness tester (model GYZJ 934-1, USA) for cured specimens having ~3 mm thickness. Hardness was determined at five different positions on the specimen with the measurement points taken at least 6 mm apart.

RESULTS AND DISCUSSION

Thermal Analysis (TG-DTA and DSC)

To investigate the polymerization of benzoxazine monomer and polyester resin in the presence of BPO (initiator), DSC analysis has been performed as shown in Figure 1. For pure benzoxazine monomer the presence of an exothermic peak at ~217°C (onset 153°C and offset 270°C) indicated the curing of benzoxazine by the ring opening polymerization (Figure 1(a)) [5]. In the case of polyester resin with BPO, an exothermic peak at 105°C (onset 84°C and offset 125°C) was observed (Figure 1(b)), which can be attributed to the polymerization of the vinyl double bonds of styrene and unsaturated double bonds of polyester.

In the DSC thermogram of uncured blends it was observed that the exothermic peak (at ~217°C), for the curing of benzoxazine, slowly diminished with an increasing PER concentration in the blend. Complete disappearance of this peak was observed for PB-60/PER-40 composition and onwards. This might be due to the dilution of benzoxazine in the blend Figure 2.

To investigate the thermal stability of the cured blends with various composition thermogravimetric analysis (TGA) was performed. From TGA thermogram of cured pure polyester resin, pure polybenzoxazine and blends are shown in Figure 3. It was observed that:

- (a) Thermal decomposition of pure polyester occurred in three steps: (i) first weight loss of ~24% in the temperature range of 150–300°C, might be

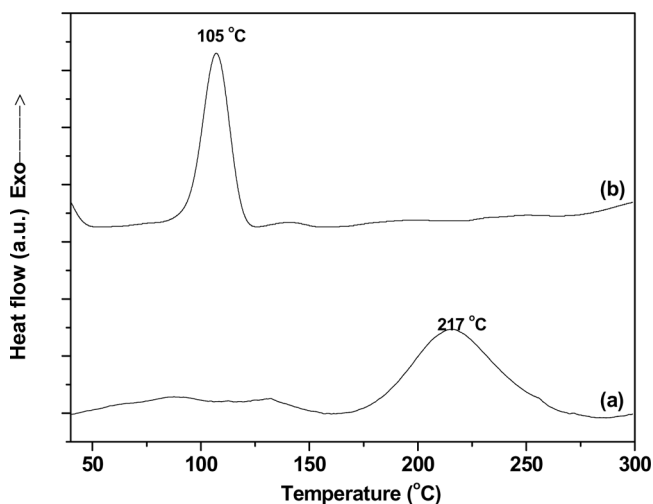


Figure 1: DSC of (a) BA-a and (b) PER with BPO.

due to decomposition of untreated styrene and some unreacted monomer, (ii) major weight loss of $\sim 52\%$ in the temperature range $300\text{--}400^\circ\text{C}$ may be attributed to the decomposition of carbonyl groups in the main chain [20], and (iii) $\sim 14\%$ weight loss in $400\text{--}550^\circ\text{C}$ region might be due to the decomposition of aromatic ring units in the polymer chain [21].

- (b) In the case of pure cured polybenzoxazine, decomposition started at $\sim 365^\circ\text{C}$ and $\sim 69\%$ weight loss occurred in the temperature range at $365\text{--}650^\circ\text{C}$.

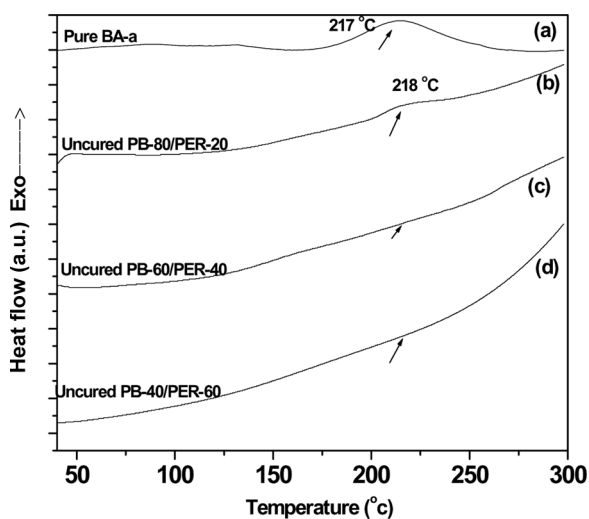


Figure 2: DSC of (a) BA-a, (b) uncured PB-80/PER-20, (c) uncured PB-60/PER-40, and (d) uncured PB-40/PER-60.

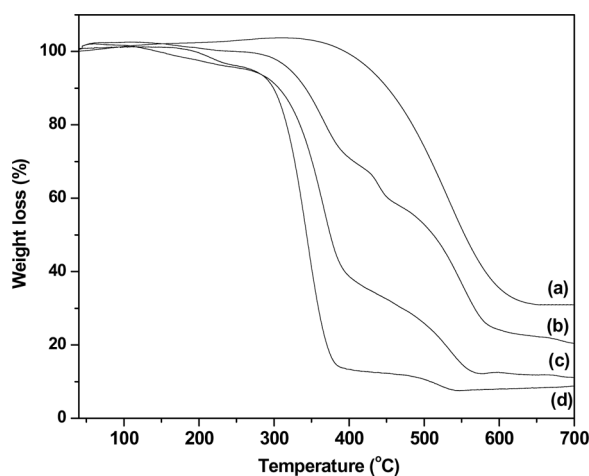


Figure 3: TGA of cured samples (a) PB-100/PER-0 (pure cured PB), (b) PB-80/PER-20, (c) PB-20/PER-80, and (d) PB-0/PER-100 (pure cured PER).

- (c) Thermal stability of cured blends was found to be increased with increasing the amount of benzoxazine in the blend. For example, when 20 wt% polybenzoxazine (PB-20/PER-80) ~36% weight loss occurred in the temperature region of 300–400°C, where as when 80 wt% polybenzoxazine was present in the sample (PB-80/PER-20), ~6% weight loss was observed in the same temperature region.
- (d) Major weight loss due to thermal decomposition occurred for all the blend compositions in the temperature range of 315–600°C but char yield of the blends was found to be increasing with increasing the benzoxazine amount in the blend.
- (e) Initial decomposition temperature (T_i) of the cured blend was found to be increasing with an increasing benzoxazine concentration in the blend. Initial decomposition temperature (T_i), temperature for 5% weight loss, 10% weight loss and char yield for all the compositions of the blends have been listed in Table 3.

DTA thermogram of all the compositions of the blend is shown in Figure 4. From DTA, it was observed that:

- (i) For pure polybenzoxazine, an exothermic peak at 555°C (onset 464°C and offset 627°C) appeared due to degradation of the aromatic ring units of polymer chain [21].
- (ii) For cured polyester, the appearance of two exothermic peaks (a) at 360°C (onset 248°C and offset 434°C) for degradation of C=O group [20] and (b) at 515°C (onset 434°C and offset 584°C) for degradation of aromatic ring units [21].

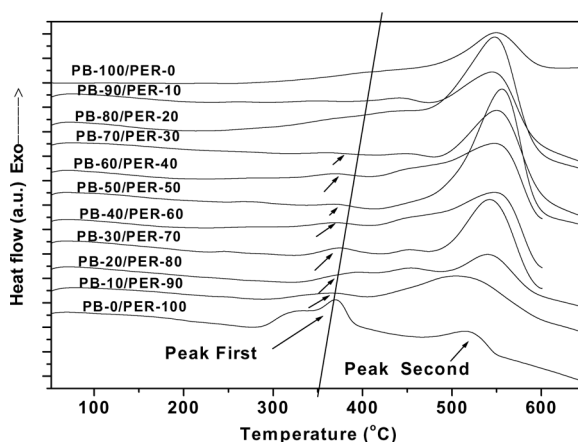
Table 3: Comparison of T_i , $T_{5\%}$, $T_{10\%}$, and char yield values for all blend compositions.

Sample code	Initial decomposition temperature (T_i) ($^{\circ}\text{C}$)	$T_{5\%}$	$T_{10\%}$	Char yield (%) at 650°C
PB-100/PER-0	365	421	450	31
PB-90/PER-10	331	405	430	26
PB-80/PER-20	312	382	424	23
PB-70/PER-30	273	340	380	21
PB-60/PER-40	257	315	335	20
PB-50/PER-50	248	305	328	19
PB-40/PER-60	245	282	324	18
PB-30/PER-70	240	268	319	16
PB-20/PER-80	235	242	300	11
PB-10/PER-90	230	233	276	9
PB-0/PER-100	177	226	259	8

- (iii) With the increasing amount of polybenzoxazine in the blend, the exothermic peak at 360°C started decreasing and disappeared for the composition when 60 wt% polybenzoxazine was present in the composition (PB-60/PER-40).
- (iv) The exothermic peak, responsible for aromatic ring unit degradation, was found to be shifted from 515 to 555°C with an increasing benzoxazine amount in the blends. This indicated thermal stability of blends increased with increasing benzoxazine concentration in the blend.

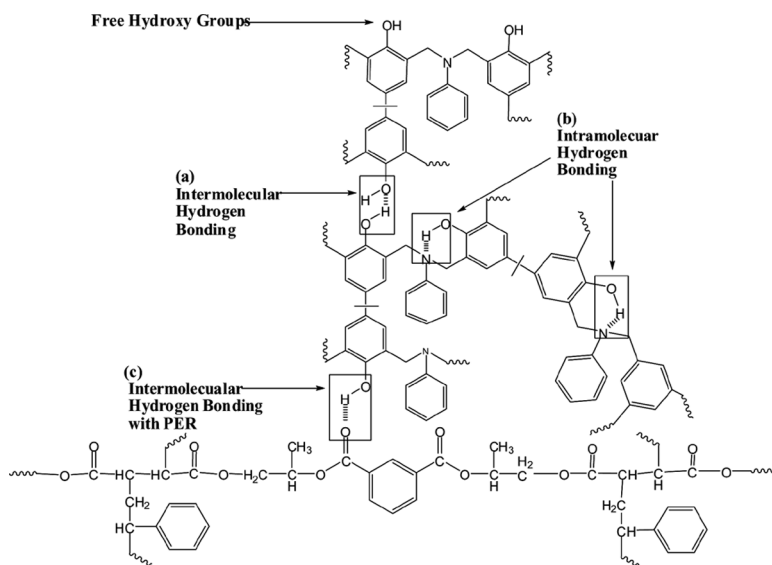
FTIR Analysis

It has been reported by Huang et al. [10] and Ishida et al. [11,12] that the hydroxyl group of polybenzoxazine is capable of forming hydrogen bonding with

**Figure 4:** DTA thermograms of cured blends showing the effect of PB concentration on the thermal degradation of blend compositions.

the C=O group of poly(ϵ -caprolactone) and polycarbonate polymers [10–12]. There are three types of hydrogen bonding which could possibly occur in PB/PER blends, which are shown in Scheme 2. Possible hydrogen bonds are (i) intermolecular hydrogen bonding, between two hydroxy groups of polybenzoxazine (Scheme 2(a)), (ii) intramolecular hydrogen bonding between hydroxy group and nitrogen atoms on the Mannich Bridge (Scheme 2(b)), (iii) intermolecular hydrogen bonding between carbonyl groups of polyester and a hydroxy group of polybenzoxazine (Scheme 2(c)). These hydrogen bonds can be identified in FTIR spectra of the blends. FTIR spectra of pure benzoxazine monomer, uncured pure PER, cured pure PER, and cured blend (PB-30/PER-70) are shown in Figure 5.

From FTIR spectra it has been observed that: (i) in the case of pure benzoxazine monomer, IR peaks appeared at 945 cm^{-1} and 1497 cm^{-1} , which can be attributed to the tri-substituted benzene ring in benzoxazine monomer [9]. (ii) For uncured PER, a peak at 1652 cm^{-1} for C=C bond and a sharp peak at 1732 cm^{-1} along with a very small shoulder peak at 1717 cm^{-1} for C=O group were present. (iii) In the case of cured blends, the absence of peak at 1652 cm^{-1} (C=C) indicated the crosslinking of the double bonds occurred due to curing. The presence of peaks at 1732 cm^{-1} and 1717 cm^{-1} can be attributed to the C=O group. It is important to note that, for the cured blend sample peak at 1717 cm^{-1} , it was observed for uncured PER as a small shoulder peak which appeared as a high intensity peak and splitted from 1732 cm^{-1} peak (Figure 6).



Scheme 2: Three types of hydrogen bonding that could possibly occur in polyester/polybenzoxazine blend: (a) intermolecular hydrogen bonding between two hydroxy groups of polybenzoxazine, (b) intramolecular hydrogen bonding between hydroxy groups and nitrogen atom on the Mannich bridge, and (c) intermolecular hydrogen bonding between carbonyl groups of polyester and hydroxyl groups of polybenzoxazine.

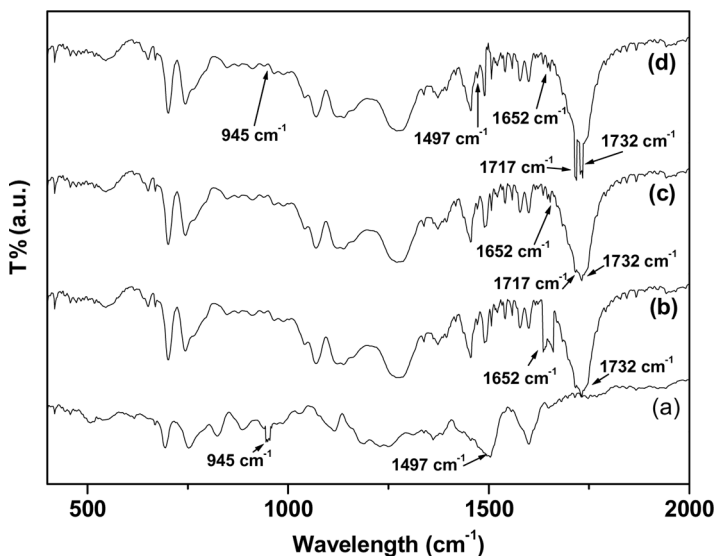


Figure 5: FTIR of (a) BA-a, (b) uncured PER, (c) cured PER, and (d) cured PB-70/PER-30.

This might be due to the formation of hydrogen bonding between C=O group of PER with -OH group of PB. The peaks at 1717 cm^{-1} and 1732 cm^{-1} were assigned for hydrogen bonded and non-hydrogen bonded carbonyl groups of PB/PER blends, respectively [10–12].

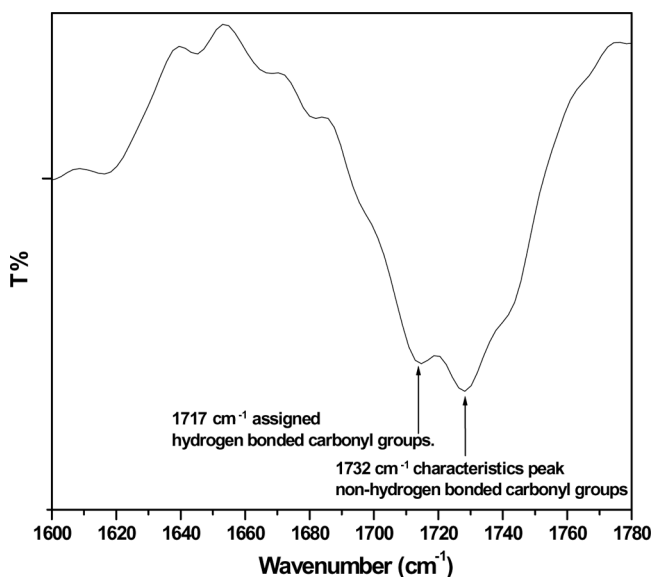


Figure 6: FTIR of cured PB-70/PER-30 carbonyl group region showing the effect of hydrogen bonding.

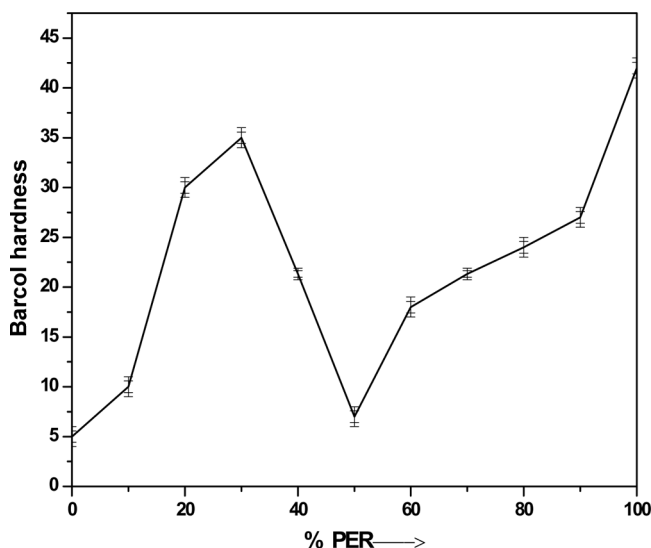


Figure 7: Hardness of all blend compositions.

Barcol Hardness Testing

The effect of composition of blends on the hardness of cured blends was determined by Barcol Hardness testing. Change of hardness with composition is shown in Figure 7. The hardness value of pure polybenzoxazine was found to be very less (about 5). The hardness values of the blends increased with an increasing amount of PER in the blend. The highest value of hardness 35 was observed for 30 wt% of polyester resin (PB-70/PER-30) composition. Then the values decreased for 40 wt% PER (PB-60/PER-40) and 50 wt% PER (PB-50/PER-50) concentration in the blend. The increase of hardness up to PB-70/PER-30 composition might be due to an increase of crosslinking density of polybenzoxazine in the presence 30 wt% PER. Hydrogen bonding between C=O group of PER with –OH group of polybenzoxazine played a critical role in this case. It has been observed that a further increase of PER concentration in the blend (up to 50 wt% PER) caused a decrease in hardness value. This might be due to the influence of a significant amount of PB in blend, which affected the crosslinking density of PER. But, a further increase of PER concentration (above 50 wt%) resulted in an increase of hardness, because in these cases PER played a dominating role.

CONCLUSIONS

The preparation of polybenzoxazine-polyester blends (with a wide range of composition) by using a simple solution blending method has been reported

in this paper. Thermal stability of the blends have been investigated by using TG-DTA and DSC. Formation of hydrogen bonding between carbonyl group of polyester and $-OH$ group of polybenzoxazine was detected by using FTIR spectroscopy. Hardness of the cured blend was determined by using Barcol Hardness testing. The important observations of this investigation are (i) thermal stability of the blends increased with increasing the amount of polybenzoxazine in the composition. This was reflected in the increasing values of T_i , $T_{5\%}$, $T_{10\%}$, and char yield with increasing amount of polybenzoxazine, (ii) hardness of the polybenzoxazine was found to increase from 5 to 35 due to blending with 30 wt% polyester resin. The composition having 70 wt% polybenzoxazine and 30 wt% polyester resin possesses highest hardness with comparatively good thermal stability ($T_i = 274^\circ\text{C}$ and char yield = 21%). During preparation of blends benzoxazine monomers were mixed with semi-viscous unsaturated polyester resin to form a liquid blend solution. This may be helpful for easier processing and preparation of complex structures. Comparatively high thermal stability and good mechanical properties make these materials suitable candidates for various applications. A detailed investigation on mechanical properties using DMA, universal testing machine is in progress.

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