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Poly(benzoxazine-*co*-urethane)s: A new concept for phenolic/urethane copolymers via one-pot method

Mohamed Baqar [a,1], Tarek Agag [b,*], Hatsuo Ishida [b], Syed Qutubuddin [a,b]

[a] *Department of Chemical Engineering, Case Western Reserve University, Cleveland, OH 44106-7202, USA*
[b] *Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106-7202, USA*

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ABSTRACT

Historically, applications for traditional phenolic resin/polyurethane materials are limited due to the inherently weak thermal stability of urethane-phenolic linkage and slow reaction rate. A novel concept has been developed to produce phenolic resin/polyurethane copolymers via benzoxazine chemistry. Through one-pot synthesis, a series of linear poly(benzoxazine-*co*-urethane) materials has been synthesized via the reaction of a newly developed dimethylol functional benzoxazine monomer with 4,4′-methylene diphenyl diisocyanate and poly(1,4-butyleneadipate). The structure of the copolymers has been characterized by Fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance spectroscopy (NMR). The copolymers in the film forms have been further thermally treated for crosslinking to produce crosslinked poly(benzoxazine-*co*-urethane) via the ring opening polymerization of cyclic benzoxazine moieties in the main-chain. The tensile properties of the films have been studied and compared with those of traditional high performance materials. The thermal properties of the crosslinked copolymers have also been studied by dynamic mechanical analysis, and thermogravimetric analysis (TGA).

1. Introduction

Polyurethanes (PUs) represent one of the most versatile classes of polymers due to their advantages, which include excellent low temperature flexibility, superb oil and abrasion resistance, and extraordinary easy processability [1–3]. PUs are segmented polymers that consist of soft segments derived from polyols and hard segments derived from isocyanate and chain extenders. The hard segments offer stiffness to the resulting materials, whereas the soft segments act as flexible connectors between the hard segments. PUs also have a wide variety of properties, ranging from elastic to plastic behavior, which make them suitable for a broad number of applications, such as coatings and paints, flexible foams, insulations, adhesives, and sealants. Nonetheless, the use of PUs is associated with some disadvantages, including high water up-take, poor resistance to polar solvents, and poor thermal stability. They also undergo dissociation of urethane linkages at elevated temperatures [4]. As a result, tremendous research efforts have been reported to improve the thermal stability of PUs. Most of the reported approaches are based on copolymerization or blending with other polymers of high thermal stability such as polyimides [5–8], polyurea [9,10], polyamide [11,12], epoxy [13], and polydiacetylene [14].

Polybenzoxazines, as a newly developed class of high performance polymers, have attracted much interest of academia and industries. They are characterized by many useful properties, such as low moisture absorption, excellent mechanical properties, self-extinguishing properties, and excellent dimensional stability [15–18]. They also offer a remarkable flexibility in molecular design of monomers and, consequently, a versatile performance as polymers [19–21]. Benzoxazine monomers are polymerized by the thermally activated cationic ring opening polymerization of benzoxazine without any added initiators, catalysts, or by-product formation [22–26]. The potential application areas of polybenzoxazines include coatings, electronic packaging materials, printed circuit boards, frictional materials, catalysis, and matrices for composite materials.

Due to the excellent thermal and mechanical properties of polybenzoxazines, they have been incorporated into PUs aiming at improving their thermal and mechanical properties. The flow chart shown in Fig. 1 represents all reported routes for preparing polybenzoxazine/PU materials. The concept adapted in all the previous studies is based on blending of either preformed

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[*] Corresponding author. Tel.: +1 20 40 3326357; fax: +1 20 40 3350804.
E-mail address: taa16@cwru.edu (T. Agag).

[1] On leave from Nasser International University-Libya

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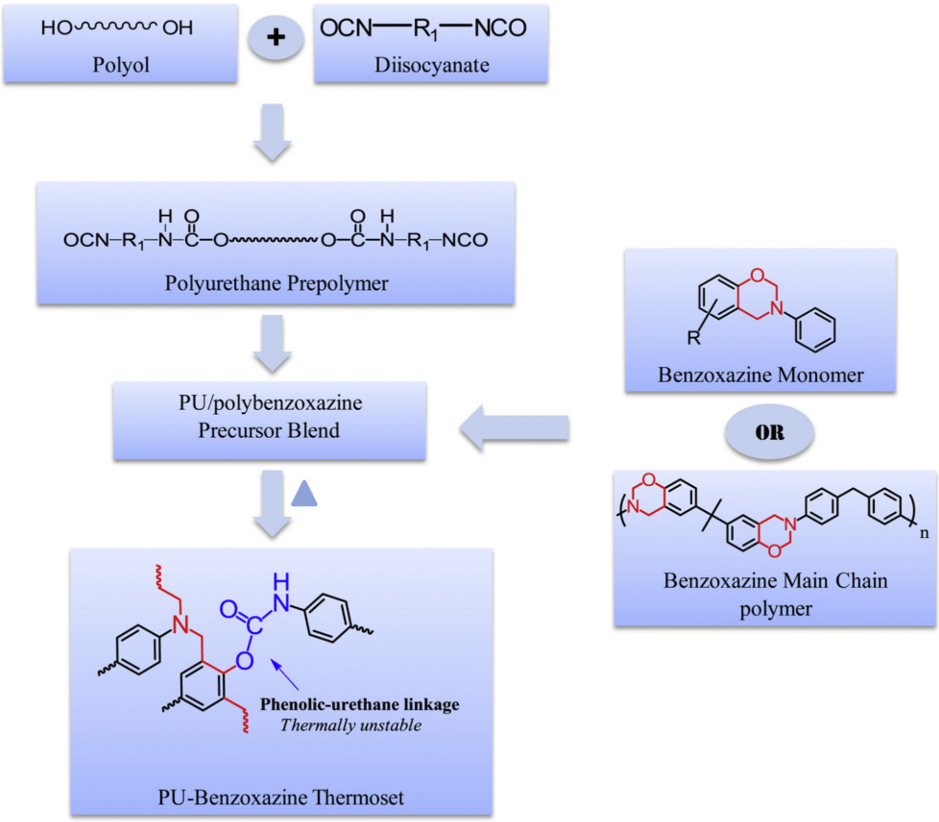


Fig. 1. Previous approaches of polybenzoxazine/PU materials.

benzoxazine monomers or main-chain benzoxazine polymers as polybenzoxazine precursors, with NCO-terminated PUs followed by thermal treatment. As a result, the phenolic groups produced upon ring opening polymerization of benzoxazine react with the NCO groups of PU prepolymer, leading to the formation of phenolic-urethane linkage.

The first study of polybenzoxazine/PU systems was reported by Takeichi et al. [27,28]. They blended bisphenol A/aniline-type benzoxazine monomer (BA-a) and phenol/aniline-type monomer (P-a) with NCO-terminated PU prepolymer. The results of thermal and mechanical properties indicated that polybenzoxazine/PU materials with elastomeric properties can be obtained by adding ca. 10–15% of polybenzoxazine, whereas films with greater plasticity can be produced by increasing the polybenzoxazine content. They also further improved the tensile modulus by adding organoclay to produce polybenzoxazine/PU nanocomposites [29]. Wang et al. [30] prepared interpenetrating polymer networks (IPNs) of polybenzoxazine/PU system. Their morphological studies indicated that the copolymer networks exhibit only physical bonding with slight phase separation behavior. Rimdusit et al. investigated various aspects of polybenzoxazine/PU systems. They found that a system with 10 wt.% PU content exhibited improved flexural strength without deterioration of the thermal degradation temperature [31]. The char yield was slightly increased by using a polyol of higher molecular weight [32]. They also studied the effect of various isocyanates on the properties of a polybenzoxazine/PU system and the reinforcement of the system by carbon fiber [33]. Yeganeh et al. studied various polybenzoxazine/PU systems for electrical insulation applications by blending BA-a monomer and main-chain benzoxazine polymer (BA-ddm) with epoxy-terminated PU prepolymer [34,35]. They have also recently prepared phenolic-terminated PU prepolymer by end-capping of NCO-terminated PU prepolymer with bisphenol A, which was then mixed with BA-a to form polybenzoxazine/PU materials [36].

Despite the known slow kinetics of isocyanate reacting with phenolic compounds and the poor thermal stability of the urethane linkages produced, most of the aforementioned methods of synthesizing polybenzoxazine/PU materials used similar concept of reacting NCO-terminated PU prepolymers with the phenolic groups of polybenzoxazine [27–36]. It is known that the nature of the group attached to a urethane linkage controls its thermal stability. In general, the thermal stability increases in the presence of electron donating groups and decreases in the presence of electron withdrawing groups in the following order; aryl-NHCOO-aryl < alkyl-NHCOO-aryl < aryl-NHCOO-alkyl < alkyl-NHCOO-alkyl [4,37,38]. Thus, urethane-phenolic linkage produced through the previous approaches is considered to have lowest thermal stability. As a result of these disadvantages, phenolic/PU materials have historically limited applications.

Thus, it is believed that the use of an aliphatic hydroxyl-functional benzoxazine for urethane linkage formation instead of a phenolic hydroxyl group will lead to polybenzoxazine/PU materials of fundamentally different structure and properties than the previously reported approaches. This new approach preserves the oxazine ring upon main-chain polymer formation, which can then be used to further crosslink the copolymer to produce polybenzoxazine/PU network that contains free phenolic moieties. Preservation of the phenolic moieties will maintain the well-known advantages of polybenzoxazines by allowing the formation of intramolecular 6-membered ring hydrogen bonding that offers polybenzoxazines the unique characteristics [22,23]. In the current study, a newly developed hydroxymethyl functional benzoxazine monomer has been used to produce poly(benzoxazine-*co*-urethane)s as a main-chain type benzoxazine polymers. The reaction of aliphatic hydroxymethyl functionalities with isocyanate groups is expected to produce thermally stable urethane linkages. Applying this concept of one-pot method will also lead to avoid the drawbacks associated with the use of NCO-terminated PU prepolymer, such as poor shelf life due to their high sensitivity towards moisture and susceptibility to undesirable side reactions. Furthermore, the unique advantage of the recently developed concept of thermoplastic-thermosetting crossover of main-chain type benzoxazine polymers [39,40] will be highly beneficial in designing varieties of poly(benzoxazine-*co*-urethane)s with unique characteristics in terms of processability and performance. The preparation, characterization, crosslinking and properties of this new class of copolymers are discussed in the current study.

2. Experimental

2.1. Materials

4,4′-Methylenediphenyldiisocyanate (**MDI**) (>99%), 4,4′-diaminodiphenylmethane (**DDM**) (98%), and paraformaldehyde (96%) were obtained from Acros Organics USA and used as received. 4-Hydroxybenzyl alcohol (**4HBA**) (98%) was purchased from Sigma Aldrich. Poly(1,4-butylene adipate) (**PBA**) with molecular weight of 1000 was purchased from Sigma Aldrich and dried at 80 °C for 10 h under vacuum just before use. *N,N*-dimethylformamide (**DMF**) was purchased from Fisher and dried over molecular sieves prior to use.

2.2. Synthesis of methylol-functional benzoxazine monomer (4HBA-ddm)

In a 500 mL flask, **4HBA** (19 g, 150 mmol), **DDM** (15.02 g, 75 mmol), and paraformaldehyde (9.01 g, 300 mmol) were mixed together and heated at 140 °C in xylenes (175 mL) for 5 h. The reaction was allowed to cool to room temperature followed by washing with hexane to afford a yellow product. The product was then recrystallized in chloroform, (Yield: 80–85%).

IR spectra (KBr, cm^{-1}): 1228 (asymmetric stretching of Ar–O–C), 1076 (asymmetric stretching of C–O–C), 952 (out-of-plane vibration, benzene ring to which oxazine is attached).

^{1}H NMR spectra (DMSO-d_6, frequency: 600 MHz, ppm: δ) 4.36 (d, $-CH_2-O$), 4.57 (s, $C-CH_2-N$), 4.99 (t, –OH), 5.36 (s, $N-CH_2-O-$).

^{13}C NMR spectra (DMSO-d_6, ppm, δ): 49.23 ($C-CH_2-N-$), 62.61 (s, $-CH_2-OH$), 78.87 ($N-CH_2-O$).

2.3. Synthesis of model compound

The model compound has been synthesized by dissolving **4HBA-ddm** (0.5 g, 1 mmol) and phenyl isocyanate (0.238 g, 2 mmol) in a 50 mL dry three neck flask in extra dry DMF (<50 ppm, 20 mL) containing dibutyltindilaurate (0.02 g) under nitrogen atmosphere. The mixture was heated at 70 °C for 30 min to afford a yellow solution. The solution was then cooled and precipitated in cold water, washed by ethanol, and dried in a vacuum oven at room temperature for 24 h to afford a white powder, (Yield: 84%).

IR spectra (KBr, cm^{-1}): 1224 (asymmetric stretching of Ar–O–C), 1037 (asymmetric stretching of C–O–C), 950 (out-of-plane vibration, benzene ring to which oxazine is attached).

^{1}H NMR spectra (DMSO-d_6, ppm: δ, frequency: 600 MHz): 4.59 (s, $C-CH_2-N-$), 4.98 (s, $-CH_2-O$), 5.38 (s, $N-CH_2-O-$), 9.67 (s, –NH).

^{13}C NMR spectra (DMSO-d_6, ppm, δ): 49.15 ($C-CH_2-N-$), 65.62 (s, $-CH_2-OH$), 79.03 ($N-CH_2-O$).

2.4. Synthesis of poly(benzoxazine-co-urethane)s

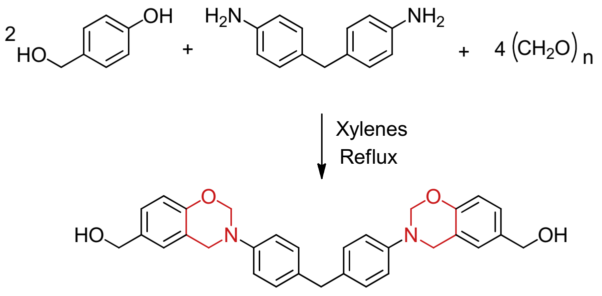
The following is an example of the synthesis of poly(benzoxazine-*co*-urethane)s with a 1:0.8:0.2 M ratio of MDI:4HBA-ddm:PBA respectively. Into a 50 mL dried three neck flask was dissolved **4HBA-ddm** (0.594 g, 1.2 mmol), and **PBA** (0.3 g, 0.3 mmol) in an extra dry DMF (<50 ppm, 35 mL) solvent containing dibutyltindilaurate (0.02 g), under dry nitrogen atmosphere. The mixture was stirred until clear solution was obtained, followed by adding **MDI** (0.376 g, 1.5 mmol). The mixture was then continually stirred at 70 °C for 30 min. The resulting solution was precipitated in water to afford a slightly yellowish powder, which was dried under vacuum at room temperature for 24 h.

IR spectra (KBr, cm^{-1}): 1733 (the C=O stretching of non-hydrogen bonded carbonyl group of urethane and ester groups), 1540 (the C–N stretching, combined with N–H out-of-plane bending), 1414 (the stretching of C–NH), 1228 (the asymmetric stretching of Ar–O–C), 1076 (the asymmetric stretching of C–O–C), 955 (the out-of-plane vibration of benzene ring to which oxazine is attached).

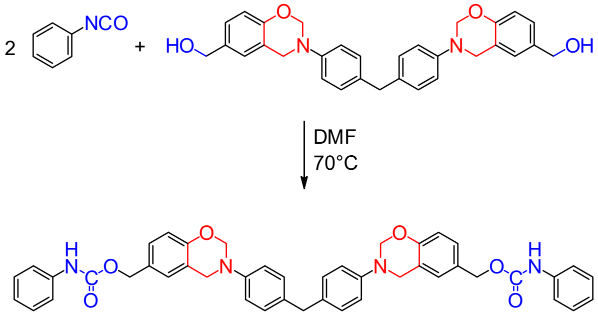
^{1}H NMR spectra (DMSO-d_6, ppm: δ, frequency: 600 MHz): 4.58 (s, $C-CH_2-N-$), 4.99 (s, $-CH_2-O$), 5.38 (s, $N-CH_2-O-$).

2.5. Crosslinking of poly(benzoxazine-co-urethane)s

Solutions of the copolymers in DMF were cast onto glass plates that were pretreated by methylmethoxysilane and dried in an air-circulating oven at 70 °C for 24 h. The produced films were then crosslinked at various temperatures in the air-circulating oven. The temperature profile used to crosslink the samples was as follows: 90 °C/2 h, 120 °C/2 h, 150 °C/2 h, and 180 °C/3 h. The color of the film changed from yellow to red during the crosslinking process.



Scheme 1. Preparation of dimethylol benzoxazine monomer (4HBA-ddm).



Scheme 2. Preparation of model compound.

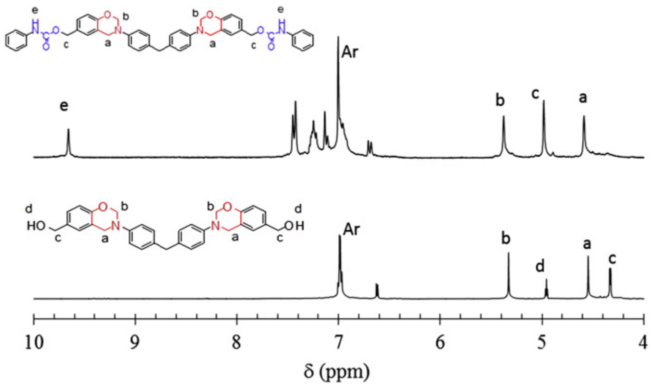


Fig. 2. ^{1}H NMR spectrum of model compound and benzoxazine monomer.

Table 1
Compositions of poly(benzoxazine-*co*-urethane)s.

Copolymer code	MDI (g, mmol)	4HBA-ddm (g, mmol)	PBA (g, mmol)	4HBA-ddm (mol%, wt.%)
I-0	0.25, 1	0.495, 1	0, 0	50, 66.4
I-10	0.25, 1	0.396, 0.8	0.2, 0.2	40, 46.8
I-20	0.25, 1	0.297, 0.6	0.4, 0.4	30, 31.4
I-30	0.25, 1	0.198, 0.4	0.6, 0.6	20, 18.9
I-40	0.25, 1	0.099, 0.2	0.8, 0.8	10, 8.6

2.6. Measurements

Both proton (^{1}H) and carbon (^{13}C) NMR spectra were obtained by Varian Oxford AS600 spectrometer, operating at a proton frequency of 600 MHz and a corresponding carbon frequency of 150.9 MHz. Deuterated dimethylsulfoxide (DMSO-d$_6$) was used as a solvent.

Fourier transform infrared spectra (FTIR) were obtained using a Bomem Michelson MB-100 FT-IR spectrometer, which was equipped with a deuterated triglycine sulfate (DTGS) detector. Thirty two scans were recorded at a resolution of 4 cm^{-1} after purging with dry air. The spectrum was taken by casting a film from polymer solution onto a KBr crystal.

Thermal analysis was performed with differential scanning calorimetry (DSC) using TA Instruments DSC model 2920 to study the curing behavior and thermal stability. The temperature was ramped at 10 °C/min and a nitrogen flow rate of 65 mL/min was used for all tests. All samples were crimped in hermetic aluminum pans with lids.

The thermal stability was studied by thermogravimetric analysis (TGA) with a TA Instruments High Resolution 2950 thermogravimetric analyzer using nitrogen as a purging gas. A heating rate of 10 °C/min and nitrogen flow rate of 60 mL was used for all tests.

Dynamic mechanical behavior (DMA) was performed on a TA Instruments Q800 DMA applying controlled strain tension mode with amplitude of 10 μm and a temperature ramp rate of 3 °C/min.

Atomic force microscopy (AFM) experiments were performed by tapping mode at ambient temperature in air. Phase and height images of the cross sections were recorded simultaneously using the Nanoscope IIIa instrument Multi-Mode scanning probe (Digital Instruments, Santa Barbara, CA). A tip made of silicon (110–140 μm in length with ca. 327–383 kHz resonant frequency and at 20–80 N/m of force) was used. In these images, the height of any spot in the phase image together with the corresponded height of the same spot in the topography image was used to study the morphology of any specific system under study.

Mechanical properties of crosslinked films were evaluated in uniaxial tension on an Instron 5565 universal tester. Dog bone shaped specimens were punched from the films using an ASTM D638 punch tool. An average of four to five specimens were cut and tested at ambient temperature using 1 mm/min as a strain rate. The reported modulus values were calculated from the initial slope of the stress-strain curve at 1% strain.

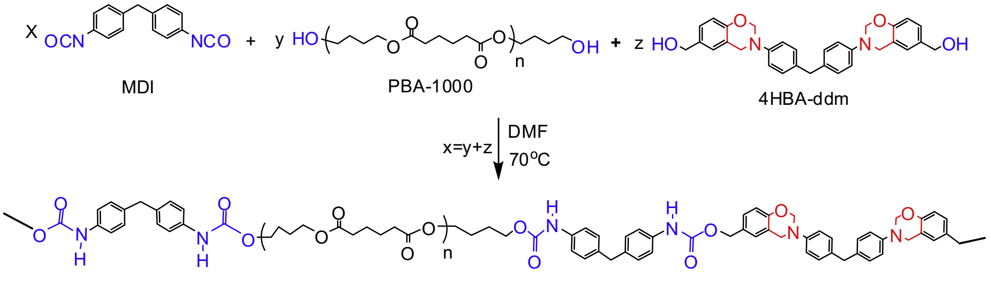
3. Results and discussion

3.1. Synthesis of dimethylol-functional benzoxazine monomer (4HBA-ddm)

4HBA-ddm as a novel benzoxazine monomer has been synthesized following the newly developed method in our laboratory for the synthesis of difficult benzoxazine monomers [41]. Scheme 1 shows the preparation of 4HBA-ddm. The structure of the monomer has been confirmed by ^{1}H NMR, ^{13}C NMR, and FT-IR spectra. In the ^{1}H NMR spectrum, the characteristic resonances attributed to cyclic benzoxazine structure are observed at 4.57 ppm (s, C–CH$_2$–N) and 5.36 ppm (s, N–CH$_2$–O–), whereas the resonances of methylol group are observed at 4.36 ppm (d, –CH$_2$–O) and 4.99 ppm (t, –OH). ^{13}C NMR spectra showed the typical resonances for benzoxazine structure at 49.23 ppm (C–CH$_2$–N–) and 78.87 ppm (N–CH$_2$–O) that further support the formation of benzoxazine monomer. The FT-IR spectra further show the characteristic absorption bands of benzoxazine structure at 1228 cm^{-1} due to the stretching of C–O–C and at 952 cm^{-1} due to the out-of-plane bending vibration of the benzene ring attached to the oxazine ring [42,43].

3.2. Synthesis of model compound

A model compound has been synthesized from the reaction of **4HBA-ddm** and phenyl isocyanate. The reaction was carried out in dry DMF under nitrogen atmosphere as illustrated in Scheme 2. This model compound helps to understand the reaction condition at which the methylol groups (–CH$_2$OH) of the benzoxazine monomer react with the isocyanate group (–NCO) to form urethane linkages and to confirm the stability of cyclic benzoxazine structure under the reaction condition. The structure of the model



Scheme 3. Preparation of main-chain poly(benzoxazine-*co*-urethane)s.

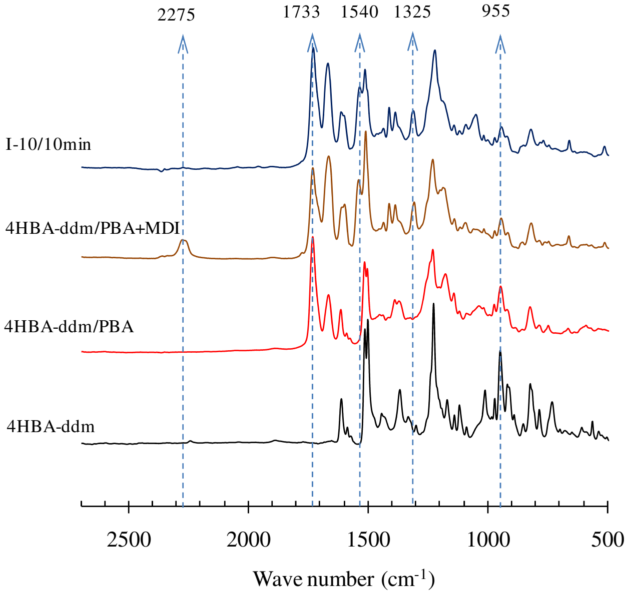


Fig. 3. FT-IR spectra of I-10 and related compounds.

compound has been confirmed by ^{1}H NMR, ^{13}C NMR, and FT-IR spectra. ^{1}H NMR spectrum depicted in Fig. 2 shows the characteristic resonances at 4.59 ppm (s, C–CH$_2$–N) and 5.38 ppm (s, N–CH$_2$–O–) due to benzoxazine structure, indicating its stability at this reaction condition. A new resonance was observed at 9.67 ppm attributed to the –NH of urethane linkage. In the FT-IR spectra, benzoxazine structure was confirmed by the characteristic absorption bands at 1224 cm^{-1} due to the stretching of C–O–C and the band at 950 cm^{-1} due to the out-of-plane bending vibration of the benzene ring that is attached to the oxazine ring. This confirms the high reactivity of the methylol group in a benzoxazine monomer towards the isocyanate group to form urethane linkage in a short time at relatively low reaction temperature.

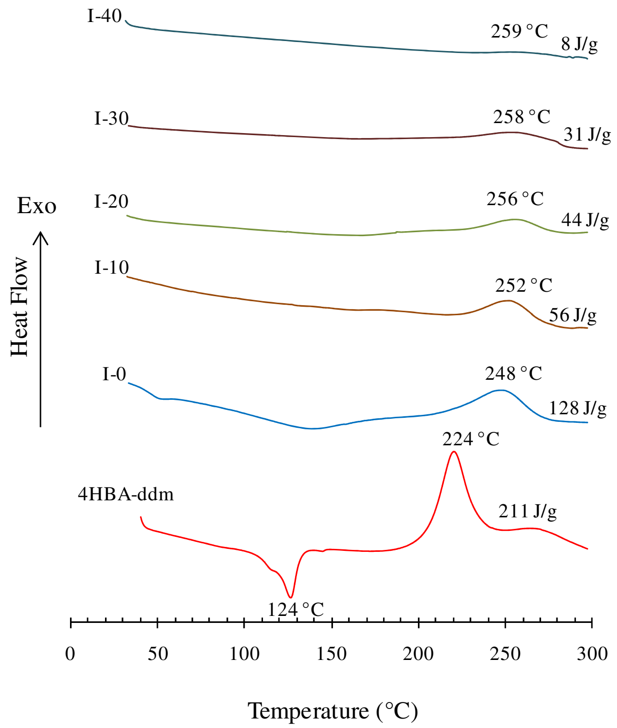


Fig. 4. DSC thermograms of uncrosslinked films at different benzoxazine molar ratio.

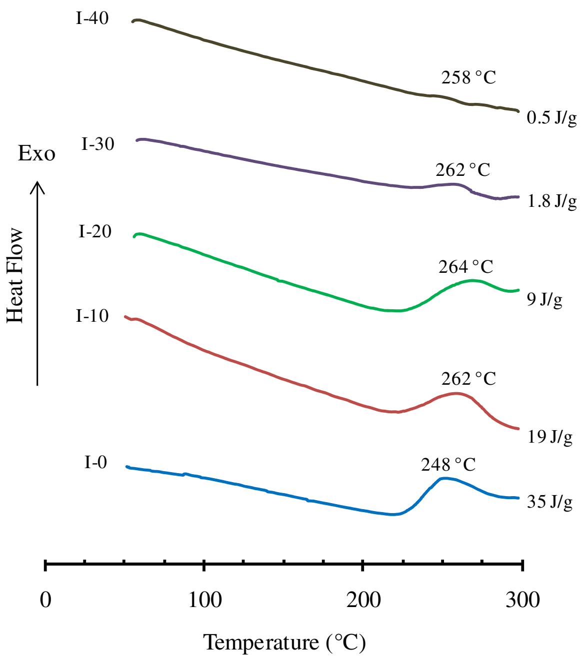


Fig. 5. DSC thermograms of crosslinked films at different benzoxazine molar ratio.

3.3. *Synthesis of main-chain type poly(benzoxazine-co-urethane)s*

Main-chain type poly(benzoxazine-*co*-urethane)s have been prepared by the reaction of **MDI**, **PBA** and different molar ratio of **4HBA-ddm**. The proposed structure is depicted in Scheme 3. This structure does not represent the exact structures of the copolymers, but rather idealized structure is shown. The compositions of the synthesized copolymers and their nomenclature are illustrated in Table 1. The uncrosslinked copolymers will be abbreviated as I# and the crosslinked forms will be poly(I#). The number (#) is used to indicate the molar percent of polyol in copolymer.

The consumption of the NCO groups of MDI due to the reaction with the OH groups of both **4HBA-ddm** and **PBA** to produce urethane linkages has been followed by FT-IR. Fig. 3 illustrates the FT-IR spectra of I-10, as an example. FT-IR spectra indicate that the typical absorption at 2275 cm^{-1} due to –NCO group disappeared

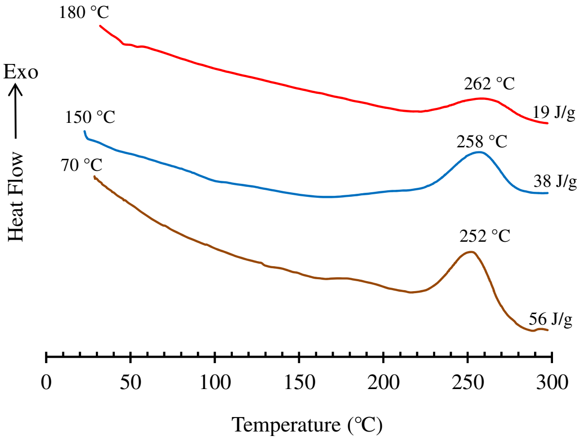


Fig. 6. DSC thermograms for I-10 at various polymerization temperatures.

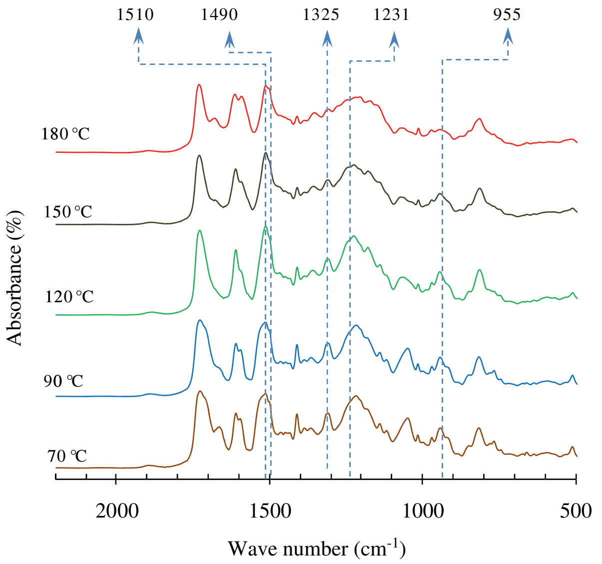


Fig. 7. FT-IR spectra of I-10 film after polymerizing at different temperature.

quickly within 10 min. It was also observed that the C═O stretching of non-hydrogen bonded carbonyl group of urethane and ester groups at 1733 cm^{-1} and the C–N stretching combined with N–H out-of-plane bending at 1540 cm^{-1} attributed to the formation of urethane linkage increased. Also, the band at 955 cm^{-1} due to the out-of-plane bending vibration of the benzene ring attached to oxazine ring is maintained intact, confirming the presence of benzoxazine structure in the resulting polymer [27,34,38,42,43].

3.4. Polymerization behavior of poly(benzoxazine-co-urethane)s

Differential scanning calorimetry (DSC) has been used to monitor the crosslinking behavior of the main-chain type poly(benzoxazine-*co*-urethane). Fig. 4 shows the DSC thermograms of copolymers containing different content of cyclic benzoxazine in the main-chain after drying at 70 °C. The DSC thermograms indicate that as the content of benzoxazine in copolymers increases, the amount of the exothermic heat increases. The heat of polymerization of benzoxazine for crosslinking are 128, 46, 41, 31, and 8 J/g for I-0, I-10, I-20, I-30 and I-40, respectively. This exothermic heat is attributed to the crosslinking reaction of poly(benzoxazine-*co*-urethane)s via ring opening polymerization of benzoxazine structure.

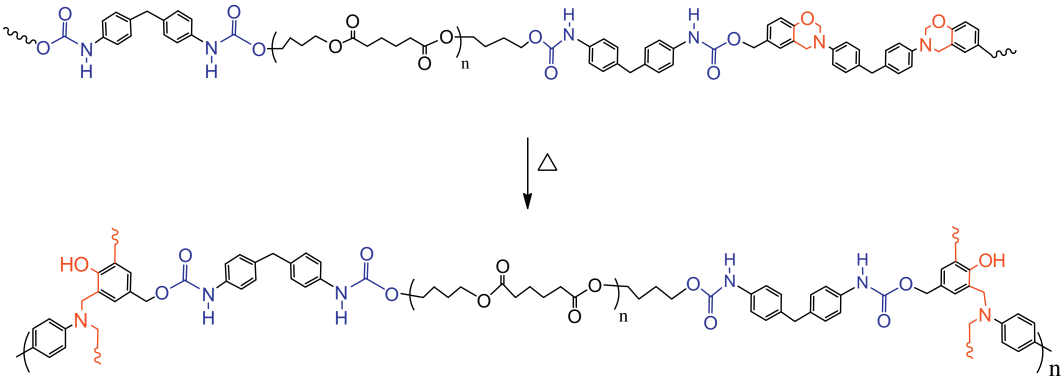
DSC thermograms have been used to monitor the residual benzoxazine in the main-chain of the crosslinked copolymers after thermal treatment up to 180 °C as depicted in Fig. 5. The residual exothermic peaks represent the remaining unpolymerized benzoxazine in the copolymers. Since the amount of benzoxazine is varied in the main-chain copolymer, there is a gradual decrease in the remaining exothermic peaks with decreasing the benzoxazine content in the copolymers. By comparison of the amount of exotherm before and after the crosslinking (Figs. 4 and 5), we can conclude that the copolymers with low benzoxazine content such as poly(I-40) and poly(I-30) showed the completion of polymerization of more than 93%, whereas copolymers with higher benzoxazine content such as poly(I-20), poly(I-10) and poly(I-0) showed the completion of polymerization of ~66–80%.

The crosslinking of I-10 as an example has been studied by DSC and FT-IR after each thermal treatment cycle. Fig. 6 shows the DSC thermograms of the films at various thermal treatments. The DSC thermograms show that the heat of polymerization decreases from 56 J/g to 19 J/g as the temperature increases from 70 to 180 °C, indicating the presence of residual benzoxazine structure. Further thermal curing has been avoided to eliminate the possibility of partial degradation of aliphatic segment of PUs copolymer [1,4,27,28].

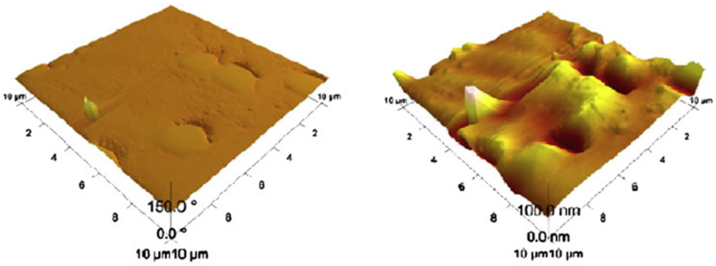
To further confirm the crosslinking of the copolymers, FT-IR spectra of the copolymers have been studied. Fig. 7 shows the FT-IR spectra of I-10 after various thermal treatments. A gradual decrease of the characteristic absorption bands of benzoxazines with thermal treatment was observed at 1510 cm^{-1} of trisubstituted benzene, 1325 cm^{-1} of CH_2 of benzoxazine ring, and 1231 cm^{-1} of ether linkage. Meanwhile, a new band appeared at 1490 cm^{-1} of tetrasubstituted benzene rings, indicating the formation of polybenzoxazine and hence the crosslinking of the copolymer [18,25]. However, a residual absorption band at 955 cm^{-1} due to the out-of-plane bending vibration of benzene ring is still observed. Nonetheless, thermal treatment up to 180 °C has been fixed as last polymerization cycle to avoid any partial degradation of the aliphatic component of PU [1,4]. Scheme 4 shows the proposed structure of the crosslinked copolymer network structure. As a result of the thermally activated ring opening polymerization of cyclic benzoxazine in the main-chain, crosslinking is achieved through the formation of polybenzoxazine as crosslinkers between copolymer chains.

3.5. Morphology studies

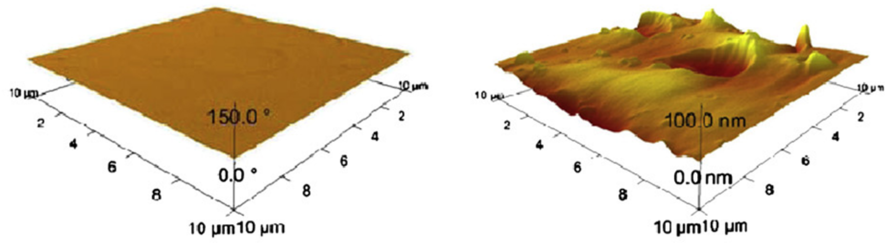
The surface morphologies of main-chain poly(benzoxazine-*co*-urethane) films were monitored by AFM in tapping mode and are displayed in Fig. 8. It was obvious, by comparing the images (a)–(e), that the higher benzoxazine ratio creates more wrinkled surface



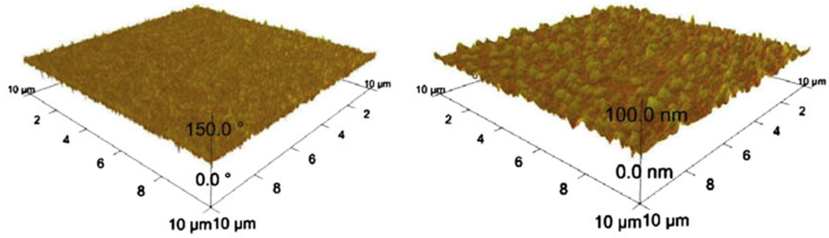
Scheme 4. Proposed idealized, crosslinked structure of the main-chain poly(benzoxazine-*co*-urethane).



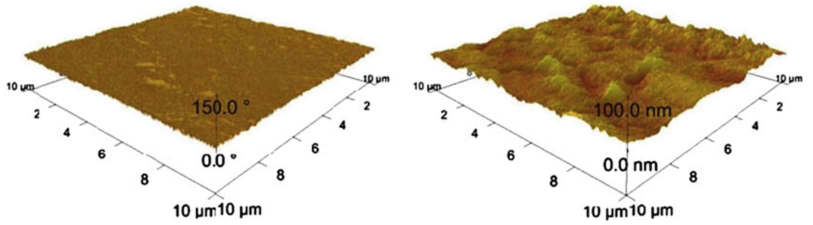
a I-0 cured at 180 °C



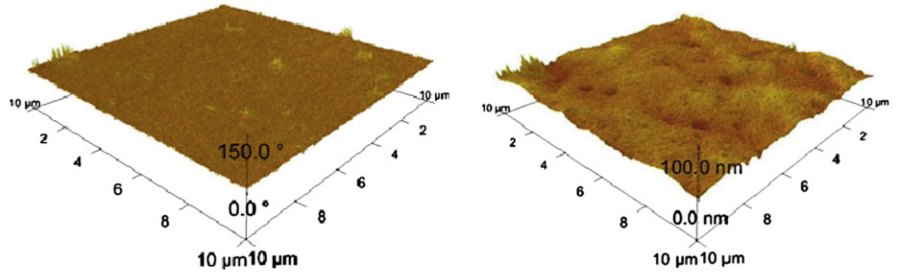
b I-10 cured at 180°C



c I-20 cured at 180°C



d I-30 cured at 180°C



e I-40 cured at 180°C

Fig. 8. AFM morphology of crosslinked films at 180 °C for 3 h: a) poly(I-0), b) poly(I-10), c) poly(I-20), d) poly(I-30), and e) poly(I-40). Left: phase images and right: topographic images.

than the system with lower benzoxazine ratio. This phenomenon was attributed to the increase in the hard segment content which is represented by aromatic structure in MDI and 4HBA-ddm in comparison to the PBA that is responsible for the soft segments in the moiety. The AFM images exhibit difference in height and phase in micro-regions around 100 nm, which indicates the presence of specific microphase-separated morphologies. These regions consist of hard segment-rich and soft segment-rich domains as in poly(I-40) and poly(I-30) samples. Besides the small phase micro-regions, many rougher domains appear in the poly(I-20) and poly(I-10) samples with the dimension of around 200 nm and more. In the case of poly(I-0) film as a control, it shows a rough surface due to the presence of hard segment-rich domains which is attributed to the high aromatics content in the molecular structure.

3.6. Tensile properties

The tensile properties of the crosslinked poly(benzoxazine-*co*-urethane) films have been evaluated. The effect of varying the thermal treatments of the main-chain poly(benzoxazine-*co*-urethane) films on the tensile properties has been studied in details for the I-20 sample. Fig. 9 shows stress-strain curves of the I-20 films after various thermal treatment cycles for crosslinking. The tensile properties data of I-20 including tensile modulus, tensile strength, and elongation at break are tabulated in Table 2. It is obvious that, as the thermal treatment temperature increases, both tensile modulus and tensile strength increase whereas the elongation at break decreases. This behavior is attributed to the increase of crosslinking density coupled with the increase of the thermal treatment temperature, which leads to further ring opening polymerization of benzoxazine structures in the main-chain to take place and the formation of a more rigid three dimensional network structure. As a result, both tensile modulus and tensile strength increased whereas elongation at break decreases.

The effect of benzoxazine content as a crosslinking agent on the tensile properties of poly(benzoxazine-*co*-urethane) films has also been studied. Fig. 10 shows the stress-strain curves of copolymers after thermally treated up to 180 °C. Table 3 summarizes the results of the tensile properties. Both the tensile modulus and tensile strength increase with an increase in the benzoxazine content in copolymers as depicted in Fig. 11. For example, the tensile modulus values are 2360, 737, 517, 54 and 18 MPa whereas the tensile strengths are 78, 40, 32, 13 and 3 MPa for samples poly(I-0), poly (I-10), poly(I-20), poly(I-30), and poly(I-40) respectively. On the other hand, the elongation at break increased with decreasing the benzoxazine content to be 4, 12, 16, 73 and 109% for samples poly (I-0), poly(I-10), poly(I-20), poly(I-30), and poly(I-40) respectively. This behavior is attributed mainly to the decrease of crosslinking density as the content of benzoxazine decreases. Thus, the more benzoxazine content in the copolymer, the greater the crosslinking density, leading to a more rigid structure. The trends in mechanical behavior are in agreement with reported studies [27,31–36]. Nonetheless, the values of tensile modulus and tensile strength of crosslinked poly(benzoxazine-*co*-urethane)s produced through the concept adapted in this study are higher than that of the reported polybenzoxazine/PU materials. For example, poly(I-30) with ca. 18 wt.% of polybenzoxazine content showed tensile strength and tensile modulus of 13.0 and 73.0 MPa. These values are significantly higher than the reported values for polybenzoxazine/PU materials containing the same content of polybenzoxazine which showed tensile strength and tensile modulus of <5 and< 20 MPa, respectively [27,34,35]. For polybenzoxazine/PU materials reported by Takeichi et al. [27], the films cured at 180 °C had higher elongation at break than the current concept and all the reported approaches for

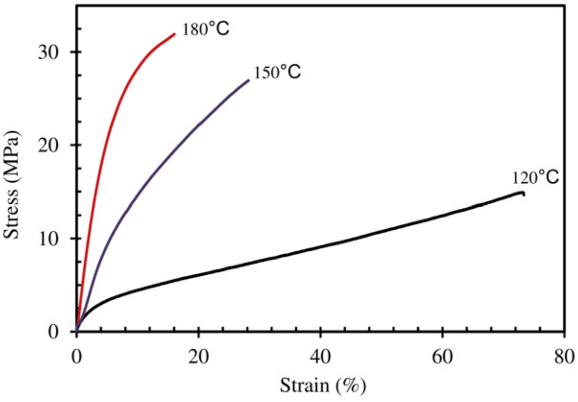


Fig. 9. Stress-strain curves of I-20 treated at different temperatures.

Table 2
Tensile properties of I-20 films after different thermal treatment.

Polymerization temp.(°C)	Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
120 °C	90	15	73
150 °C	197	27	28
180 °C	533	32	16

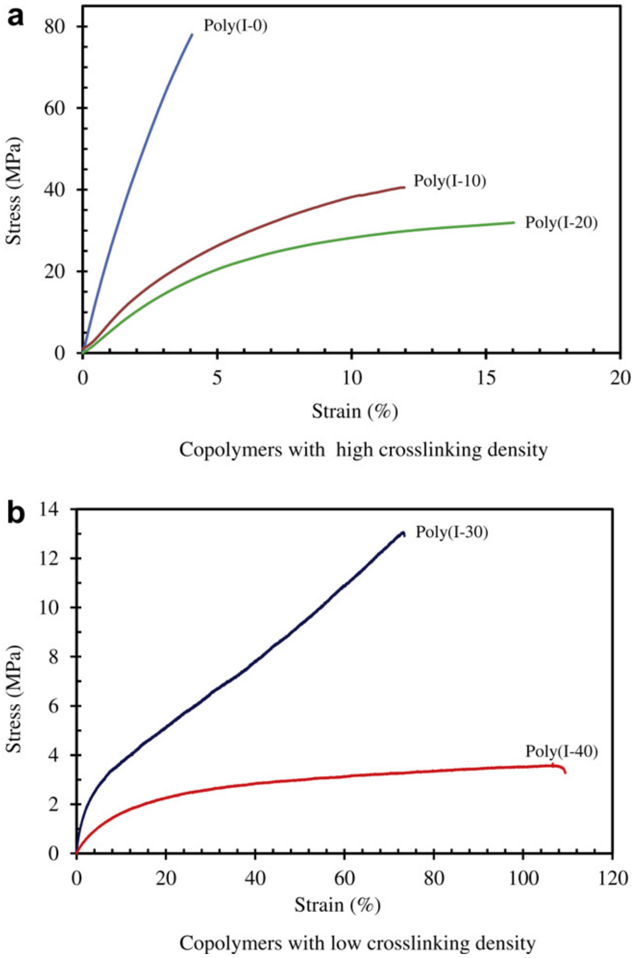


Fig. 10. Stress-strain curves of crosslinked copolymer films at different benzoxazine molar ratio.

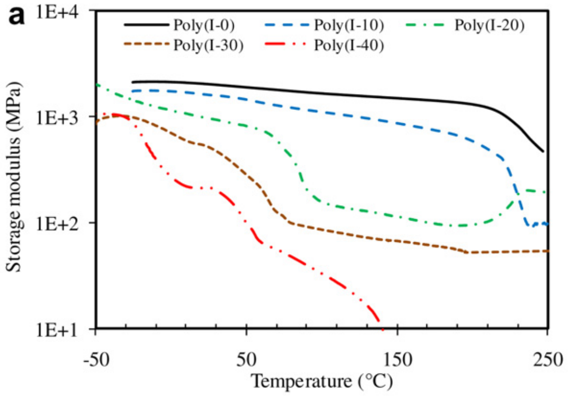
Table 3
Tensile properties of copolymer films of different benzoxazine content after thermal treatment at 180 °C.

Sample code	Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
Poly(I-0)	2358	78	4
Poly(I-10)	737	40	12
Poly(I-20)	517	32	16
Poly(I-30)	54	13	73
Poly(I-40)	18	3	109

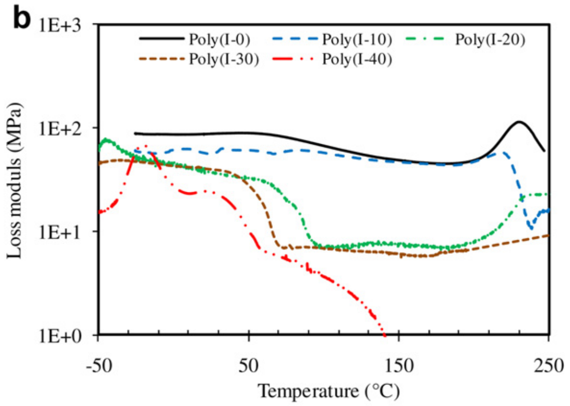
polybenzoxazine/PU materials. This high value of the elongation at break is attributed to the use of benzoxazine monomer that leads to lower crosslinking density than the current concept through the main-chain type benzoxazine polymers. In addition, the lower elongation at break in this method for polybenzoxazine/PU materials is presumably due to the role of the inter- and intra-molecular hydrogen bonding of free phenolic groups of polybenzoxazine that acts as additional physical crosslinks between the chains of the copolymer [22,44]. Moreover, most of the previously reported approaches for polybenzoxazine/PU materials used toluene diisocyanate (TDI) and 1,6-hexamethylene diisocyanate (HDI) to prepare PU prepolymer. However, in this study methylene diphenyl diisocyanate (MDI) of more rigid aromatic content has been used that adds more rigidity in the molecular structure [1,44]. Also, in comparison to well-known high performance poly(urethane-imide), the crosslinked poly(benzoxazine-*co*-urethane) copolymers showed comparable values for samples containing similar PU content. For example poly(I-20) exhibited higher tensile strength but lower elongation at break than poly(urethane-imide) of the same urethane content [5,8].

3.7. Thermal properties of crosslinked poly(benzoxazine-co-urethane)s

Dynamic mechanical analysis (DMA) of crosslinked copolymer films has been performed and the results are shown in Fig. 12. The DMA results indicate that the initial storage moduli (E`) of the copolymer films increased with increasing the content of benzoxazine in the main-chain. It was also observed that the storage modulus maintained at higher value by increasing the benzoxazine content, indicating the increase in the stiffness of the copolymers. In addition, the T_g of crosslinked poly(benzoxazine-*co*-urethane)s shifted to lower temperature with increasing the content of **PBA** as a soft segment and decreasing the crosslinking density. For example, T_g decreased from 230 to 219 °C by increasing the polyols content in the main-chain from 0 to 10 mol% for samples poly(I-0)



Storage modulus temperature relationship of polymerized films at 180 ºC



Loss modulus temperature relationship of polymerized films at 180 ºC

Fig. 12. DMA analysis for poly(benzoxazine-co-urethane) films polymerized at 180 °C.

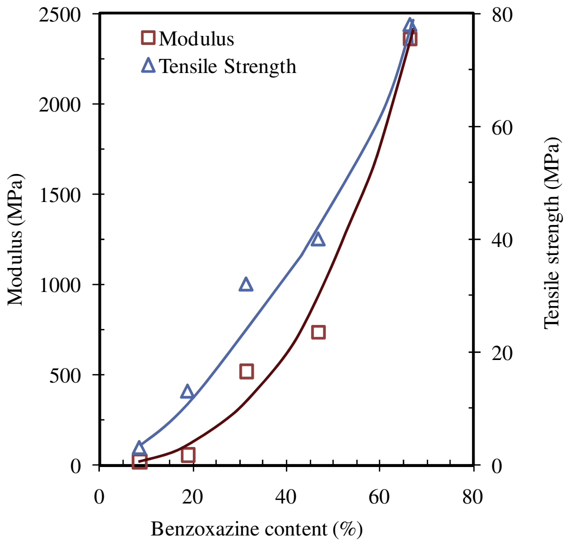


Fig. 11. The effect of benzoxazine content on the modulus and tensile strength.

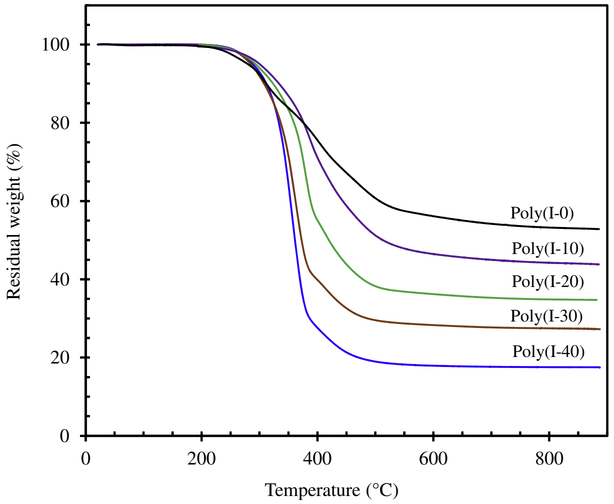


Fig. 13. TGA analysis of cured poly(benzoxazine-*co*-urethane)s films.

Table 4
TGA data of poly(benzoxazine-*co*-urethane) films cured up to 180 °C.

Sample	Td$_5$ (°C)	Td$_{10}$ (°C)	Char yield (%)
Poly(I-0)	280	311	53.0
Poly(I-10)	300	333	44.3
Poly(I-20)	293	323	35.0
Poly(I-30)	287	310	27.5
Poly(I-40)	285	309	17.5

and poly(I-10), respectively. This behavior is attributed to the increased chain mobility of the copolymer as a result of decreasing the crosslinking density that leads to decreased T_g.

Thermogravimetric analysis (TGA) has been used to investigate the thermal stability of the crosslinked poly(benzoxazine-*co*-urethane) films. Fig. 13 shows the TGA profiles of copolymer films after 180 °C treatment. The results of TGA are summarized in Table 4. The thermal stability of poly(I-0), which can be used as a control, shows an early weight loss from 280 °C. 4HBA-ddm monomer which has been used in this study is a methylol functional end-capped benzoxazine which, by thermal treatment, will condensate to produce water at about 200 °C, similar to traditional resole. Since the copolymer poly(I-0) contains the highest content of 4HBA-ddm and the thermal treatment did not exceed 180 °C, the early weight lost is attributed to the condensation reaction of methylol end groups in the copolymer which will be discussed in details elsewhere [41]. For the rest of the crosslinked copolymers, a higher benzoxazine content led to an improvement in the onset of the degradation as can be seen from the 5 and 10% weight loss temperatures, Td$_5$ and Td$_{10}$. For example, Td$_5$s are 300, 293, 287, and 285 °C whereas Td$_{10}$s are 333, 323, 310, and 309 °C for samples poly(I-10), poly(I-20), poly(I-30), and poly(I-40), respectively. The onset of degradation is higher than the control due to the absence of methylol groups that are consumed for urethane linkage formation. Although depolymerization of urethane bonds occurred at about 240 °C [8], the incorporation of benzoxazine in the poly(benzoxazine-*co*-urethane) copolymer shifted the decomposition temperature to $\sim$285–300 °C, depending on the benzoxazine content. The onset of the degradation did not improve significantly, since the increase of the benzoxazine content will shift the initial weight to low temperature due to methylol condensation. On the other hand, the increase of polyol content as aliphatic component will contribute to the shift of initial weight loss to lower temperature. Despite the aforementioned reasons of the initial weight loss of the copolymers, the thermal stability of this new system is still comparable with the reported similar polybenzoxazine/PUs. For example, Td$_5$ changed from 285 °C for poly(I-40) copolymer of 8.6 wt.% benzoxazine weight percent to 300 °C for poly(I-10) copolymer of 46.8 wt.%, respectively. The char yield also showed significant increase upon increasing the benzoxazine content in the main-chain. For example samples poly(I-0), poly(I-10), poly(I-20), poly(I-30) and poly(I-40) have char yield of ca. 53.0, 44.3, 35.0, 28.0 and 18.0%, respectively. Thus, this new concept of crosslinked poly(benzoxazine-*co*-urethane) copolymer is shown to be effective for producing polybenzoxazine/PU materials of significant higher thermal stability than the previously reported approaches. For example, sample poly(I-20) of ca. 70 wt.% of PU has char yield of 35.0%, whereas the previously reported polybenzoxazine/PU materials of similar PU content showed a char yield in the range of 22-25% [27,28,36] and not more than 30% for systems of ca. 30 wt.% of PU [32,33]. This enhancement in thermal stability is attributed to the presence of polybenzoxazine as a part of the copolymer main-chain and the thermal stability of urethane linkage that result in better thermal properties than the reported polybenzoxazine/PU materials.

4. Conclusions

A new concept to produce polybenzoxazine/PU copolymers has been developed by incorporating oxazine and urethane groups in one molecule through main-chain type poly(benzoxazine-*co*-urethane)s. These copolymers have been synthesized via copolymerization of diisocyanate monomer with a dimethylol-functional benzoxazine monomer and polyol to afford a linear main-chain type polymer. The produced copolymers were further crosslinked through thermally activated ring opening polymerization of benzoxazine to produce network structure. Films were subjected to mechanical and thermal tests and the results were associated with the chemical structure of corresponding films according to the content of benzoxazine in the moiety. This novel class of polybenzoxazine/PU materials is characterized by the following:

- One-pot synthesis of phenolic-urethane materials that avoids the drawbacks associated with the use of preformed NCO-terminated PU prepolymers.
- Superior thermal stability compared to previous approaches.
- Excellent mechanical integrity as can be seen from high tensile modulus and tensile strength due to the presence of polybenzoxazine as part of the main-chain.
- These copolymers showed thermal and mechanical properties that are comparable to the well-known high performance poly(urethane-imide).

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