Form-stable benzoxazine-urethane alloys for thermally reversible light scattering materials

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Abstract. Thermally reversible light scattering (TRLS) materials based solely on benzoxazine-urethane (BA-a/PU) alloys were successfully fabricated and demonstrated in this work. The alloys displayed the opaque state below 40 °C. The alloys were transformed to the transparent state upon exposing to the transition temperature of 60–130 °C, depending on the molecular weights and mass concentrations of urethane prepolymers in the BA-a/PU alloys. The optical state transitions were reversible with small hystereses. BA-a/PU alloys exhibited a good optical contrast with 0%T at the light scattering state and almost 100%T at the transparent state. The alloys were glassy and form-stable up to 250 °C, due to the synergistic behavior in the glass transition temperatures. The reaction-induced phase separation effectuated by the incorporation of urethane prepolymer into thermosetting polybenzoxazine, the sizes and local concentrations of the phase-separated urethane microdomains in the supporting polybenzoxazine matrix, and the reversible dissolution and demixing of urethane microdomains and polybenzoxazine phase played crucial roles on TRLS properties of the developed benzoxazine-urethane alloys.

Keywords: polymer blends and alloys, smart polymers, polybenzoxazine, urethane, thermally reversible light scattering

1. Introduction

Polybenzoxazines are one of the few thermosetting polymers that have been adopted and commercialized in the composites industry since the early 1990s. Polybenzoxazines possess multitudinous preferable characteristics including low melt viscosity, low water absorption, high thermal stability, outstanding mechanical properties, and good chemical resistance [1]. Benzoxazine resins can be prepared by the patented solventless synthesis technique from formaldehyde, primary amines, and phenols, offering high purity monomers and enormous molecular design flexibilities [2]. Benzoxazine resin can be self-polymerized through thermally activated ring-opening polymerization without any additional initiators and

catalysts [3]. Polybenzoxazines exhibit superior characteristics upon polymerization including dimensional stability, near-zero volumetric shrinkage, and no volatile by-product elimination [4]. Furthermore, polybenzoxazines can be alloyed with various chemicals including epoxy [5–7], polyurethane [8], poly(imide-siloxane) [9], and bismaleimides [10, 11], suppressing the inherent brittleness of polybenzoxazines and meeting the requirement of numerous applications with tailor-made properties. Promising applications of polybenzoxazines, their copolymers, and their composites have been demonstrated, including coating [12–14], proton conductive porous substrate [15], optical probe [16], bipolar plates in fuel cell [17], superinsulating materials for space applications

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[18], shape memory polymer [19], halogen-free flame retardant material [20], porous carbon anode [21], and self-healing polymers [22].

Even though thermal, mechanical, and electrical properties of polybenzoxazines have been widely explored and well-documented, their optical properties have not been thoroughly investigated and utilized. Rajamanikam and coworkers [23] fabricated benzoxazine terminated silane functionalized zinc oxide/ polybenzoxazine nanocomposites displaying ultraviolet shielding properties. Liu *et al.* [24] investigated the photoluminescence properties of hybrid materials based on benzoxazine-bridged polysilsesquioxanes. Lin *et al.* [25] observed the bathochromic shifts in the UV-visible and photoluminescent spectra of thermally polymerizable triphenylamine-benzoxazine dendrimers. Li *et al.* [26] firstly reported the benzoxazine-based polyfluorene displaying reversible temperature-sensitive fluorescent properties. Recently, we discovered that benzoxazine-urethane alloys also possessed the unique optical properties called thermally reversible light scattering (TRLS) properties [27].

Thermally reversible light scattering (TRLS) materials are smart materials exhibiting the temperature-dependent transparency across some specific temperature ranges. TRLS materials with good optical contrasts based on β -hydroxyester organogels [28], eicosane dissolved in poly(dodecyl methacrylate) [29], polyether urethane diacrylate with dispersed 1-octadecanol [30], epoxy resin modified with a low molecular weight liquid crystal [31], dispersed polystyrene/naphthalene domains in epoxy matrixes [32], epoxy resin modified with polystyrene-*block*-poly(ethylene oxide) and a low molecular weight liquid crystal [33], meso/nanocomposite films [34], dispersed diphenyl crystals in an epoxy matrix [35], and 4'-(hexyloxy)-4-biphenyl-carbonitrile and polystyrene in diglycidylether of bisphenol-A epoxy resin [36] were previously fabricated. The optical state transitions in these systems mainly based on melting/crystallization of organic crystals or nematic/isotropic transition of liquid crystals. Reversible opaque/transparent state transitions were observed at the temperature below 100 °C, depending on the employed crystalline or liquid crystalline dispersive centers and the polymer matrixes. However, the TRLS materials based solely on polybenzoxazine alloys have never been reported.

In this work, bisphenol-A-based benzoxazine (BA-a)/urethane (PU) alloys possessed the unique optical

properties i.e. TRLS properties were fabricated and explored. Among other thermoplastic [37–41] and thermosetting [5–7] modifiers, urethane prepolymers appropriately modified the polybenzoxazine networks, endowing the BA-a/PU alloys with unique optical properties. Interestingly, TRLS properties were intrinsically associated with the BA-a/PU alloys without incorporating additional organic crystals or liquid crystals. The TRLS materials based on benzoxazine-urethane alloys could be prepared with easy processability because BA-a monomers with specified mass concentrations could be melted and homogeneously mixed with urethane prepolymers at the relatively low temperature (130 °C). In addition, the optical state transition temperatures in the range of 60–130 °C can be selectively optimized through the molecular weights and mass concentrations of urethane prepolymers without intervening the optical contrasts. BA-a/PU alloys were considerably rigid and exhibited the synergistic behavior in the glass transition temperatures up to 250 °C. Therefore, TRLS materials based on BA-a/PU alloys were form-stable and can be employed for demanding applications at high temperatures.

2. Materials and methods

2.1. Materials

The copolymers exhibited thermally reversible light scattering properties in this research were prepared from benzoxazine resin and urethane prepolymer. Benzoxazine resin was based on bisphenol-A, para-formaldehyde, and aniline. Bisphenol-A (polycarbonate grade) was supplied by PTT Phenol Co., Ltd. (Bangkok, Thailand). Para-formaldehyde (AR grade) was purchased from Merck Co., Ltd. (Darmstadt, Germany). Aniline (AR grade) was obtained from Panreac Quimica S.A. (Barcelona, Spain). Urethane prepolymer was prepared by reacting polyether polyol with toluene diisocyanate (TDI). TDI and poly(propylene glycol) with the molecular weights (M_w) of 1000, 2000, and 3000 g/mol were supported from IRPC Public Company Limited (Rayong, Thailand).

2.2. Benzoxazine resin preparation

Benzoxazine monomer (BA-a) was synthesized by the patented solventless synthesis technique [2] from bisphenol-A, para-formaldehyde, and aniline at the molar ratio of 1:4:2 (Figure 1). Briefly, the three reactants were continuously mixed in an aluminum pan at 110 °C for 40 minutes. Subsequently, the reaction

Figure 1. Solventless synthesis of benzoxazine resin (BA-a).

mixture was cooled-down to room temperature and the benzoxazine monomer (BA-a) was formed as a transparent yellowish solid. The product was then pulverized to fine powder and kept in a refrigerator for future-use.

2.3. Urethane prepolymer preparation

The urethane prepolymer was synthesized by mixing poly(propylene glycol) ($M_w = 1000, 2000, \text{ or } 3000$) and 2,4-toluene diisocyanate (TDI) at a molar ratio of 1:2 in a four-necked round-bottomed flask. The mixture was then stirred under a nitrogen stream at 80°C for 2 hours without any addition of a catalyst. The obtained transparent and viscous urethane prepolymer was cooled down to room temperature and kept in a refrigerator to prolong its shelf life. The urethane prepolymers were labeled as PU1K, PU2K, and PU3K, according to the molecular weights of poly(propylene glycol) of 1000, 2000, and 3000 g/mol, respectively (Figure 2).

2.4. Preparation of TRLS materials based on benzoxazine-urethane alloys

The benzoxazine monomer (BA-a) was mixed with PU1K, PU2K, or PU3K prepolymer at a specified mass ratio (BA-a:PU) of 100:0, 90:10, 80:20, 70:30, 60:40, 50:50, and 40:60. The binary mixtures was sequentially heated at 130°C for 1 hour and at 150°C for 1 hour in an aluminum pan while thoroughly mixed until clear homogeneous resin mixture was obtained. The molten resin was thermally cured in an air-circulated oven with a step heating profile at 160, 170, 180, and 200°C for 2 hours at each temperature

(Figure 3). The specimen was finally left to cool down to room temperature and was ready for characterizations. Based on the developed fabrication procedure, we could systematically investigate effects of molecular weights and mass concentrations of urethane prepolymers on the TRLS properties of the benzoxazine-urethane alloys. The alloys were labelled according to the mass concentrations of urethane prepolymers ($x\%$) and the molecular weight of poly(propylene glycol) employed for the urethane prepolymer preparation ($y\text{K}$; $y = 1, 2, \text{ or } 3$) as $(100 - x)\text{BA-a}/x\text{PU}y\text{K}$.

2.5. Characterization techniques

Molecular information of all specimens was acquired with attenuated total reflection Fourier transform infrared (ATR FT-IR) spectroscopy and Raman microspectroscopy. A Nicolet iS5 FT-IR spectrometer (Thermo Scientific, Massachusetts, USA) equipped with a fast recovery deuterated triglycine sulfate (DTGS) detector was employed for all infrared spectral acquisition. An iD5 single-bounce ATR accessories with a laminate-diamond crystal was employed as a sampling probe. To acquire an infrared spectrum, the specimen surface was placed onto a flat diamond crystal IRE with sampling diameter of 1.5 mm. The specimen was pressed against the flat diamond crystal with a pressure device until the maximum allowable pressure was obtained. All ATR FT-IR spectra were collected at 4 cm^{-1} resolution with 32 co-addition scans.

Raman spectra of all specimens were acquired with a DXR Raman Microscope (Thermo Scientific,

Figure 2. Urethane prepolymer (PU) preparation.

Figure 3. Copolymerization of benzoxazine resin (BA-a) and urethane prepolymer (PU).

Massachusetts, USA) with a 780 nm excitation laser. The specimens were analyzed under a 10X-objective lens with a laser spot size of 3.1 μm . The laser power was set to 14.0 mW. A 50 μm slit type aperture was utilized for a spectral acquisition. The exposure time for measuring was 2.0 seconds with 32 accumulated sample exposures. 4th-degree polynomials were employed for spectral fluorescence correction. To obtain a Raman spectrum, the tested specimen was mounted onto the sample stage beneath the objective lens. The spectral acquisition at a specified point was conducted by focusing the excitation laser on the surface. The surface of specimens should be flat and smooth. The thickness of the specimen was 2 mm.

Differential scanning calorimeter model DSC1 Module (Mettler-Toledo (Thailand) Ltd., Bangkok, Thailand) was employed to study the curing behavior of BA-a/PU mixtures. A sample with a mass in range of 5–10 mg was sealed in an aluminum pan with lid and was systematically scanned from 30 to 300°C at the heating rate of 10°C/min under a nitrogen steam with a purging rate 50 ml/min.

Thermal stability of fully cured benzoxazine-urethane specimens was investigated by a Mettler Toledo thermogravimetric analyzer model TGA1 STARE System (Mettler-Toledo (Thailand) Ltd., Bangkok, Thailand). The testing temperature program was ramped at a heating rate of 20°C/min from 30 to 800°C under a nitrogen atmosphere with a constant $\text{N}_2(\text{g})$ purging at a flow rate of 50 ml/min. The sample mass was approximately 5–10 mg. The degradation temperature at 5% weight loss ($T_{d,5}$) and char yield at 800°C were recorded for each specimen.

A dynamic mechanical analyzer (DMA) model DMA242 from NETZSCH, Inc. (Bavaria, Germany) was employed to investigate the thermo-mechanical properties of the specimens polymerized to a full conversion. The dimensions of each specimen were 50×10×2 mm³. The test was performed under the three-point bending mode. The temperature was scanned from –100°C to the temperature beyond the glass transition temperature (T_g) of each specimen with a heating rate of 2°C/min under a nitrogen atmosphere. The strain was applied sinusoidally with

a frequency of 1 Hz. The storage modulus (G'), loss modulus (G''), and loss tangent ($\tan \delta$) of fully cured samples were then obtained. The glass transition temperatures were obtained from the local maxima of the loss factor curves and the loss modulus curves.

Thermo-optical properties of benzoxazine-urethane alloys were investigated by a homemade laser light scattering measurement apparatus (Figure 4). The insulator chamber had dimensions of $16 \times 21 \times 23 \text{ cm}^3$. In order to suppress a stray light, the interior wall of the test chamber was coated with black paint. The apparatus mainly consisted of a 500 W ceramic heater plate (Zhengxi (Shanghai) Industrial, Co., Ltd., Shanghai, China (mainland)), an Omron E5CC panel mount PID temperature controller (Misumi (Thailand), Co., Ltd., Rayong, Thailand), a type K thermocouple (PK ONE Enterprise (Thailand) Co., Ltd., Nonthaburi, Thailand) a BPW21 visible light Si photodiode (RS Components Ltd., Birkirkara, Malta), a UT61E digital multimeter (Uni-Trend Group Limited, Kowloon, Hong Kong), and a laser diode (Class IIIA Laser Product (FDA0612577-00)). The heating temperature up to 300°C can be precisely controlled. The laser generated from the laser source had a wavelength within the range from 630 to 680 nm. The dynamic range of the photodiode was 460–750 nm. Dimensions of each specimen were $50 \times 10 \times 2 \text{ mm}^3$. The transmittance of all specimens was measured under the same isothermal conditions. After repeated calibrations, the average heating rate and the average cooling rate of the instrument were determined to be $10^\circ\text{C}/\text{min}$ and $1^\circ\text{C}/\text{min}$, respectively.

Optical micrographs in reflection, transmission, and cross-polarized transmission modes of specimens were obtained with an Axio Scope.A1 coupled with an AxioCam HRc CCD camera (Carl Zeiss Co., Ltd., Bangkok, Thailand). Specimens were prepared as thin films with the thickness of $100 \mu\text{m}$ on microscope slides. Photographic images of BA-a/PU alloys were

captured by a Canon IXUS 960 IS digital camera (Canon Inc., Tokyo, Japan) with a resolution of 12.1 megapixels.

3. Results and discussion

3.1. Molecular information

TRLS materials developed in this research were based on the alloys of benzoxazine resin (BA-a) and urethane resin (PU). The molecular characteristics of benzoxazine resin, urethane prepolymer, and benzoxazine-urethane alloys were characterized by ATR FT-IR spectroscopy and Raman microspectroscopy. The urethane prepolymer synthesized with poly(propylene glycol) possessing a molecular weight of 3000 g/mol (PU3K) was selected as a representative for the study. ATR FT-IR spectra and Raman spectra of BA-a resin, polybenzoxazine, PU3K prepolymer, and BA-a/PU3K alloys at various PU3K mass concentrations are shown in Figure 5. Some important vibrational characteristics are summarized in Table 1 [42]. The infrared absorption peaks of BA-a resin at 942 and 1229 cm^{-1} were attributed to the benzene mode of the benzene ring and the trisubstituted benzene that is adjacent to the oxazine ring, respectively [43]. The infrared absorption peak at 1599 cm^{-1} and the Raman shift at 1600 cm^{-1} of BA-a resin were assigned to the benzene ring C=C stretching vibrations [44]. The Raman shift at 3063 cm^{-1} and the infrared band in the region from 2990 – 3110 cm^{-1} came from the aromatic =C–H stretching vibrations of BA-a resin. Alkane C–H deformations from the $-\text{C}(\text{CH}_3)_2$ functional group of BA-a were exhibited in the infrared absorption peaks at 1382 and 1362 cm^{-1} and the Raman band centered at 1372 cm^{-1} . The infrared absorption peak and the Raman shift of BA-a at 1156 cm^{-1} were assigned to C–C skeletal vibrations of $-\text{C}(\text{CH}_3)_2$. Tertiary aromatic amines from the oxazine ring of BA-a resin showed C–N stretching vibrations at 1302 cm^{-1} in the Raman spectrum and at 1325 cm^{-1} in the infrared spectrum. The Raman shift at 1031 cm^{-1} and the infrared absorption peak at 1029 cm^{-1} of BA-a resin were attributed to the symmetric C–O–C stretching from the benzoxazine ring. Polybenzoxazine was formed from BA-a resin by thermal-triggered ring-opening polymerization [3]. Benzoxazine monomers were transformed from a ring structure to a nearly infinite three-dimensional network. The C–O–C stretching peak was disappeared in the Raman spectra of polybenzoxazine because the oxazine rings in BA-a resin were opened

Figure 4. Light scattering measurement apparatus.

Figure 5. ATR FT-IR spectra (a) and Raman spectra (b) of BA-a resin, polybenzoxazine, PU3K prepolymer, 70BA-a/30PU3K alloy, and 40BA-a/60PU3K alloy.

Table 1. Important vibrational characteristics of benzoxazine resin (BA-a), polybenzoxazine, urethane prepolymer (PU3K), and benzoxazine-urethane alloys [42, 43].

IR absorption [cm ⁻¹]	Raman shift [cm ⁻¹]	Vibrational characteristics
Benzoxazine resin (BA-a)		
2964	2969	methyl C–H stretching vibrations
1599	1600	benzene ring C=C stretching vibrations
1382, 1362	1372	alkane C–H deformations from –C(CH ₃) ₂
1325	1302	C–N stretching vibrations from tertiary aromatic amines of oxazine ring
1229	–	trisubstituted benzene that is adjacent to the oxazine ring
1156	1156	C–C skeletal vibrations of –C(CH ₃) ₂
942	–	benzene mode of the benzene ring that is adjacent to the oxazine ring
1029	1031	symmetric C–O–C stretching from the benzoxazine ring
Polybenzoxazine (Poly(BA-a))		
3372 (broad)	–	self-associated phenolic hydroxyl groups
1176	–	deformation vibrations of hydroxyl groups
PU3K Prepolymer		
2970	2974	asymmetric C–H stretching vibrations of aliphatic CH ₃ –
2930	2932	acyclic symmetric –CH ₂ – stretching vibrations
2867	2871	symmetric C–H stretching vibrations of aliphatic CH ₃ –
2272	–	asymmetric aryl isocyanate (–N=C=O) stretching vibrations
1092	–	ether C–O stretching vibration of –CH ₂ –O–CH ₂ –
Benzoxazine-urethane alloys (70BA-a/30PU3K and 40BA-a/60PU3K)		
1705 or 1709	–	urethane C=O stretching vibrations (Amide I band) of solid phase <i>N</i> -aryl urethanes

by the breakage of C–O bonds. In addition, broad infrared absorption band situated around 3372 cm^{-1} was observed in the polybenzoxazine spectra. The band was attributed to self-associated hydroxyl groups of polybenzoxazine [38]. The shoulder band centered at 3569 cm^{-1} was ascribed to the stretching vibration of free phenolic hydroxyl groups. The combination of deformation vibrations of hydroxyl groups and C–O stretching vibrations was observed at 1176 cm^{-1} in the infrared spectra of polybenzoxazine. This intense peak was not observed in the infrared spectra of BA-a resin. Trisubstituted benzene ring in BA-a resin was transformed into 1,2,3,5-tetrasubstituted benzene ring in polybenzoxazine after the polymerization. This transformation was confirmed by the complete disappearance of the infrared absorption peaks at 942 and 1229 cm^{-1} in polybenzoxazine spectra.

In situ generated phenolic hydroxyl groups during the thermal curing of BA-a resin can be employed for the cross-linking with urethane prepolymer to generate BA-a/PU3K alloys. Urethane prepolymer was prepared by reacting poly(propylene glycol) and toluene diisocyanate at the molar ratio of 1:2 under a nitrogen atmosphere. The intense infrared absorption peaks at 2970 and 2867 cm^{-1} and the Raman shifts at 2974 and 2871 cm^{-1} in the PU3K prepolymer spectra were attributed to the asymmetric C–H stretching and symmetric C–H stretching of aliphatic methyl groups, respectively. Acyclic symmetric $-\text{CH}_2-$ stretching vibrations were observed at 2930 cm^{-1} in the infrared spectra and at 2932 cm^{-1} in the Raman shift of PU3K prepolymer spectra. An ether C–O stretching vibration of $-\text{CH}_2-\text{O}-\text{CH}_2-$ was observed at 1092 cm^{-1} as the intense peak in the infrared spectra of PU3K prepolymer. PU3K prepolymer was terminated with free isocyanate groups because the intense infrared absorption peak attributed to the asymmetric aryl isocyanate ($-\text{N}=\text{C}=\text{O}$) stretching vibrations was observed at 2272 cm^{-1} . BA-a resin and urethane prepolymer can be alloyed through the formation of urethane linkage ($-\text{NH}-\text{CO}-\text{O}-$). The terminal isocyanate groups in urethane prepolymer were reacted with *in situ* generated phenolic hydroxyl groups of poly(BA-a) during thermal ring-opening polymerization [45]. The complete disappearance of the peak at 2272 cm^{-1} of the infrared spectra of 70BA-a/30PU3K and 40BA-a/60PU3K alloys indicated that isocyanate groups in PU3K prepolymer were completely consumed during the alloy formation process. Additionally, the infrared absorption peak

ascribed to the stretching vibration of free phenolic hydroxyl groups of polybenzoxazine was not observed in the ATR FT-IR spectra of the alloys. Interestingly, the infrared absorption peak attributed to the self-associated hydroxyl groups of polybenzoxazine centered at 3365 cm^{-1} was still observed in the ATR FT-IR spectra of 70BA-a/30PU3K alloy and 40BA-a/60PU3K alloy. This result suggested that the phenolic hydroxyl groups of polybenzoxazine were not hydrogen-bonded with the oxygen atoms of ether linkages in the urethane prepolymer [38]. Urethane C=O stretching vibrations (Amide I band) of solid phase *N*-aryl urethanes of 70BA-a/30PU3K and 40BA-a/60PU3K alloys were observed in the infrared spectra at 1705 and 1709 cm^{-1} , respectively. ATR FT-IR spectra and Raman spectra of BA-a/PU3K alloys greatly resembled the vibrational characteristics of both polybenzoxazine and urethane prepolymer. These results indicated that poly(BA-a) and PU3K prepolymer were alloyed through the formation of the urethane linkage under the polymerization profile employed in our fabrication.

3.2. Curing behavior

Benzoxazine-urethane (BA-a/PU) alloys were fabricated by thermal curing of binary mixtures of benzoxazine monomers and urethane prepolymers. The binary mixtures were prepared by mixing urethane prepolymers with specified mass concentrations (0–60 wt%) and molecular weights (PU1K, PU2K, or PU3K) with benzoxazine monomers (BA-a) in aluminum molds. The binary mixtures were then thermally cured in an air circulated oven. The representative curing behavior of the BA-a/PU3K binary mixtures at various PU3K mass concentrations was investigated by differential scanning calorimetry (Figure 6a). The heating rate was $10^\circ\text{C}/\text{min}$. The temperature was in the range of 30 – 300°C . Only a single exothermic peak indicating the curing reaction was observed for all BA-a/PU3K binary mixtures at various PU3K mass concentrations. The results suggested that the network forming reactions, i.e. thermal ring-opening polymerization of BA-a resin and the formation of urethane linkages by the reaction of *in situ* generated phenolic hydroxyl groups of poly(BA-a) and isocyanate groups of PU3K prepolymer took place simultaneously. The curing reaction of these binary system proceeded without any catalysts or curing agents.

Figure 6. DSC thermograms of benzoxazine resin and BA-a/PU3K binary mixtures at various PU3K mass concentrations (a) and DSC thermograms of 40BA-a/60PU3K resin mixture at various curing conditions (b).

When the PU3K mass concentrations in the BA-a/PU3K resin mixtures increased from 0 to 10, 20, 30, 40, 50, and 60%, the exothermic peak was shifted from 233 to 238, 243, 247, 253, 256 and 262 °C, respectively. The curing retardation was attributed to the dilution effect of the urethane prepolymer [43]. The area under the exothermic peak also systematically decreased with increasing PU3K mass concentrations in the BA-a/PU3K binary mixtures as revealed in the DSC thermograms. The result suggested that the network forming reaction between BA-a monomer and PU3K prepolymer possessed a lower heat of reaction per mole of the reactant when it was compared to the network forming reaction between BA-a and BA-a monomers.

Since 40BA-a/60PU3K alloy exhibited the highest curing temperature, the alloy was selected for further investigations in order to determine the fully-cured condition for other binary mixture compositions. The DSC thermograms of 40BA-a/60PU3K alloy at various thermal curing conditions are shown in Figure 6b. The degree of conversion of the sample was calculated by Equation (1):

$$\% \text{Conversion} = \left(1 - \frac{H_{rxn}}{H_0} \right) \cdot 100\% \quad (1)$$

where H_{rxn} is the heat of reaction of a partially cured specimen, H_0 is the heat of reaction of an uncured specimen. Both H_{rxn} and H_0 values were obtained from the DSC experiments by calculating the area under the exothermic peaks of a partially cured specimen and an uncured specimen, respectively. The fully-cured condition of the BA-a/PU3K binary mixtures corresponded to the complete disappearance of the exothermic peak in DSC thermograms. Theoretically, the fully-cured thermosetting polymer was reported to provide high thermal and mechanical properties. The uncured 40BA-a/60PU3K binary mixture exhibited the heat of reaction (H_0) of 105.5 J/g (0% conversion). The heat of reaction (H_{rxn}) reduced to 82.8 J/g (22% conversion) and 79.4 J/g (25% conversion) after 40BA-a/60PU3K binary mixture was pre-melted at 130 °C for 1 hour and 150 °C for 1 hour, respectively. 40BA-a/60PU3K binary mixture rapidly underwent the network forming reactions when the mixture was thermally cured at 160 °C ($H_{rxn} = 64.2$ J/g; 39% conversion), 170 °C ($H_{rxn} = 26.3$ J/g; 75% conversion), and 180 °C ($H_{rxn} = 10.1$ J/g; 90% conversion) for 2 hours at each step. The fully-cured 40BA-a/60PU3K alloy was obtained after a post-curing step at 200 °C for another 2 hours since the exothermic peak in the DSC thermogram was

completely disappeared. Therefore, to ensure the complete and uniform network forming reactions of the BA-a/PU alloys, the step-curing conditions starting from 130 °C for 1 hour, 150 °C for 1 hour, 160 °C for 2 hours, 170 °C for 2 hours, 180 °C for 2 hours, and 200 °C for 2 hours were employed as the optimum polymerization profile for other BA-a/PU binary mixture compositions.

3.3. TRLS properties

The fully-cured BA-a/PU alloys at some specific mass concentrations and molecular weights of urethane prepolymers exhibited the thermally reversible light scattering properties. For example, 70BA-a/30PU3K alloy was opaque when the temperature of the specimen was below 40 °C (Figure 7). When the temperature of the specimen was elevated above 150 °C, the specimen was transparent and ‘Phra Kieo’ (the symbol of Chulalongkorn University) laid behind the specimen was observable.

Figure 7. Digital photographs of 70BA-a/30PU3K alloy at the opaque state and the transparent state.

The thermo-optical properties of BA-a/PU alloys at various PU mass concentrations and molecular weights were systematically investigated with a home-made light scattering measurement apparatus. The dimensions of all specimens were 50×10×2 mm³. The thermo-optical curves of BA-a/PU3K alloys with PU3K mass concentrations of 30, 40, and 50 wt% are shown in Figures 8a–8c. The thermo-optical curves of BA-a/PU2K alloys with PU2K mass concentrations of 30, 40, and 50 wt% are shown in Figures 8d–8f. The transition temperatures of heating and cooling steps were determined from the midpoint of the optical state transitions in thermo-optical curves of each BA-a/PU2K and BA-a/PU3K alloy specimens.

At room temperature, BA-a/PU3K alloys at PU3K mass concentrations of 30–50 wt% and BA-a/PU2K alloys at PU2K mass concentrations of 30–40 wt% exhibited the opaque state. Only 50BA-a/50PU2K alloy was transparent at room temperature. When the temperature of the tested specimens was raised, the opaque-to-transparent transition was observed for BA-a/PU3K alloys at PU3K mass concentrations of 30–50 wt% and for BA-a/PU2K alloys at PU2K mass concentrations of 30–40 wt%. There was no opaque-to-transparent transition in 50BA-a/50PU2K alloy and the transmittance of the specimen (~96%T) was invariable within the tested temperature range. The opaque-to-transparent transition temperatures of the

Figure 8. Thermo-optical curves of BA-a/PU3K alloys (a–c) and BA-a/PU2K alloys (d–f) at PU mass concentrations of 30–50 wt%. The insets are digital photographs of the corresponding specimens at 30 °C.

alloys are summarized in Table 2. In BA-a/PU3K alloys, the opaque-to-transparent transition temperatures decreased from 128 to 104 °C when PU3K mass concentrations increased from 30 to 50 wt%. The opaque-to-transparent transparent transition temperatures for BA-a/PU2K alloys at PU2K mass concentrations of 30 and 40 wt% were 84 and 67 °C, respectively. The opaque-to-transparent transition temperatures of BA-a/PU3K alloys were significantly higher than those of BA-a/PU2K alloys at the same PU mass concentrations. Noticeably, the transmittance values at the transparent state for BA-a/PU3K and BA-a/PU2K alloys at PU mass concentrations of 30 and 40 wt% were higher than 95%T. High transparency of BA-a/PU alloys indicated that the alloy components, i.e. polybenzoxazine (poly(BA-a)) and urethane prepolymer, were miscible at elevated temperatures, forming a single phase [28]. The experimental bulk refractive indices of PU3K prepolymer was measured to be 1.465. The bulk refractive index of poly(BA-a) predicted from additive group contributions [46] was 1.671. The calculated refractive index of poly(BA-a) was reasonable because the values could be employed to precisely predict the measured refractive index of 40BA-a/60PU3K alloy (1.54) by a simple rule of mixtures. As far as we know, the temperature-dependent refractive index of polybenzoxazine has not been reported in any literature yet. This might be due to the complication in the accurate determination of the molecular weight of the cross-linked thermosetting network of polybenzoxazine and the preparation of the free standing film of poly(BA-a) with a controllable thickness. Nevertheless, we anticipated that the refractive indices of poly(BA-a) (1.671) and PU3K prepolymer (1.465) should be converged to the common value at an elevated temperature [47] and facilitated the transmittance process of BA-a/PU alloys. In addition, the transmittance values at the transparent state of the

alloys were not affected by PU mass concentrations and molecular weights.

When the alloy specimens were left to cool down to room temperature, the specimens were reversibly transformed to the opaque state again. These results indicated that there was a refractive index mismatch in the alloy components at the opaque state [46]. In BA-a/PU3K alloys, the transparent-to-opaque transition temperatures were decreased from 114 to 82 °C when PU3K mass concentrations increased from 30 to 50 wt%. Even though the optical state transitions were reversible, increasing hystereses of 14, 15, and 22 °C were observed for 70BA-a/30PU3K, 60BA-a/40PU3K, and 50BA-a/50PU3K alloys, respectively. In the case of BA-a/PU2K alloys, when PU2K mass concentrations increased from 30 to 40 wt%, the transparent-to-opaque transition temperatures decreased from 73 to 63 °C. Hystereses of 11 and 4 °C were observed for 70BA-a/30PU2K and 60BA-a/40PU2K alloys. The transmittance values at the opaque state of BA-a/PU3K and BA-a/PU2K alloys exhibiting the TRLS properties were approximately the same at 0%T. Again, there was no transparent-to-opaque state transition in 50BA-a/50PU2K alloy in the cooling step. The opaque-to-transparent or transparent-to-opaque transitions of the developed benzoxazine-urethane (70BA-a/30PU3K) alloys with TRLS properties could be carried out reversibly for several cycles without altering the optical contrasts. The transmittance values were ~0%T at the opaque state and ~96%T at the transparent state after each test cycle. The reversibility of our developed TRLS material was comparable with the TRLS material based on UV cured polyether urethane diacrylate films with dispersed octadecanol [30].

Normally, TRLS materials are fabricated by dispersing a crystalline or liquid crystalline phase in a polymeric continuous matrix. The optical state transitions were mainly based on the dissolution and crystallization of

Table 2. Optical state transition temperatures and transition temperature gaps of BA-a/PU3K alloys and BA-a/ PU2K alloys at PU mass concentrations of 30–50 wt%.

Specimen	Opaque-to-transparent transition temperatures [°C]	Transparent-to-opaque transition temperature [°C]	Transition temperature gap [°C]
70BA-a/30PU3K	128	114	14
60BA-a/40PU3K	119	104	15
50BA-a/50PU3K	104	82	22
70BA-a/30PU2K	84	73	11
60BA-a/40PU2K	67	63	4
50BA-a/50PU2K	No observable optical state transitions		

the dispersed crystallites or nematic/isotropic transition of liquid crystals in the supporting matrixes. However, there were only amorphous 3D interconnected polymeric networks in BA-a/PU alloys. In addition, there were no endothermic peaks indicating the melting of crystalline species observed in the DSC thermograms of BA-a/PU alloys. Noticeably, the optical contrasts of BA-a/PU3K and BA-a/PU2K alloys at various mass concentrations of urethane prepolymers were approximately the same for the heating and cooling cycles, while the optical contrasts of TRLS materials based on the crystallization/melting of organic crystals [29] were drastically affected by dissimilar rates of heating and cooling. Therefore, the optical state transitions observed in our BA-a/PU alloys were possibly brought about by a different mechanism. To elucidate the underlying mechanism of TRLS phenomena in BA-a/PU alloys, further investigation by dynamic mechanical analysis and optical microscopy were carried out. BA-a/PU3K alloys were selected as representative TRLS materials.

3.4. Dynamic mechanical analysis

Fully-cured poly(BA-a), PU3K resin, and BA-a/PU3K alloys were subjected to the dynamic mechanical analysis under a flexural mode from -100 to 350 °C. The dynamic mechanical spectra of the fully-cured poly(BA-a), PU3K resin, and BA-a/PU3K alloys at the PU3K mass concentrations of 30–50 wt% are shown in Figure 9. The $\tan \delta$ or loss factor curves were obtained from the ratio of energy loss or viscous part (G'') to storage energy or elastic part (G') of dynamic modulus of materials. The glass transition temperatures (T_g) of the polymers were determined from the local maxima of the $\tan \delta$ curve or the loss modulus curve of each specimen. T_g depends largely on molecular structure, chain flexibility, branching and cross-linking, and molar mass [48]. There was only a single peak maximum, i.e. a single T_g , in the loss tangent curves of fully-cured poly(BA-a) and PU3K resin at 168 and -63 °C, respectively (Figure 9c). In contrast, there were two peak maxima in the loss tangent curves of BA-a/PU3K alloys at PU3K mass concentrations of 30–50 wt%. The results indicated that there was a phase separation in BA-a/PU3K alloys. The immiscibility of the alloys suggested that the polymer components did not mix on the molecular level. Two peak maxima in the loss tangent curves indicated that there were two phases

Figure 9. Storage modulus (a), loss modulus (b), and loss tangent (c) curves of poly(BA-a) (●), 70BA-a/30PU3K alloy (■), 60BA-a/40PU3K alloy (◆), 50BA-a/50PU3K alloy (▲), and PU3K resin (▼). All specimens were in the fully-cured stage.

in BA-a/PU3K alloys. The first peak maxima were found at -63 , -61 , and -63 °C when the PU3K mass concentrations in BA-a/PU3K alloys were 30, 40,

and 50 wt%, respectively. The first peak maxima corresponded to the PU3K phase in BA-a/PU3K alloys. The second peak maxima were found at 273, 278, and 289 °C when the PU3K mass concentrations in BA-a/PU3K alloys were 30, 40, and 50 wt%, respectively. The second peak maxima exhibited much higher values than the glass transition temperatures of both fully-cured BA-a (168 °C) and PU3K resin (−63 °C). Rimdusit *et al.* [8] previously reported the synergistic behavior in the glass transition temperature of benzoxazine-urethane alloys. Therefore, the second peak maxima should correspond to the poly(BA-a) phase that was cross-linked with PU3K prepolymer. Peak-shift in the dynamic mechanical spectra also indicated that there was a strong interaction between poly(BA-a) and PU3K prepolymer [41]. The ATR FT-IR spectra of BA-a/PU3K alloys revealed that poly(BA-a) and PU3K resin were covalently cross-linked through the urethane linkages. In the pre-melting step at 130 °C, the binary mixtures of benzoxazine monomer (BA-a) and urethane prepolymer (PU) remained clear and transparent. The clearness suggested that the BA-a/PU blends were completely miscible in the amorphous state, i.e. no phase separation occurred. The miscibility of the BA-a/PU blends is attributed to the non-negligible entropy contribution to free energy of mixing as the molecular weight of BA-a is rather low [40, 49]. As discussed earlier in the ATR FT-IR results, polybenzoxazine and urethane prepolymer did not possess favorable intermolecular specific interactions (i.e. hydrogen bonding) which are crucial to the miscibility of thermosetting polymer blends [38–41]. Therefore, the phase separation between poly(BA-a) and PU3K prepolymer was brought about by a reaction-induced phase separation mechanism. The macroscopic phase separation was also encountered in polybenzoxazine blends with poly(ethylene oxide) [40] and poly(ϵ -caprolactone) [38, 41]. In addition, the reaction-induced phase separation for polybenzoxazine and urethane prepolymer took place in the macroscopic scale since the polymeric modifier was a homopolymer. The degree of phase separation between poly(BA-a) and PU3K prepolymer in BA-a/PU3K alloys could also be determined from the differences in the glass transition temperatures determined from the loss factor curves and the loss modulus curves [41]. The glass transition temperatures determined from the loss modulus curves of 70BA-a/30PU3K, 60BA-a/40PU3K, and 50BA-a/50PU3K

alloys were 258, 268, and 284 °C, respectively. The differences in the glass transition temperatures determined from the loss factor curves and the loss modulus curves of 70BA-a/30PU3K, 60BA-a/40PU3K, and 50BA-a/50PU3K alloys were 15, 10, and 5 °C, respectively. The results indicated that the degree of phase separation between poly(BA-a) and PU3K prepolymer decreased with increasing mass concentration of PU3K prepolymer.

The degree of phase separation between poly(BA-a) and PU3K prepolymer might affect the TRLS properties of BA-a/PU3K alloys. The opaque-to-transparent transition temperatures of BA-a/PU3K alloys decreased from 128 to 104 °C when PU3K mass concentrations increased from 30 to 50 wt% (Table 2). The transparent state of BA-a/PU3K alloys at higher PU3K mass concentrations was attained faster at lower opaque-to-transparent transition temperatures because the poly(BA-a) phase and the PU3K phase in BA-a/PU3K alloys were less phase-separated. In contrast, the opaque state of the BA-a/PU3K alloys at higher PU3K mass concentrations was achieved slower at lower transparent-to-opaque transition temperatures. The transparent-to-opaque transition temperatures of BA-a/PU3K alloys decreased from 114 to 82 °C when PU3K mass concentrations increased from 30 to 50 wt%. Higher miscibility of the poly(BA-a) phase and the PU3K phase in BA-a/PU3K alloys at higher PU3K mass concentrations might retard the demixing of the two phases at the transparent-to-opaque transition.

Cross-link density of a polymer network can be calculated from rubbery plateau modulus as suggested by Nielsen [41, 50], as shown in Equation (2):

$$\log G' = 7.0 + 293\rho_x \quad (2)$$

where G' is a storage modulus in a rubbery plateau region [dyn/cm²], ρ_x is a cross-link density defined as the mole of network chains per unit volume of the polymer [mol/cm³]. The rubbery plateau modulus values of 70BA-a/30PU3K, 60BA-a/40PU3K, and 50BA-a/50PU3K alloys at 340 °C were 143, 192, and 211 MPa, respectively. The cross-link densities calculated by Equation (2) were $7.4 \cdot 10^{-3}$, $7.8 \cdot 10^{-3}$, and $7.9 \cdot 10^{-3}$ mol/cm³ for 70BA-a/30PU3K, 60BA-a/40PU3K, and 50BA-a/50PU3K alloys, respectively. The cross-link densities of BA-a/PU3K alloys increased with increasing PU3K mass concentrations. Moreover, the magnitude of the $\tan \delta$ peak at high

temperatures reflects the large-scale mobility associated with alpha relaxation of polybenzoxazine [41]. The peak heights of the cross-linked poly(BA-a) phase in the loss factor curves tended to decrease with increasing PU3K mass concentrations. This suggested the reduction in the chain's segmental mobility and fewer relaxation species due to a higher cross-link density. Increased cross-link densities and reduced chain mobility might also account for the increased hysteresis as observed in the thermo-optical curves of BA-a/PU3K alloys (Figure 8 and Table 2). Effects of the urethane prepolymer molecular weights (1000, 2000, and 3000 g/mol) and mass concentrations (0–60 wt%) on the phase behavior of BA-a/PU alloys were also investigated (Table 3). The published work of Ishida and Lee [41] clearly demonstrated that either the macrophase separation or the microphase separation in the polymer blend could be clearly justified by the transparency of the specimens coupled with the dynamic mechanical analysis. After completing the thermal curing reaction, BA-a/PU2K alloys at the PU2K mass concentrations of 30 and 40 wt% and BA-a/PU3K alloys at the PU3K mass concentrations of 30, 40, and 50 wt% became opaque, suggesting the occurrence of macrophase separation. As demonstrated earlier, these alloys exhibited the TRLS properties. The results implied that reaction-induced phase separation in BA-a/PU alloys was essential for endowing polybenzoxazine with TRLS properties. Even though BA-a/PU3K alloys with PU3K mass concentrations of 10 and 60 wt% appeared transparent at room temperature, there was a phase separation in the alloys as revealed by the dynamic mechanical analysis (results not shown). In 2008, Rimdusit reported that the BA-a/PU alloys at the weight ratio BA-a:PU of 90:10 exhibited the synergistic

behavior in the flexural strength for all molecular weights of the polyol (1000, 2000, 3000, and 5000 g/mol) employed [8]. Ruiz-Pérez *et al.* [51] also demonstrated that the formation of the nanostructures in the multi-component thermosets can significantly improve the mechanical properties of the materials. Therefore, it was possible that the microphase separation also occurred in our benzoxazine-urethane alloy systems that were transparent at room temperature. As previously demonstrated, the transparent 50BA-a/50PU2K alloy did not exhibit the TRLS properties. It could be implied that the transparent benzoxazine-urethane alloy with a microphase separation should not exhibit the TRLS properties.

3.5. Optical microscopy results

The macrophase separation in the BA-a/PU alloys with TRLS properties could possibly create the phase-separated species in the alloys. The transmittance values at the opaque state of the BA-a/PU2K and BA-a/PU3K alloys with TRLS properties were approximately 0%T. To observe the phase-separated morphology in the alloys at room temperature, the selected BA-a/PU alloys were fabricated to 100 μm thick films on glass substrates and were observed with an optical microscope in normal and cross-polarized transmission modes. The polymeric films of the neat poly(BA-a) and the neat PU3K prepolymer were also investigated for comparison.

In the normal transmission mode, polyurethane (PU3K) and polybenzoxazine (poly(BA-a)) films transmitted the visible light originated from a halogen lamp (Figure 10a and 10c). When the polarized light was employed, both polyurethane and poly(BA-a) did not exhibit any optical activities (Figure 10b and 10d). Similarly, 40BA-a/60PU3K alloy film, which

Table 3. Effects of urethane prepolymer molecular weights and mass concentrations on the transparency of BA-a/PU alloys at room temperature.

M_w of Urethane Prepolymer [g/mol]	Mass concentrations of urethane prepolymers [wt%]						
	0	10	20	30	40	50	60
PU1K (1000 g/mol)							
PU2K (2000 g/mol)							
PU3K (3000 g/mol)

Figure 10. Optical micrographs of 100 μm thick films of PU3K resin (a and b), polybenzoxazine (poly(BA-a)) (c and d), 40BA-a/60PU3K alloy (e and f), and 70BA-a/30PU3K alloy (g–j) in normal transmission and cross-polarized transmission modes. Magnifications and scale bars are specified for each micrograph.

was transparent at room temperature, did not distort the polarized light and the dark area in the micrograph was only observed (Figure 10f). In contrast, visible light cannot totally transmit through 70BA-a/30PU3K alloy film when it was observed in the normal transmission mode (Figure 10g). The film also appeared opaque when it was observed with the naked eyes. In contrast, 70BA-a/30PU3K alloy film displayed some optical activities with the polarized light (Figure 10h). When we closely investigated the optical micrograph in the cross-polarized transmission mode of 70BA-a/30PU3K alloy film at a 50× magnification (Figure 10j), we observed that there were numerous polymeric microdomains uniformly dispersed within the support polymeric matrix. The polymeric microdomains were capable of distorting the plane-polarized light and they were exhibited as bright spots in the cross-polarized transmission micrographs (Figure 10h and 10j). The polymeric microdomains with the size in the range of 2–10 μm were possibly generated by the reaction-induced phase separation during the polymerization process. The macrophase separation between urethane prepolymer and cross-linked polybenzoxazine was verified by the dynamic mechanical analysis and discussed previously. Visible light was scattered by these phase-separated microdomains as observed in the normal transmission mode (Figure 10g and 10i) and the magnitude of light scattering depended on the local concentration of the microdomains (Figure 10h and 10j)). Therefore, the dispersive centers causing the light scattering state for the BA-a/PU alloys were the phase-separated polymeric microdomains. The phase-separated polymeric microdomains were possibly urethane microdomains and the supporting matrix were cross-linked polybenzoxazine phase [38, 40]. The urethane microdomains were miscible with the cross-linked polybenzoxazine phase at elevated temperatures and the transparent state of the BA-a/PU alloy was achieved [27]. Even though 40BA-a/60PU3K alloy film appeared transparent at room temperature (Figure 10e), the microphase separation was still existed as discussed earlier. It was possible that the dispersive centers possessed the sizes that were much smaller than the wavelengths of visible light. Therefore, we did not observe the phase-separated morphology with the optical microscope (Figure 10e and 10f).

From the optical microscopy results and dynamic mechanical analysis results, we proposed the TRLS

mechanisms exhibited by the benzoxazine-urethane alloys as follows. The incorporation of urethane prepolymer with an appropriate composition (both molecular weight and mass concentration) into thermosetting polybenzoxazine led to the reaction-induced phase separation within the obtained benzoxazine-urethane alloy. The phase-separated urethane microdomains played a role as light scattering centers in the alloy. The alloy appeared opaque at room temperature because visible light was scattered by the microdomains and the opaque state of the alloy was attained. The transparent state of the alloy was brought about by the dissolution of the urethane microdomains into the cross-linked polybenzoxazine phase at the elevated temperature, forming a single phase. The reversible dissolution and demixing of urethane microdomains and the cross-linked polybenzoxazine phase was the principal mechanism accounted for TRLS properties of the benzoxazine-urethane alloys.

3.6. Thermal stability

BA-a/PU alloys developed in our system not only exhibited special optical effects, they were also form-stable at rather high temperatures. BA-a/PU3K alloys at PU3K mass concentrations of 30–50 wt% were at their glassy state up to 250 °C (Figure 9). The storage modulus values at room temperature for BA-a/PU3K alloys at PU3K mass concentrations of 30, 40, and 50 wt% were 1857, 1546, and 1066 MPa, respectively. Comparing to the storage modulus value at room temperature of polybenzoxazine i.e. 6627 MPa, incorporating PU3K prepolymer into the BA-a/PU3K alloys made the materials more flexible. The thermal stability of BA-a/PU3K alloys was also investigated with thermogravimetric analysis. The TGA thermograms of polybenzoxazine and BA-a/PU3K alloys at various PU3K mass concentrations are shown in Figure 11. The degradation temperature at 5% weight loss ($T_{d,5}$) of the neat polybenzoxazine was determined to be 334 °C. The $T_{d,5}$ of BA-a/PU3K alloys at PU3K mass concentrations of 30, 40, and 50 wt% were determined to be 355, 365, and 374 °C, respectively. Incorporation of the urethane resin into the benzoxazine resin raised the thermal degradation temperatures of the obtained alloys. Therefore, the thermal stability of the polybenzoxazine was improved. The enhanced thermal stability was, in part, due to the relatively more stable chemical bonds in the polyether polyol in contrast to a polybenzoxazine network containing less stable Mannich bridge.

Figure 11. TGA thermograms of BA-a/PU3K alloys at various BA-a:PU3K mass ratios of 100:0 (●), 70:30 (■), 60:40 (◆), and 50:50 (▲).

The char yield, which is the total residual weight at 800 °C under nitrogen, of the neat polybenzoxazine was determined to be 27 wt%. When the PU3K mass concentrations in the alloys were 30, 40, and 50 wt%, the char yield values were found to be 23.5, 22.9, and 21 wt%, respectively. The char yield values of the BA-a/PU3K alloys decreased when PU3K mass concentrations increased. This result comes from the fact that the chemical structure of the urethane prepolymers composes of a less char forming aliphatic structure of poly(propylene glycol) compared to the prevalent aromatic benzene rings in the network structure of polybenzoxazine [43, 45, 52]. The results from dynamic mechanical analysis and thermogravimetric analysis collectively indicated that BA-a/PU3K alloys could endure high temperatures up to 250 °C without considerable deformation and degradation. Therefore, BA-a/PU3K alloys could be potentially employed as the form-stable TRLS materials at high temperatures.

4. Conclusions

Benzoxazine-urethane polymer alloys exhibiting thermally reversible light scattering (TRLS) properties were successfully fabricated. The optical state transition temperatures in the range of 60–130 °C can be optimized through the proper selection of urethane prepolymer molecular weights (2000 or 3000 g/mol) and mass concentrations (30–50 wt%). The benzoxazine-urethane alloys with TRLS properties displayed very good optical contrasts with 0%T at the light

scattering state and nearly 100%T at the transparent state. The benzoxazine-urethane alloys also possessed superior thermal stability in the temperature range of 30–250 °C due to the synergistic behavior in the glass transition temperatures. They were rigid at their glassy state and form-stable under the operating temperature range. The reaction-induced phase separation brought about by the incorporation of urethane prepolymer, the sizes and local concentrations of the light-scattered urethane microdomains, and the reversible dissolution and demixing of the phase-separated urethane microdomains and the cross-linked polybenzoxazine phase were the three crucial factors accounted for the TRLS properties of the alloys. The developed benzoxazine-urethane alloys can be potentially employed as form-stable TRLS materials and the alloys are suitable for opto-thermal sensing applications at high temperatures.

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References

- [1] Rimdusit S., Jubsilp C., Tiptipakorn S.: *Alloys and composites of polybenzoxazines: Properties and applications*. Springer, Singapore (2013).
<https://doi.org/10.1007/978-981-4451-76-5>
- [2] Ishida H.: Process for preparation of benzoxazine compounds in solventless systems. U.S. Patent 08245478, USA (1996).
- [3] Ning X., Ishida H.: Phenolic materials *via* ring-opening polymerization: Synthesis and characterization of bisphenol-A based benzoxazines and their polymers. *Journal of Polymer Science Part A: Polymer Chemistry*, **32**, 1121–1129 (1994).
<https://doi.org/10.1002/pola.1994.080320614>
- [4] Ishida H., Allen D. J.: Physical and mechanical characterization of near-zero shrinkage polybenzoxazines. *Journal of Polymer Science Part B: Polymer Physics*, **34**, 1019–1030 (1996).
[https://doi.org/10.1002/\(SICI\)1099-0488\(19960430\)34:6<1019::AID-POLB1>3.0.CO;2-T](https://doi.org/10.1002/(SICI)1099-0488(19960430)34:6<1019::AID-POLB1>3.0.CO;2-T)
- [5] Jubsilp C., Takeichi T., Hiziroglu S., Rimdusit S.: High performance wood composites based on benzoxazine-epoxy alloys. *Bioresource Technology*, **99**, 8880–8886 (2008).
<https://doi.org/10.1016/j.biortech.2008.04.057>

- [6] Rimdusit S., Kunopast P., Dueramae I.: Thermomechanical properties of arylamine-based benzoxazine resins alloyed with epoxy resin. *Polymer Engineering and Science*, **51**, 1797–1807 (2011).
<https://doi.org/10.1002/pen.21969>
- [7] Zhang L., Wang M., Wu J.: Study on an amine-containing benzoxazine: Homo- and copolymerization with epoxy resin. *Express Polymer Letters*, **10**, 617–626 (2016).
<https://doi.org/10.3144/expresspolymlett.2016.56>
- [8] Rimdusit S., Mongkhonsi T., Kamonchaivanich P., Sujirote K., Thiptipakorn S.: Effects of polyol molecular weight on properties of benzoxazine–urethane polymer alloys. *Polymer Engineering and Science*, **48**, 2238–2246 (2008).
<https://doi.org/10.1002/pen.21171>
- [9] Takeichi T., Agag T., Zeidam R.: Preparation and properties of polybenzoxazine/poly(imide-siloxane) alloys: *In situ* ring-opening polymerization of benzoxazine in the presence of soluble poly(imide-siloxane)s. *Journal of Polymer Science Part A: Polymer Chemistry*, **39**, 2633–2641 (2001).
<https://doi.org/10.1002/pola.1240>
- [10] Takeichi T., Uchida S., Inoue Y., Kawauchi T., Furukawa N.: Preparation and properties of polymer alloys consisting of high-molecular-weight benzoxazine and bismaleimide. *High Performance Polymers*, **26**, 265–273 (2014).
<https://doi.org/10.1177/0954008313510958>
- [11] Li S., Yan H-X., Jia Y., Liu T-Y.: Synthesis of a novel phosphorus-containing benzoxazine-monomer and its polymer alloys based on bismaleimides. *Journal of Polymer Research*, **23**, 186/1–186/7 (2016).
<https://doi.org/10.1007/s10965-016-1030-5>
- [12] Patil D. M., Phalak G. A., Mhaske S. T.: Synthesis and characterization of bio-based benzoxazine oligomer from cardanol for corrosion resistance application. *Journal of Coatings Technology and Research*, **14**, 517–530 (2017).
<https://doi.org/10.1007/s11998-016-9892-3>
- [13] Patil D. M., Phalak G. A., Mhaske S. T.: Enhancement of anti-corrosive performances of cardanol based amine functional benzoxazine resin by copolymerizing with epoxy resins. *Progress in Organic Coatings*, **105**, 18–28 (2017).
<https://doi.org/10.1016/j.porgcoat.2016.10.027>
- [14] Escobar J., Poorteman M., Dumas L., Bonnaud L., Dubois P., Olivier M-G.: Thermal curing study of bisphenol a benzoxazine for barrier coating applications on 1050 aluminum alloy. *Progress in Organic Coatings*, **79**, 53–61 (2015).
<https://doi.org/10.1016/j.porgcoat.2014.11.004>
- [15] Kim K., Choi S-W., Park J. O., Kim S-K., Lim M-Y., Kim K-H., Ko T., Lee J-C.: Proton conductive cross-linked benzoxazine-benzimidazole copolymers as novel porous substrates for reinforced pore-filling membranes in fuel cells operating at high temperatures. *Journal of Membrane Science*, **536**, 76–85 (2017).
<https://doi.org/10.1016/j.memsci.2017.04.058>
- [16] Su Y., Shi W., Chen X., Zhao S. Y., Hui Y. H., Xie Z. F.: An aggregation-induced emission enhancement fluorescent benzoxazine-derived macromolecule: Catalyst-free synthesis and its preliminary application for the determination of aqueous picric acid. *RSC Advances*, **6**, 41340–41347 (2016).
<https://doi.org/10.1039/c6ra06942h>
- [17] Plengudomkit R., Okhawilai M., Rimdusit S.: Highly filled graphene-benzoxazine composites as bipolar plates in fuel cell applications. *Polymer Composites*, **37**, 1715–1727 (2016).
<https://doi.org/10.1002/pc.23344>
- [18] Berthon-Fabry S., Hildenbrand C., Ilbizián P.: Light-weight superinsulating resorcinol-formaldehyde-aptres benzoxazine aerogel blankets for space applications. *European Polymer Journal*, **78**, 25–37 (2016).
<https://doi.org/10.1016/j.eurpolymj.2016.02.019>
- [19] Tanpitaksit T., Jubsilp C., Rimdusit S.: Effects of benzoxazine resin on property enhancement of shape memory epoxy: A dual function of benzoxazine resin as a curing agent and a stable network segment. *Express Polymer Letters*, **9**, 824–837 (2015).
<https://doi.org/10.3144/expresspolymlett.2015.77>
- [20] Krishnadevi K., Selvaraj V.: Development of halogen-free flame retardant phosphazene and rice husk ash incorporated benzoxazine blended epoxy composites for microelectronic applications. *New Journal of Chemistry*, **39**, 6555–6567 (2015).
<https://doi.org/10.1039/c5nj00364d>
- [21] Guo D-C., Han F., Lu A-H.: Porous carbon anodes for a high capacity lithium-ion battery obtained by incorporating silica into benzoxazine during polymerization. *Chemistry A European Journal*, **21**, 1520–1525 (2015).
<https://doi.org/10.1002/chem.201405068>
- [22] Štirn Ž., Ručigaj A., Krajnc M.: Characterization and kinetic study of diels-alder reaction: Detailed study on *n*-phenylmaleimide and furan based benzoxazine with potential self-healing application. *Express Polymer Letters*, **10**, 537–547 (2016).
<https://doi.org/10.3144/expresspolymlett.2016.51>
- [23] Rajamanikam R., Pichaimani P., Kumar M., Muthukaruppan A.: Optical and thermomechanical behavior of benzoxazine functionalized zno reinforced polybenzoxazine nanocomposites. *Polymer Composites*, **38**, 1881–1889 (2017).
<https://doi.org/10.1002/pc.23758>

- [24] Liu H., Fu Z-E., Song F., Liu Q., Chen L.: The controllable construction and properties characterization of organic–inorganic hybrid materials based on benzoxazine-bridged polysilsesquioxanes. *RSC Advances*, **7**, 3136–3144 (2017).
<https://doi.org/10.1039/c6ra26150g>
- [25] Lin R-C., Mohamed M. G., Kuo S-W.: Benzoxazine/triphenylamine-based dendrimers prepared through facile one-pot mannich condensations. *Macromolecular Rapid Communications*, **38**, 1700251/1–1700251/7 (2017).
<https://doi.org/10.1002/marc.201700251>
- [26] Li W., Yuan X., Huang J., Peng B., Zhou F., Ma J., Jia X.: Synthesis of heat-resistant benzoxazine-based polyfluorene and its reversible temperature-sensitive fluorescence. *Polymer*, **109**, 126–136 (2017).
<https://doi.org/10.1016/j.polymer.2016.12.038>
- [27] Kasemsiri P., Wakita J., Ando S., Rimdusit S.: Thermally reversible light scattering characteristics of benzoxazine-urethane alloy. in ‘Multidisciplinary International Student Workshop 2009. Tokyo Institute of Technology, Tokyo, Japan’, p1 (2009).
- [28] Puig J., dell’ Erba I. E., Schroeder W. F., Hoppe C. E., Williams R. J.: Epoxy-based organogels for thermally reversible light scattering films and form-stable phase change materials. *ACS Applied Materials and Interfaces*, **9**, 11126–11133 (2017).
<https://doi.org/10.1021/acsami.7b00086>
- [29] Puig J., Williams R. J. J., Hoppe C. E.: Poly(dodecyl methacrylate) as solvent of paraffins for phase change materials and thermally reversible light scattering films. *ACS Applied Materials and Interfaces*, **5**, 9180–9185 (2013).
<https://doi.org/10.1021/am402680q>
- [30] Cao L-C., Mou M., Feng G., Wang Y-C.: Thermo-optical study of UV cured polyether urethane diacrylate films with dispersed octadecanol. *European Polymer Journal*, **45**, 2587–2593 (2009).
<https://doi.org/10.1016/j.eurpolymj.2009.06.015>
- [31] Tercjak A., Mondragon I.: Relationships between the morphology and thermoresponsive behavior in micro/nanostructured thermosetting matrixes containing a 4’-(hexyloxy)-4-biphenylcarbonitrile liquid crystal. *Langmuir*, **24**, 11216–11224 (2008).
<https://doi.org/10.1021/la8015244>
- [32] Zucchi I. A., Resnik T., Oyanguren P. A., Galante M. J., Williams R. J. J.: Comparison of optical properties of thermally reversible light scattering films consisting in dispersions of polystyrene/naphthalene domains or polystyrene/liquid crystal (EBBA) domains in epoxy matrixes. *Polymer Bulletin*, **58**, 145–151 (2007).
<https://doi.org/10.1007/s00289-006-0516-4>
- [33] Tercjak A., Serrano E., Mondragon I.: Multifunctional thermally reversible nanostructured thermosetting materials based on block copolymers dispersed liquid crystal. *Macromolecular Rapid Communications*, **28**, 937–941 (2007).
<https://doi.org/10.1002/marc.200600893>
- [34] Tercjak A., Serrano E., Garcia I., Ocando C., Mondragon I.: Self-assembled block copolymers as matrix for multifunctional materials modified with low-molecular-weight liquid crystals. *Acta Materialia*, **55**, 6436–6443 (2007).
<https://doi.org/10.1016/j.actamat.2007.08.007>
- [35] Zucchi I. A., Galante M. J., Williams R. J. J.: Thermally reversible light scattering films based on the melting/crystallization of organic crystals dispersed in an epoxy matrix. *European Polymer Journal*, **42**, 815–822 (2006).
<https://doi.org/10.1016/j.eurpolymj.2005.09.030>
- [36] Tercjak A., Serrano E., Mondragon I.: Thermally reversible materials based on thermosetting systems modified with polymer dispersed liquid crystals for optoelectronic application. *Polymers for Advanced Technologies*, **17**, 835–840 (2006).
<https://doi.org/10.1002/pat.832>
- [37] Chu W-C., Li J-G., Kuo S-W.: From flexible to mesoporous polybenzoxazine resins templated by poly(ethylene oxide-*b*- ϵ -caprolactone) copolymer through reaction induced microphase separation mechanism. *RSC Advances*, **3**, 6485–6498 (2013).
<https://doi.org/10.1039/c3ra23447a>
- [38] Zheng S., Lü H., Guo Q.: Thermosetting blends of polybenzoxazine and poly(ϵ -caprolactone): Phase behavior and intermolecular specific interactions. *Macromolecular Chemistry and Physics*, **205**, 1547–1558 (2004).
<https://doi.org/10.1002/macp.200400054>
- [39] Su Y-C., Kuo S-W., Yei D-R., Xu H., Chang F-C.: Thermal properties and hydrogen bonding in polymer blend of polybenzoxazine/poly(*n*-vinyl-2-pyrrolidone). *Polymer*, **44**, 2187–2191 (2003).
[https://doi.org/10.1016/s0032-3861\(02\)00928-x](https://doi.org/10.1016/s0032-3861(02)00928-x)
- [40] Lü H., Zheng S. X.: Miscibility and phase behavior in thermosetting blends of polybenzoxazine and poly(ethylene oxide). *Polymer*, **44**, 4689–4698 (2003).
[https://doi.org/10.1016/s0032-3861\(03\)00401-4](https://doi.org/10.1016/s0032-3861(03)00401-4)
- [41] Ishida H., Lee Y. H.: Synergism observed in polybenzoxazine and poly(ϵ -caprolactone) blends by dynamic mechanical and thermogravimetric analysis. *Polymer*, **42**, 6971–6979 (2001).
[https://doi.org/10.1016/s0032-3861\(01\)00051-9](https://doi.org/10.1016/s0032-3861(01)00051-9)
- [42] Socrates G.: *Infrared and Raman characteristic group frequencies: Table and charts*. Wiley, Chichester (2001).
- [43] Rimdusit S., Pirstpindvong S., Tanthapanichakoon W., Damrongsakkul S.: Toughening of polybenzoxazine by alloying with urethane prepolymer and flexible epoxy: A comparative study. *Polymer Engineering and Science*, **45**, 288–296 (2005).
<https://doi.org/10.1002/pen.20273>
- [44] Andronesu C., Biru E. I., Radu I. C., Gărea S. A., Iovu H.: Kinetics of benzoxazine polymerization studied by Raman spectroscopy. *High Performance Polymers*, **25**, 634–640 (2013).
<https://doi.org/10.1177/0954008313477667>

- [45] Takeichi T., Guo Y., Agag T.: Synthesis and characterization of poly(urethane-benzoxazine) films as novel type of polyurethane/phenolic resin composites. *Journal of Polymer Science Part A: Polymer Chemistry*, **38**, 4165–4176 (2000).
[https://doi.org/10.1002/1099-0518\(20001115\)38:22<4165::Aid-pola170>3.0.Co;2-s](https://doi.org/10.1002/1099-0518(20001115)38:22<4165::Aid-pola170>3.0.Co;2-s)
- [46] van Krevelen D. W., te Nijenhuis K.: *Properties of polymers: Their correlation with chemical structure; their numerical estimation and prediction from additive group contributions*. Elsevier, Amsterdam (2009).
- [47] Krause S., Lu Z.-H.: Refractive index–temperature measurements on anionically polymerized polystyrene. *Journal of Polymer Science: Polymer Physics Edition*, **19**, 1925–1928 (1981).
<https://doi.org/10.1002/pol.1981.180191211>
- [48] Cowie J. M. G., Arrighi V.: *Polymers: Chemistry and physics of modern materials*. CRC Press, Boca Raton (2007).
- [49] Hu D., Zheng S.: Reaction-induced microphase separation in polybenzoxazine thermosets containing poly(*n*-vinyl pyrrolidone)-block-polystyrene diblock copolymer. *Polymer*, **51**, 6346–6354 (2010).
<https://doi.org/10.1016/j.polymer.2010.10.047>
- [50] Nielsen L. E., Landel R. F.: *Mechanical properties of polymers and composites*. CRC Press, Boca Raton (1993).
- [51] Ruiz-Pérez L., Royston G. J., Fairclough J. P. A., Ryan A. J.: Toughening by nanostructure. *Polymer*, **49**, 4475–4488 (2008).
<https://doi.org/10.1016/j.polymer.2008.07.048>
- [52] Takeichi T., Guo Y.: Preparation and properties of poly(urethane-benzoxazine)s based on monofunctional benzoxazine monomer. *Polymer Journal*, **33**, 437–443 (2001).
<https://doi.org/10.1295/polymj.33.437>