Macromolecules

Benzoxazine-Based Thermosets with Autonomous Self-Healing Ability

Mustafa Arslan,[†] Baris Kiskan,^{*,†} and Yusuf Yagci^{*,†,‡}

[†]Department of Chemistry, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey

[‡]Center of Excellence for Advanced Materials Research and Chemistry Department, Faculty of Science, King Abdulaziz University, 80203, Jeddah 21589, Saudi Arabia

Supporting Information

ABSTRACT: A self-healing strategy for poly(propylene oxide)s bearing benzoxazine units (PPO-Benz) through supramolecular attractions is described. Poly(propylene oxide) bisamine (PPO) with a molecular wieght of 2000 Da was reacted with formaldehyde and bisphenol A to yield desired PPO-Benz with 12 360 Da. The cross-linked polymer films were then prepared by solvent casting of suitable compositions of PPO-Benz and carboxlic acid containing benzoxazine monomer (Carb-Benz) in chloroform followed by



thermal ring-opening reaction of benzoxazine groups at 200 $^{\circ}$ C. Thermal curing and thermal stability of the film and final products were investigated. It was demonstrated that the self-healing capacity of the films was improved by employing Carb-Benz in the formulation.

INTRODUCTION

Polybenzoxazines are relatively new phenolic resins and offer a superior alternative to novolac and resole type systems. Thus, the interest in polybenzoxazines is continuously increasing in the polymer science field as reflected by the scientific publication and patents. Most of the superior properties of these addition-cure resins are stemming from the Mannich base bridges $-CH_2-N(R)-CH_2-$ and the intra- and intermolecular hydrogen bonds between phenolic -OH and amine groups. These noncovalent attractions are the reason for the low humidity uptake and high glass transition temperatures (T_{α}) of these systems. Moreover, upon ring-opening polymerization (ROP) the cyclic structure of the monomers generally inhibits shrinkage of the resin which is a common problem for many curable systems. Noncatalytic polymerization, high char yield, and limited release of byproducts during curing are additional benefits of the polybenzoxazine-based resins. The synthesis of polybenzoxazines from its corresponding 1,3-benzoxazine monomers can simply be achieved by thermally activated ROP with or without a catalyst (Scheme 1).¹ In noncatalytic conditions the ROP temperatures vary in a range of 160-250 °C.^{2–6}

The properties of polybenzoxazines resins can be controlled by three common methodologies that are (i) synthesis of monomers, (ii) forming their composites by adding fillers or additives, and (iii) synthesis of polybenzoxazine monomers containing hydroxyl,¹² alkyl,¹³ phenyl,¹⁴ maleimide,^{15,16} propargyl,¹⁷ nitrile, allyl,¹⁸ and carboxyl¹⁹ groups were synthesized. The synthesis can easily be facilitated by using suitable phenols, Scheme 1. Thermally Activated Ring-Opening Polymerization of a Bisbenzoxazine Monomer



primary amines, and formaldehyde as starting materials (Scheme 2). $^{20-26}$

The other widespread approach to regulate the properties is based on the preparation of polybenzoxazine prepolymers.^{27–34} Such polymeric precursors generate high cross-linking degree, reduce cold flow, and increase the toughness of the resin. Various chemistries were successfully used to synthesize

Scheme 2. Synthesis of a Monofunctional 1,3-Benzoxazine Monomer from a Phenol and a Primary Amine



Received:December 14, 2014Revised:February 16, 2015

polybenzoxazine prepolymers including coupling reactions, alternating copolymerization of donor-acceptor monomers, Diels–Alder,³⁵ Mannich reactions,³⁶ polyesterification,³⁷ poly-etherification,³⁸ hydrosilylation,^{39,40} etc. These synthetic approaches essentially yield diverse polybenzoxazines with designed properties. Although polybenzoxazines were used in many applications, the use of polybenzoxazines in the synthesis of self-healing materials has scarcely been investigated. In this direction, recent publications from the authors' laboratory reported the first usage of polybenzoxazine precursors as a selfhealing additive for polysulfones⁴¹ and coumarin functional polybenzoxazines.⁴² In these systems, heat- and light-induced intrinsic self-healing was accomplished through covalent bond formations. In contrast to such healing mechanism, supramolecular networks that generally associate with reversible supramolecular interactions exhibit a higher dynamic healing behavior. It appears that these materials display autonomous healing upon damage and have numerous potential applica-tions.^{43,44} So far, such self-healing has been reported in a claydendrimer mixture,⁴⁵ metal ion–polymer systems,^{46,47} supra-molecular gels,^{48,49} π – π stacking networks,^{50,51} disulfide–thiol exchange,⁵² and multicomponent systems.⁵³ Additionally, selfhealing polymers based on hydrogen bonding can also generate supramolecular network systems that contain highly dynamic noncovalent bonds. These bonds show a reversible "stickerlike" behavior enabling connection and reconnection between several hydrogen bonding regions. Typical examples include ureido-pyrimidone bonding, nucleobases and similar systems, Leibler bond, butylurea of guanosine and 2,7-diamido-1,8naphtyridine attractions, polystyrene grafted with polyacrylamide, and quadruple hydrogen bonding.54 In the view of supramolecular attraction concept, the intra- and intermolecular hydrogen bonding in polybenzoxazines can be utilized to design a novel self-healing system. To demonstrate the feasibility of this strategy, we report poly(propylene oxide)based polybenzoxazine networks with embedded carboxylic acid containing benzoxazines as the stimuli to form efficient autonomous healing though both covalent and supramolecular network.

EXPERIMENTAL SECTION

Materials. 4,4'-Isopropylidenediphenol (bisphenol A) (Aldrich, 97%), paraformaldehyde (Acros, 96%), poly(propylene glycol) bis(2-aminopropyl ether) ($M_n \sim 2000$ Da, Aldrich), 4-aminobenzoic acid (\geq 99%, Aldrich), ethanol (\geq 99.5%, Aldrich), toluene (Carlo Erba, 99.5%), chloroform (Acros, 99+%), hexane (Aldrich, 95%), 1,4-dioxane (Riedel-de Haen 99.5%), and diethyl ether (\geq 98%, Aldrich) were used as received.

Characterization. ¹H NMR spectra were recorded in CDCl₃ with Si(CH₃)₄ as internal standard, using a Bruker AC250 (250.133 MHz) instrument. FT-IR spectra were recorded on a PerkinElmer FT-IR Spectrum One spectrometer. Differential scanning calorimetry (DSC) was performed on PerkinElmer Diamond DSC from 30 to 320 °C with a heating rate of 20 °C min under nitrogen flow. Thermal gravimetric analysis (TGA) was performed on a PerkinElmer Diamond TA/TGA with a heating rate of 10 °C min under nitrogen flow. Molecular weights were determined by gel-permeation chromatography (GPC) instrument equipped with a Waters styragel column (HR series 2, 3, and 5E) with THF as the eluent at a flow rate of 0.3 mL/min and a Waters 410 differential refractometer detector. Uniaxial elongation measurements were performed on polymeric film samples (approximately 16.4 mm length and 8.6 mm² cross-section area). Measurements were carried out using a PerkinElmer Pyris Diamond DMA (SII Nanotechnology Inc.) at 25 °C under 50 mN/

min load speed. The tensile strength and percentage elongation at break were recorded.

Synthesis of Poly(propylene oxide)benzoxazine (PPO-Benz). In a 250 mL round bottomed flask, paraformaldehyde (10.0 mmol, 0.30 g), bisphenol A (2.6 mmol, 0.60 g), and poly(propylene oxide) bisamine (PPO) (2.5 mmol, 5 g) were dissolved with 50 mL of toluene and 25 mL of ethanol mixture. The reaction mixture was refluxed for 24 h. The solvent was evaporated under vacuum, and a blondish oily product was precipitated in cold *n*-hexane. The precipitation process has been done two times. Final oily product was dried at room temperature in a vacuum for 1 day.

Synthesis of Carboxyphenylbenzoxazine (Carb-Benz). Carb-Benz was synthesized according to the procedure in the literature:⁵⁵ In a 500 mL round bottomed flask, paraformaldehyde (105.0 mmol, 3.2 g), phenol (53.0 mmol, 5 g), and 4-aminobenzoic acid (51.0 mmol, 7 g) were dissolved in 200 mL of 1,4-dioxane and refluxed for 5 days. After cooling at room temperature, the solvent removed at reduced pressure. Ethyl ether (150 mL) was added to the oil with magnetic stirring, and a yellow precipitate was obtained. The yellow solid was filtered and dried under reduced pressure. For spectral and thermal characterization data see Figures S1–S3.

Film Preparations. To obtain polybenzoxazine films, PPO-Benz was mixed with Carb-Benz monomer in $CHCl_3$ in three different w/w ratios: 1:0.1, 1:0.05, and 1:0.025. These solutions were charged into a Teflon mold. The solvent was evaporated at room temperature for 5 days. After the solvent removal, films were exposed to thermal curing at 200 °C for 1 h in oven. Finally brownish, transparent polybenzoxazine cross-linked films were obtained.

RESULTS AND DISCUSSION

In general, the elementary steps of supramolecular self-healing systems are interdiffusion and entanglement of polymer chains. Accumulation of hydrogen bonding sites on the cut edge, surface approach, and wetting are important. For spontaneous repair of material as a response to damage a balanced dynamic system for formation of a network should be chosen. In other words, a sufficiently high molecular flexibility must be established to form dynamic networks. Strong interacting functional groups in the supramolecular system can result in high mechanical stability but at the same time slow down or reduce the healing capacity. Weak interactions enhance molecular dynamics, but in such cases can generate only soft materials that could not meet required mechanical properties. Thus, for efficient healing, we have deliberately selected poly(propylene oxide) with a molecular weight of 2000 Da as the matrix material in polybenzoxazine precursor synthesis so as to introduce sufficient dynamics to the healable system. Such propylene oxide amines have high chain mobility and could provide softness to the networks that they were incorporated.^{56,57} Hence, a successful synthesis of poly(propylene oxide)-based polybenzoxazines (PPO-Benz) were performed using poly(propylene oxide) bisamine (PPO) $(M_n: 2000)$ and bisphenol A as difunctional phenol source (Scheme 3). A toluene/ethanol mixture (2:1, v:v) was used as the solvent in order to prevent possible gelation during precursor synthesis.²⁸ It is known that depending on the solvent used, formaldehyde with primary amines can readily form 1,3,5-dihydrotriazines.

The chemical structure of the PPO-Benz was confirmed by ¹H NMR and FT-IR spectral analysis. As can be seen from Figure 1 where the ¹H NMR spectrum of PPO-Benz is presented, the appearance of the protons resonating at 4.92 ppm (O-CH₂-N) and 4.01 ppm (Ar-CH₂-N) is clear evidence for the benzoxazine ring formation on poly(propylene oxide). Moreover, the peak at 1.59 ppm (-CH₃) discloses the bisphenol A moiety. The integration ratios of the characteristic

Scheme 3. Synthesis of Benzoxazine Containing Poly(propylene oxide)s (PPO-Benz)s



Figure 1. ¹H NMR spectra of PPO and the corresponding PPO-Benz.

peaks agree with the proposed structure. FT-IR spectra of the correponding polymers also give evidence for the formation of benzoxazine functional PPO-Benz precursor (Figure 2). The consumption of amino groups of poly(propylene)amines can be detected by the disappearances of N–H stretching vibrations in the spectra. Moreover, the stretching vibrations of aromatic C–H (3022–3055 cm⁻¹) and aromatic C=C (1511–1621 cm⁻¹) as well as the out-of-plane bending vibrations of aromatic C–H at 963 cm⁻¹ are detected for the



Figure 2. FT-IR spectra of PPO-Benz (a) and PPO (b).

precursor obtained. These results confirm successful synthesis of benzoxazine functional poly(propylene oxide).

The GPC trace of the precursor polymer is depicted in Figure S4. Clearly, successive condensation reactions resulted in the formation of PPO with relatively high molecular ($M_n = 12360 \text{ g mol}^{-1}$, PDI = 1.43). The shoulders observed in the lower molecular weight region are typical consequences of the step-growth polymerization.

It is known that depending on the functionalities present, benzoxazines have the ring-opening polymerization temperature generally between 150 and 260 $^\circ$ C. Figure 3 shows the



Figure 3. DSC thermogram of PPO-Benz under a N₂ atmosphere.

DSC profile of PPO-Benz. The precursor is curable, and its curing temperature is in accordance with many classical bisbenzoxazine monomers or main chain polybenzoxazine precursors. PPO-Benz showed an exotherm with an onset at 221 °C, end-set at 271 °C, and the curing maximum was detected as 252 °C. The total amount of curing exotherm is 20 J/g. After curing of PPO-Benz, the second run did not exhibit any curing exotherm, indicating the consumption of the benzoxazine groups in the first thermal treatment. Glass transition temperature (T_g) of polybenzoxazine films were detected by DSC with a fast scanning method (40 °C/min). Two T_g s were observed at 32 and 151 °C. These values reveal two distinct domains in a typical film.

Autonomous healing of thermally cured PPO-Benz polymer films was investigated. For this purpose, the films were prepared first by mixing PPO-Benz and Carb-Benz with the structure presented in Chart 1 in three different w/w ratios: 1:0.1, 1:0.05,

Chart 1. Structure of Carb-Benz



and 1:0.025. The abbreviations Carb-Benz10%-PPO-Benz, Carb-Benz5%-PPO-Benz, and Carb-Benz2.5%-PPO-Benz represent the respective mixing ratios. The maximum weight of Carb-Benz kept 100 mg in 1 g of PPO-Benz because excess amount of Carb-Benz generates voids in the film and phase separation takes place. While the onset of the ring-opening reaction of pristine PPO-Benz is 221 °C (Figure 3), the curing is conducted at 200 °C because ring-opening polymerization of Carb-Benz commences at around 160 °C (see Figure S3) and triggers the curing of PPO-Benz easily. In principle, the films

could heal themselves without an external stimulant through hydrogen bonding with the existing amino phenols. However, only inefficient healing was attained without addition of Carb-Benz. A possible drawback of carboxylic acid group could be decarboxylation of acid groups; it has been reported¹⁹ that the weight loss at around 300 °C increases with the carboxylic benzoxazine content. We have also observed this effect for the film which was prepared with the ratio of 1:0.1 (w/w) as the bubbles were formed after curing. However, the films with less amount of Carb-Benz were smooth (Figure S5).

Basically, healing of a polymeric material can be regarded as the recovery of its properties, and polymers exhibit various properties that can be a measure of the extent of healing. In general, recovery of the properties such as tensile strength, fracture toughness, etc., is measured to quantify the extent of healing. However, such quantification could not reflect the exact amount of the recovery, since pure mechanical properties cannot cover the overall properties of a material. Even though, in a practical manner measuring the degree of healing of polymeric systems for a defined mechanical property is commonly used as the basic method. Accordingly, the "healing efficiency" of a self-healing system the can be expressed as η

$$\eta = 100 \times \frac{K_{\text{healed}}}{K_{\text{virgin}}} \tag{1}$$

where K_{healed} and K_{virgin} are the fracture toughness (the area of stress-strain curve) of the healed and virgin specimens, respectively. Thus, tensile tests were performed to measure the ability of the damaged cured Carb-Benz and PPO-Benz mixture (Carb-Benz + PPO-Benz) to recover their strength. To do so, the damage generated by cutting the film into two separate parts. Then, the damaged specimens were kept in contact from the edges of the cut with applied pressure using a glass slip for 12 h at ambient temperature. Thereafter, the healed specimens were subjected to tests for healing efficiency, and the ratio of tensile strengths of the healed and virgin specimens were found. Figure 4 shows that tensile strengths of cross-linked films of Carb-Benz + PPO-Benz mixtures can be restored to some extent and the efficiency of the healing for cut specimens are tabulated in Table 1. A visual demonstration of



Figure 4. Stress-strain (%) behavior of virgin specimens Carb-Benz %10 + PPO-Benz (a), Carb-Benz%5 + PPO-Benz (b), and Carb-Benz %2.5 + PPO-Benz (c) and cut healed specimens (a'), (b'), and (c'), respectively.

the recovery is presented in Figure 5, and a video as Supporting Information is present.

Table 1

polymer	Young modulus (E) (kPa)	healing efficiency (η) (%)
CarbBenz%10 + PPO-Benz	182.3	96
CarbBenz%10 + PPO-Benz ^a	96.4	
CarbBenz%5 + PPO-Benz	163.7	41
CarbBenz%5 + PPO-Benz a	157.5	
CarbBenz%2.5 + PPO-Benz	136.5	26
CarbBenz%2.5 + PPO-Benz ^a	190.1	

^{*a*}Cut healed sample.



Figure 5. Photograph of cut healed specimen (1) and stretching of the same sample (2) (Carb-Benz%5 + PPO-Benz).

In polybenzoxazines, two types of hydrogen bonding can be considered: (i) intermolecular hydrogen bonding between two phenolic hydroxyl groups of polybenzoxazine and (ii) intramolecular hydrogen bonding between phenolic hydroxyl groups and nitrogen atoms on the Mannich bridge. These hydrogen bonding attractions can easily be detected in IR spectrum of polybenzoxazines as broadening of phenolic O–H stretching vibration band. Addition of Carb-Benz into PPO-Benz during film formation could generate increased number of hydrogen binding sites (Chart 2). Binding of -COOH to





phenolic –OH and tertiary amine would affect the hydrogen bonding in polybenzoxazine resin and results in a shift of –OH band toward the low-energy region in IR. Likewise, this shift is clearly detectable in Figure 6, evidencing the supramolecular healing mechanism. As stated previously, without addition of Carb-Benz, sufficient healing was not observed, indicating the importance of hydrogen bonding for successful healing.



Figure 6. FT-IR spectra of cured Carb-Benz5%-PPO-Benz film (a) and cured PPO-Benz film (b).

Thermal stability of the PPO-Benz polymers was explored by thermogravimetric analysis (TGA) under a N_2 atmosphere. The TGA and derivative TGA curves of the cured PPO-Benz and Carb-Benz + PPO-Benz are shown in Figure 7, and the results



Figure 7. TGA and derivative TGA of cured PPO-Benz (a, a') and cured Carb-Benz5% + PPO-Benz (b, b').

Table 2. Thermal Properties of the Cured^a PPO-Benz Films

film	$T_{5\%}^{\ \ b}$ (°C)	$T_{10\%}^{c}$ (°C)	T_{\max}^{d} (°C)
PPO-Benz	310	335	391
Carb-Benz5% + PPO-Benz	326	345	395

^{*a*}Curing was performed in TGA at 220 °C for 15 min under a N₂ stream (200 mL/min). ^{*b*}T_{5%}: the temperature for which the weight loss is 5%. ^{*c*}T_{10%}: The temperature for which the weight loss is 10%. ^{*d*}T_{max}: the temperature for maximum weight loss.

are tabulated in Table 2. Carb-Benz+PPO-Benz exhibited slightly higher degradation temperatures of $T_{5\%}$, $T_{\%10}$, and T_{max} than PPO-Benz polymers due to the increased the total aromatic content of the film arising from the addition of aromatic monomer. Accordingly, all films almost completely vaporized at 800 °C.

CONCLUSION

The results presented in this paper demonstrate that it is possible to take advantage of hydrogen bonding present in polybenzoxazine networks for autonomous self-healing processes. In the approach, benzoxazine bearing poly(propylene oxide) (PPO-Benz) was prepared through conventional main chain polybenzoxazine precursor synthesis methodology using poly(propylene oxide) amines, bisphenol A, and formaldehyde. Carboxylic acid containing benzoxazine monomer mixed with PPO-Benz, the film prepared from these components at suitable composition were then cross-linked by thermally activated ring-opening reactions of the benzoxazine groups. The autonomous self-healing property of the film was demonstrated on the cured films. Current work is devoted to the design and production of self-healable polymers containing polybenzoxazine networks by supramolecular attractions. The process is useful for further expanding the use of benzoxazines in high performance materials, and the chemistry shown here may be extended to other polymers apart from poly(propylene oxide)s.

ASSOCIATED CONTENT

Supporting Information

NMR spectrum, DSC thermogram, FT-IR spectrum of Carb-Benz, GPC trace of PPO-Benz, and images of the films; a visual demonstration of the recovery is presented in a video. This material is available free of charge via the Internet at http:// pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

*(Y.Y.) E-mail yagci@itu.edu.tr; Tel +90 2122853241; Fax +90 212 2856386.

*(B.K.) E-mail kiskanb@itu.edu.tr; Tel +90 2122853241; Fax +90 212 2856386.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Baris Kiskan acknowledges financial support of the Science Academy, Turkey, by means a BAGEP Research Award.

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