

Article

Synergistic Effect of PBz/Epoxy/PCLA Composite Films with Improved Thermal Properties

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Abstract: Polybenzoxazines (PBzs) are advanced forms of phenolic resins that possess many attractive properties, including thermally induced self-curing polymerization, which produces void-free polymer products without any by-product formation. They also possess a high T_g (glass transition temperature) and thermal stability, but the produced materials are brittle in nature, due to which the final form of their application is very difficult. Hence, in this paper, an attempt has been made to overcome the brittleness of PBz by blending it with epoxy and ϵ -caprolactam (CPLA) to produce free-standing PBz/Epoxy/PCLA (polycaprolactam) films. The curing process between the three components (i.e., Bzo, epoxy, and caprolactam) was monitored using differential scanning calorimetric (DSC) analysis. The results show that there is no appreciable shift in curing the exotherm observed, except a slight shift in the curing process. However, the heat liberated during the exotherm (ΔH) decreases drastically from 121 to 84 J/g, indicating that the content of benzoxazine is very important as it is involved in the polymerization process through oxazine ring-opening. The morphological studies analyzed using SEM and AFM analyses indicate that there was no observable phase separation up to 30 wt.% of CPLA loading, whereas a higher CPLA content of 50 wt.% causes agglomeration and leads to distinctive phase separation. Moreover, the thermal stability of the composite film, PBz/Epoxy/PCLA30, is also increased with a 10% degradation temperature, T_{10} , of 438 °C, when compared with an PBz/Epoxy film. From the obtained results, it is evident that the formation of a composite film through the melt blending process could produce a tough and thermally stable film without sacrificing individual properties.

Keywords: polybenzoxazine; ϵ -caprolactam; composite film; enhanced thermo-mechanical property



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1. Introduction

In recent decades, there has been a surge of interest in multicomponent thermosets. This focus stems from their potential to significantly improve polymer properties through the creation of blends or composites [1,2]. A key strategy in this area involves incorporating elastomers and thermoplastics into thermosetting polymers, such as epoxy resins. This approach aims to address two main challenges: reducing shrinkage during curing and enhancing the material's thermo-mechanical properties (i.e., how it behaves under the combined influence of heat and mechanical stress) [3]. However, achieving miscibility (good mixing at the molecular level) within these polymer blends often proves difficult. Introducing additional functional groups can offer a solution. These groups can facilitate favorable interactions between molecules, such as hydrogen bonding. This, in turn, holds promise for enhancing polymer miscibility and promoting the formation of uniform blends [1,4]. Polybenzoxazine (PBz) stands out as a fascinating class of phenolic resin due to its exceptional combination of mechanical, physical, and thermal properties. Additionally, PBz offers remarkable molecular design flexibility, allowing for the creation

of polymers with tailored properties [5]. Notably, benzoxazines can be synthesized from cost-effective raw materials through a process called Mannich condensation. They also boast several advantages during processing, including catalyst-free curing and the absence of by-products [3].

Benzoxazine monomers polymerize through a heterocyclic ring-opening process. Depending on the specific functionalities present in the benzoxazine molecule, this process can yield either linear or cross-linked structures. The resulting polybenzoxazine exhibits exceptional dimensional stability due to minimal shrinkage during polymerization. Furthermore, its wide-ranging molecular design flexibility translates to excellent processability [6,7]. Despite these merits, polybenzoxazines tend to be brittle, limiting their applicability in various situations. A crucial area of research, therefore, focuses on enhancing the toughness of PBz to fully exploit its potential benefits. Two primary approaches can be employed to achieve this goal: one is modifying the structure of benzoxazines to create novel variants and the other is preparing blends or composites with other polymers or inorganic fillers [7]. Epoxy resins are used to produce composites with other polymers, due to their diversified properties such as ease of processability, enhanced physical and mechanical properties, good adhesion with other materials, resistance towards chemicals, and electrical insulation. Despite these admirable properties, they also possess high flammability and low fire resistance, which hinders the advantage of the final product [8–10]. Epoxy resins are well known for their versatility and compatibility with various polymers, making them ideal candidates for blending with PBzs. While PBzs typically exhibit lower cross-link densities, they boast higher glass transition temperatures (T_g) and moduli compared to epoxy resins [4,11]. The extent of hydrogen bonding within these blends, both between individual molecules within the same material (intra-molecular) and between molecules of different materials (inter-molecular), can significantly impact their final physical and mechanical properties. Poly (ϵ -caprolactam) is another widely used polymer known for its miscibility with numerous other polymers, facilitated by hydrogen bonding interactions [12–15]. Notably, poly (ϵ -caprolactam) exhibits a tendency for water absorption, making it a prime candidate for blending with other polymers to create materials with improved water resistance [16–19].

Building upon previous research, this study aims to leverage the potential of ternary blends containing PBz, epoxy, and polycaprolactam. Pioneering work by Ishida et al. in the year 2000 demonstrated the development of novel polymeric systems based on such a combination. These materials showcased promising characteristics for applications like underfilling encapsulation and highly filled systems [20]. Subsequent studies explored the thermal properties and morphological effects of blends containing benzoxazine monomers with PCL and PBA-a/PCL [polybenzoxazine from bisphenol A and aniline/poly(ϵ -caprolactone)], respectively [20,21]. Additionally, investigations into the impact of system parameters on blend properties were conducted using nanofiber layers of polyester-amides with varying ratios of ϵ -caprolactam/ ϵ -caprolactone structural units [22].

This study seeks to enhance the toughness of polybenzoxazine by blending it with epoxy and ϵ -caprolactam. The investigation will focus on elucidating the impact of incorporating these flexible materials on the curing behavior, surface morphology, and thermal properties of the resulting blend. We anticipate that the synergistic combination of these three materials will lead to the formation of flexible films with superior properties compared to the properties that each individual component can achieve on its own.

2. Materials

Epoxy resin, KSR 177 (EEW = 190–220 g/eq; viscosity = 9000–15,000 cps at 25 °C), was purchased from Kukdo Chemical Co., Ltd., Geumcheon-gu, Seoul, Republic of Korea. Eugenol, ethylene diamine, p-formaldehyde, dimethyl sulfoxide (DMSO), and ϵ -caprolactam were purchased from Sigma Aldrich, Gangnam-gu, Seoul, Republic of Korea. Methyl ethyl ketone (MEK) and isopropanol were purchased from Daesung Chemical Co.,

Ltd., Hwaseong-si, Gyeonggi-do, Republic of Korea. All chemicals and solvents were used without further purification.

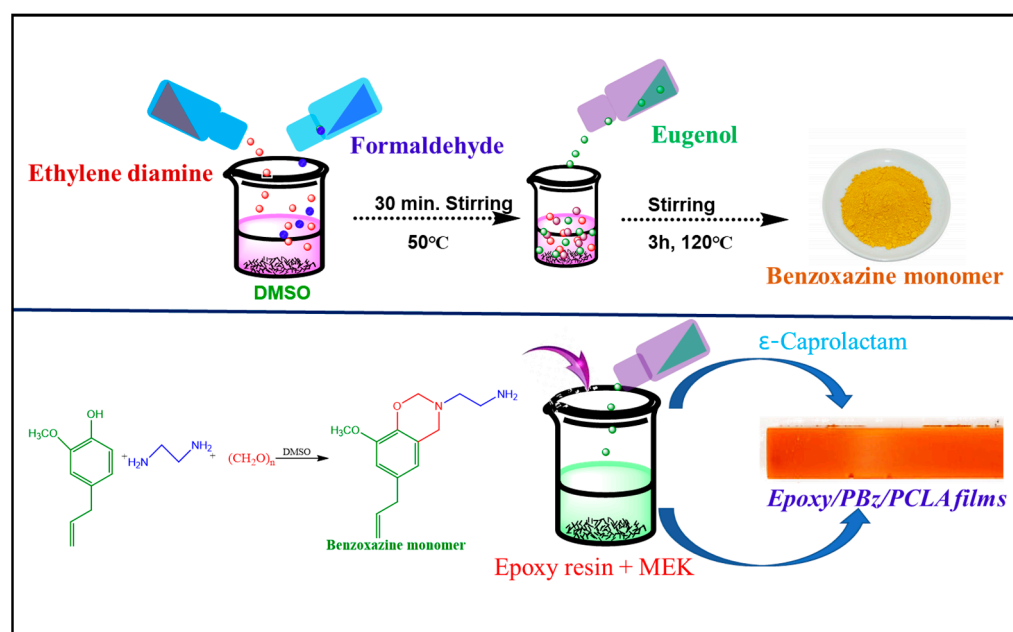
3. Methods

3.1. Synthesis of Benzoxazine Monomer (6-Allyl-8-methoxy-3-ethylamine-3,4-dihydro-1,3-benzoxazine) (Eu-Bzo)

In a three-necked round-bottom flask equipped with a magnetic stirrer and a reflux condenser, 1.8 g (0.06 moles) of paraformaldehyde was combined with 20 mL of DMSO. The mixture was stirred at 50 °C while ethylene diamine (1.34 mL, 0.02 moles) was added dropwise. Simultaneously, a separate solution of eugenol (3.28 g, 0.02 moles) in 10 mL of DMSO was prepared. Upon complete addition of ethylene diamine, the eugenol solution was also added dropwise to the reaction mixture. The temperature was then gradually raised to 120 °C, and the reaction was stirred continuously for 3 h at this temperature. Upon completion of the reaction time, a pale-yellow solution was obtained. This solution was cooled to room temperature and precipitated in 1 N NaOH solution. The resulting precipitate was washed with distilled water multiple times, filtered, and subsequently dried under vacuum at 50 °C for 12 h to yield the Eu-Bzo monomer.

3.2. Preparation of PBz/Epoxy/PCLA Films

In a beaker, equal amounts of benzoxazine monomer and epoxy resin were added, and the required amount of MEK (max. 5 mL) was added before stirring continuously to obtain a clear solution. To this, different weight percentages of ϵ -caprolactam (10, 30 and 50 wt.% of the total content of benzoxazine and epoxy) were added and stirred continuously at 50 °C until a clear solution was obtained. Separately, the PET substrate, onto which the solution was cast, was rinsed with isopropanol and dried completely. The solution was then poured into a bar coating machine and cast using an applicator, maintaining a 0.5 mm gap. The coated solution was then dried completely for 24 h in air to obtain a single-layered film. This film was then cured in an oven at 150 °C for 1 h to produce PBz/Epoxy/PCLA films. The above-mentioned procedure was followed to produce four different films—one without CPLA and the other three with different wt. percentages of CPLA. The produced films are named as follows: PBz/Epoxy, PBz/Epoxy/PCLA10, PBz/Epoxy/PCLA30, and PBz/Epoxy/PCLA50 (Scheme 1).



Scheme 1. Synthesis of benzoxazine monomer and preparation of PBz/Epoxy/PCLA films.

3.3. Instrumentation Methods

Fourier transform infrared (FT-IR) spectra were obtained with a Perkin Elmer MB3000 FT-IR spectrometer (PerkinElmer, Waltham, MA, USA). The spectra were obtained at a resolution of 4 cm^{-1} in the IR range of $4000\text{--}400\text{ cm}^{-1}$. Samples were prepared by grinding with KBr and compressed to form discs. Nuclear magnetic resonance (NMR) spectra were recorded by using an Agilent NMR, VNS600 at a proton frequency of 600 MHz for ^1H -NMR and a carbon frequency of 150 MHz for ^{13}C -NMR. Solutions were prepared by dissolving the samples in DMSO-d_6 . Optical images were taken using an Olympus BX51 optical microscope with a resolution of 600 ppi. Differential scanning calorimetric (DSC) analysis was carried out using a TA Instruments Q200 model at a heating rate of $10\text{ }^\circ\text{C/min}$ and a nitrogen flow rate of 50 mL/min . Samples weighing between 5 and 9 mg were crimped in hermetic aluminum pans with lids and used for analysis. XRD measurements were carried out using a PANalytical X'Pert3 MRD diffractometer with monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.54\text{ \AA}$) at 40 kV and 30 mA and were recorded in the range from 10 to 90° (2θ). Morphological analyses were performed on a field emission scanning electron microscope (FESEM, Hitachi S-4800, Tokyo, Japan) at an accelerating voltage of 10 kV. A Dataphysics Instrument OCA 20 model was used to determine the water contact angle of the PBz/Epoxy/PCLA films. About $2\text{ }\mu\text{L}$ of distilled water was dropped onto the film using a micro syringe, and the respective contact angle was recorded. AFM measurements were taken using Park Systems (XE-100) with a high resolution of $2\text{--}3\text{ \AA}$ lateral and $0.1\text{ \AA}$ vertical in a non-contact mode. Thermogravimetric analysis (TGA) was carried out using a TA Instruments SDT Q600 model at a heating rate of $10\text{ }^\circ\text{C/min}$ up to $800\text{ }^\circ\text{C}$ under an N_2 atmosphere.

4. Results and Discussion

4.1. Structure Analysis of Eu-Bzo

The FT-IR spectrum of the benzoxazine monomer is represented in Figure 1. A band was observed at 946 cm^{-1} due to the $-\text{CH}_2$ stretching vibration of oxazine ring. The asymmetric and symmetric stretching vibrations of C-O-C peaked at 1236 and 1220 cm^{-1} , and for C-N-C , the peaks were obtained at 1120 and 1094 cm^{-1} . The stretching vibration of the methoxy group was found at 1272 cm^{-1} . The band at 1360 cm^{-1} is due to the tetra-substituted benzene. Aliphatic C-H stretching vibrations were found at 2958 and 2856 cm^{-1} , and the $-\text{NH}$ stretching vibrations of the amine group were found at 3002 cm^{-1} . The observed vibrational bands indicate the formation of the benzoxazine monomer [23–26].

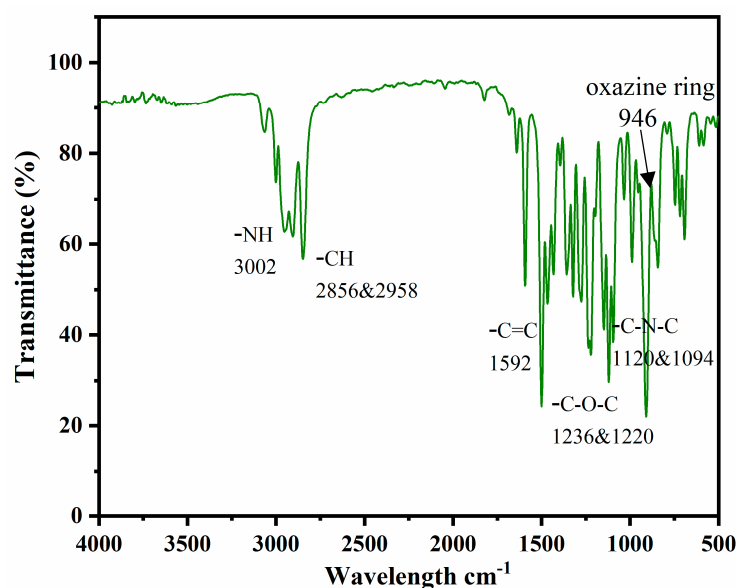


Figure 1. FT-IR spectrum of benzoxazine monomer.

The structure of the synthesized benzoxazine monomer was further confirmed by NMR spectroscopy. Figure 2a,b represents the ^1H - and ^{13}C -NMR spectra of the benzoxazine monomer. The ^1H -NMR spectrum shows two singlets at 4.75 and 3.85 ppm, confirming the presence of oxazine ring protons: $\text{O}-\text{CH}_2-\text{N}$ and $\text{N}-\text{CH}_2-\text{Ar}$, respectively. The protons of the amine group peaked at 2.8 ppm, whereas the protons of the methoxy groups peaked at 3.7 ppm. The methyl protons of the ethyl amine group resonate at 3.2 ppm, and the allyl protons resonate at 5.0 and 5.9 ppm. The aromatic protons peaked at 6.3 and 6.6 ppm. In the ^{13}C -NMR spectrum, the oxazine ring carbons gave signals at 82.3 ppm for $\text{O}-\text{C}-\text{N}$ and at 55.6 ppm for $\text{N}-\text{C}-\text{Ar}$ carbons. The methylene carbons gave signals at 49.6 and 40.1 ppm, whereas the allyl carbons gave signals at 138 and 115 ppm. The aromatic carbons resonate between 110 and 147 ppm. The observed bands and peaks from FT-IR, ^1H -NMR, and ^{13}C -NMR spectroscopy confirm the formation of the benzoxazine ring and hence confirm the successful synthesis of the benzoxazine monomer [27–30].

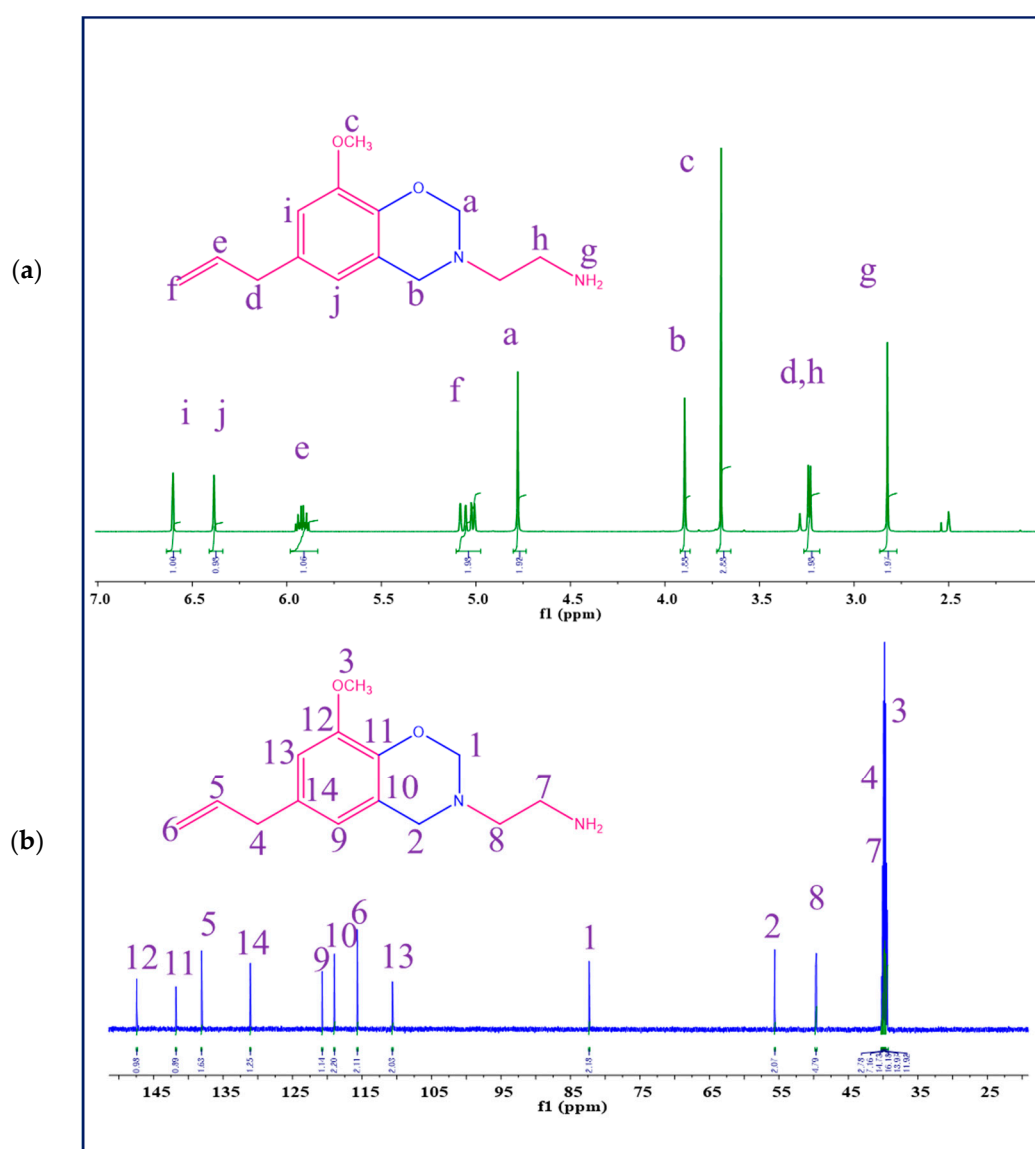


Figure 2. (a) ^1H -NMR and (b) ^{13}C -NMR spectrum of benzoxazine monomer.

4.2. Polymerization Behavior of Bzo/Epoxy/CPLA Blends

To delve deeper into the intricate dynamics of the polymerization process and reactivity of PBz/Epoxy/PCLA, a comprehensive investigation utilizing differential scanning

calorimetry (DSC) analysis was performed and is depicted in Figure 3. The DSC thermogram obtained for PBz/Epoxy showcased a distinct exothermic peak with a peak temperature of 148 °C, indicative of the ring-opening polymerization of benzoxazine. This observed curing temperature stands out significantly lower in comparison to traditional mono-benzoxazines like P-A (phenol-aniline), which exhibits a substantially higher curing temperature of 255 °C, as evidenced by its exothermic peak [31]. The distinctively lower curing temperature noted in PBz/Epoxy/PCLA is particularly intriguing as it suggests the initiation of polymerization at a more moderate temperature regime. This reduction can be ascribed to the presence of the –NH moiety within the molecular structure of caprolactam. This moiety functions as a cross-linking agent, owing to its strong affinity for the methoxy and amine groups in the Eu-Bzo monomer (derived from eugenol and ethylenediamine precursors). The existence of these groups significantly accelerates the ring-opening polymerization of benzoxazine. It is imperative to acknowledge that these effects are intricately intertwined with the specific architecture of the monomer employed. Figure 3a illustrates the DSC thermogram of Bzo/Epoxy/CPLA blends formulated with varying weight percentages of CPLA (0, 10, 30, and 50 wt%). Intriguingly, the thermograms of Bzo/Epoxy and Bzo/Epoxy/CPLA incorporated blends exhibit comparable exothermic profiles. However, a notable observation is the progressive increase in the onset temperature of polymerization from 148 to 155 °C as the CPLA content within the blend increases. Furthermore, the exothermic peaks exhibit broader characteristics with a concurrent decrease in total enthalpies. The total enthalpy for PBz/Epoxy was quantified at 121 J/g, whereas this value declined to 84 J/g for PBz/Epoxy/PCLA50. This observed reduction in ΔH values can be elucidated by the dilution effect. As the proportion of CPLA augments within the polymer blend, the contribution of the exothermic heat released during benzoxazine ring-opening polymerization proportionally diminishes, which is further confirmed by the FT-IR analysis represented in Figure 4 [32–35].

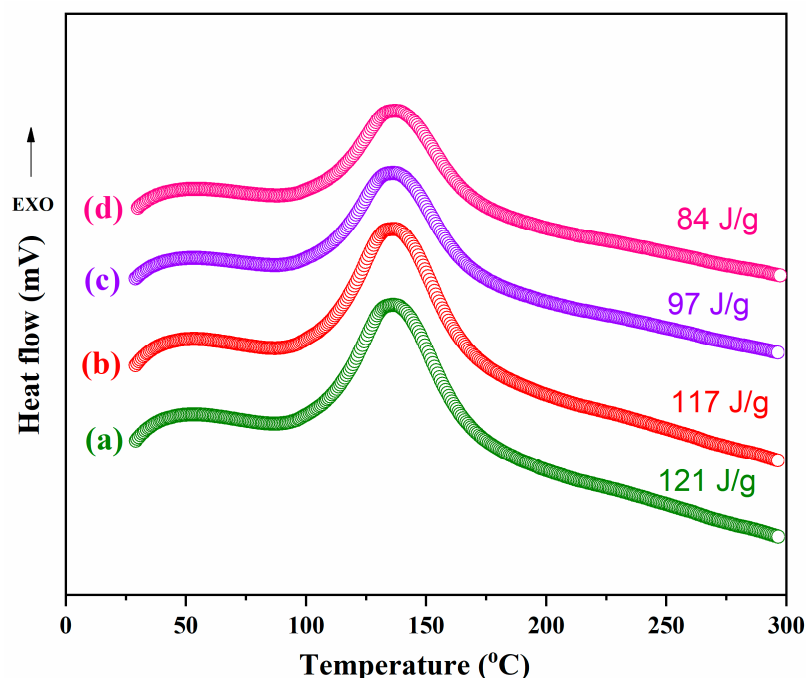


Figure 3. DSC thermograms of (a) Bzo/Epoxy, (b) Bzo/Epoxy/CPLA10, (c) Bzo/Epoxy/CPLA30 and (d) Bzo/Epoxy/CPLA50 blends.

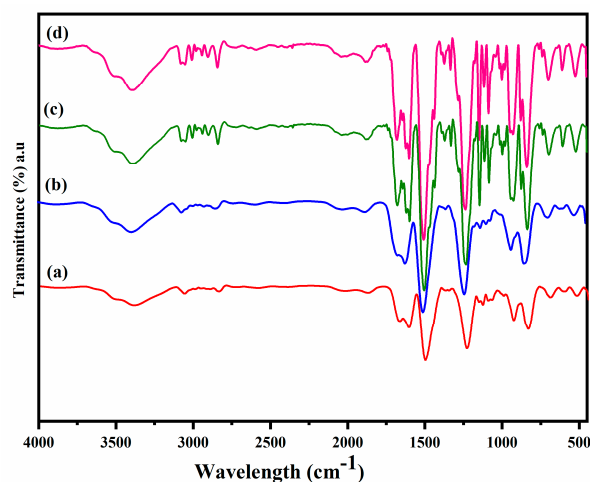


Figure 4. FT-IR spectra of (a) Bzo/Epoxy, (b) Bzo/Epoxy/CPLA10, (c) Bzo/Epoxy/CPLA30 and (d) Bzo/Epoxy/CPLA50 blends.

4.3. Structural Analysis of PBz/Epoxy/PCLA Films

The structural make up of PBz/Epoxy and PBz/Epoxy/PCLA hybrid composites was analyzed by X-ray diffraction (XRD) measurements and is illustrated in Figure 5. By analyzing the acquired spectra, we were able to glean fascinating details regarding the influence of caprolactam content on the composite's overall structure. One particularly intriguing finding was the absence of any significant changes in crystallinity with an increasing concentration of caprolactam within the PBz/Epoxy hybrids. This suggests that caprolactam disperses effectively throughout the PBz/Epoxy matrix, as evidenced by the broad and diffuse peaks observed around 20° in the spectra. This effective dispersion holds promise for improved mechanical properties and a more uniform composite structure. Furthermore, the stability observed in crystallinity signifies a high degree of compatibility between CPLA and the PBz/Epoxy matrix. This compatibility is essential for reinforcing the structural integrity of the composite. Through this comprehensive XRD characterization, we emphasize the significance of comprehending the intricate interactions between various materials within hybrid composites [36–39]. These results paved way for the development of tailored design and optimization strategies, ultimately leading to advancements in composite material engineering.

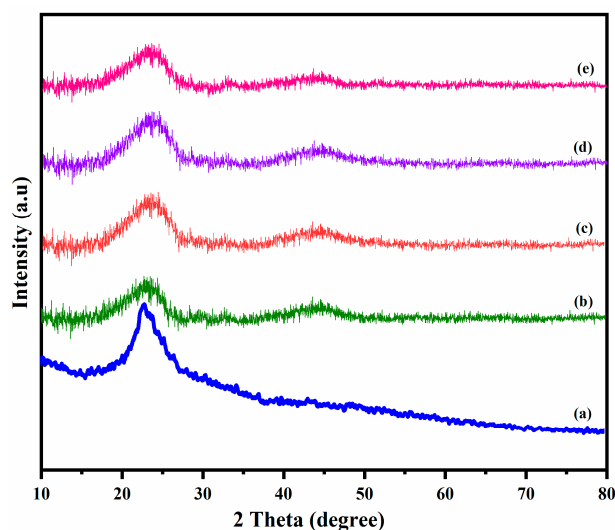


Figure 5. XRD spectra of (a) PCLA, (b) PBz/Epoxy, (c) PBz/Epoxy/PCLA10, (d) PBz/Epoxy/PCLA30 and (e) PBz/Epoxy/PCLA50 films.

4.4. Microscopic Exploration of PBz/Epoxy/PCLA Films

The microscopic morphology of PBz/Epoxy and PBz/Epoxy/PCLA composite films was analyzed utilizing scanning electron microscopy (SEM) to unveil their intricate structures. Figure 6 displays the SEM images of PBz/Epoxy/PCLA films. The SEM micrograph showcases a remarkably smooth and uniform surface, akin to a calm lake, in the case of the PBz/Epoxy film (Figure 6a). This pristine appearance signifies a highly homogeneous structure, where polybenzoxazine and epoxy resin seamlessly blend together. In stark contrast, the PBz/Epoxy/PCLA10 film presents a dramatically different morphology, displaying a roughened and fractured surface (Figure 6b). The SEM image reveals a distinct two-phase morphology, hinting at a separation of the material into two distinct regions. This phenomenon suggests microphase separation, where PBz/Epoxy and polycaprolactam tend to form separate domains within the composite. The compatibility between these constituents plays a crucial role in dictating the extent of this separation. To gain a deeper understanding of the distribution of caprolactam within the PBz/Epoxy matrix, we can focus on Figure 6b–d. These images unveil a fascinating story—a consistent and random dispersion of CPLA particles throughout all PBz/Epoxy/PCLA nanocomposites. This is particularly evident for composites with lower CPLA concentrations (10% and 30%). This remarkable uniformity underscores the exceptional miscibility achieved between CPLA and the PBz/Epoxy matrix. The secret behind this harmonious coexistence lies in robust interfacial interactions, potentially involving hydrogen bonding and favorable chemical compatibility between the components. However, it takes an interesting turn as the CPLA content increases to 50% (Figure 6d), where some agglomeration is observed on the composite surface. This observation suggests that even a minimal incorporation of CPLA can influence the properties of the resulting composite. The observed reduction in agglomeration signifies improved compatibility between CPLA and the matrix, even at higher loadings (30%). The uniform dispersion and reduced agglomeration of CPLA within the PBz/Epoxy/PCLA matrix offer a promising glimpse into the future. This improved morphology has the potential to significantly enhance the overall performance of these composites across various applications, owing to the combined benefits of PBz, epoxy, and PCLA.

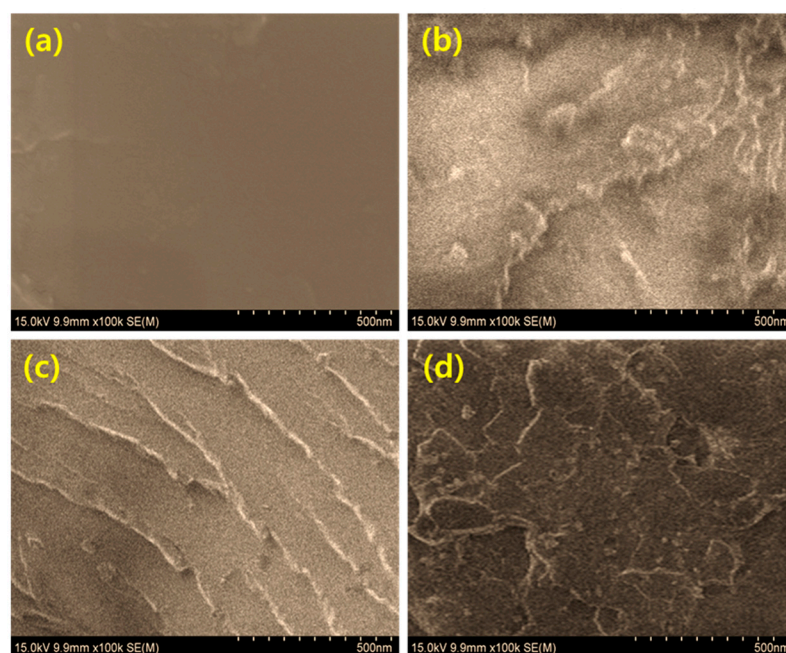


Figure 6. SEM micrographs of (a) PBz/Epoxy, (b) PBz/Epoxy/PCLA10, (c) PBz/Epoxy/PCLA30 and (d) PBz/Epoxy/PCLA50 films.

The morphological characteristics of PBz/Epoxy and PBz/Epoxy/PCLA composites were also meticulously investigated utilizing atomic force microscopy (AFM). Illustrated in Figure 7a–d are the AFM images portraying the surface of PBz/Epoxy/PCLA films with varying CPLA contents (0, 10, 30, and 50 wt.%). A discernible pattern emerges from the AFM micrographs, revealing the surface features and distribution of CPLA within the polybenzoxazine matrix. Remarkably, the AFM micrograph of PBz/Epoxy showcases a uniformly homogeneous surface, while the hybrids exhibit a notable dispersion of CPLA moieties uniformly interspersed within the polybenzoxazine framework. An intriguing observation arises as the CPLA content increases: the degree of roughness of the PBz/Epoxy hybrids amplifies, indicating a direct correlation between CPLA concentration and surface irregularities. Impressively, despite this increase in roughness, the surface remains devoid of visible defects, underscoring the robustness of the composite structure. Delving further into the nanocomposite realm, the AFM image of PBz/Epoxy/PCLA composite films unveils nodules formed by all three constituent polymers, showcasing a uniform distribution and size consistency. This uniformity, as evidenced by AFM images, underscores the meticulous integration and distribution of CPLA within the PBz/Epoxy matrix, setting a promising trajectory for tailored composite material design and applications.

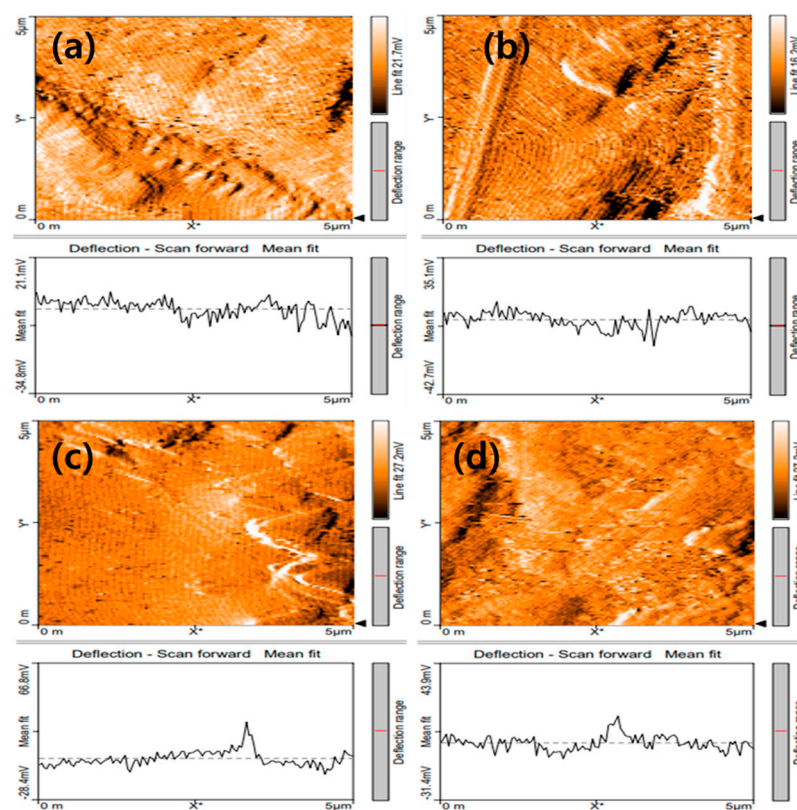


Figure 7. AFM images of (a) PBz/Epoxy, (b) PBz/Epoxy/PCLA10, (c) PBz/Epoxy/PCLA30 and (d) PBz/Epoxy/PCLA50 films.

4.5. Optical Image of PBz/Epoxy/PCLA Films

Figure 8 depicts the optical images of PBz/Epoxy/PCLA50 film at different magnifications. The incorporation of ϵ -caprolactam forms a thread-like structure that is clearly seen in all films. As can be observed from the images, there are two different structures within the PBz/Epoxy/PCLA50 film: one is the sheet form, and the other is the thread form. Furthermore, these images clearly show that the sheet-like structure comes from the combination of PBz and epoxy and the thread-like structure comes from the caprolactam. At lower magnification (Figure 8a,b), we can observe two different distributions of threads; at one place, the threads are clumped together (Figure 8a), and at the other place, they are

expanded or distributed evenly. Similar observations could be made at higher magnification (Figure 8c,d). Thus, we can say that the optical images are in good agreement with the SEM and AFM images, where the agglomeration of caprolactam is clearly visible at a higher content, 50 wt.%, of CPLA. The results also convey that the miscibility between the components is due to the even distribution of caprolactam threads in the PBz/Epoxy matrix, and the phase separation happens when there is an agglomeration of the caprolactam threads.

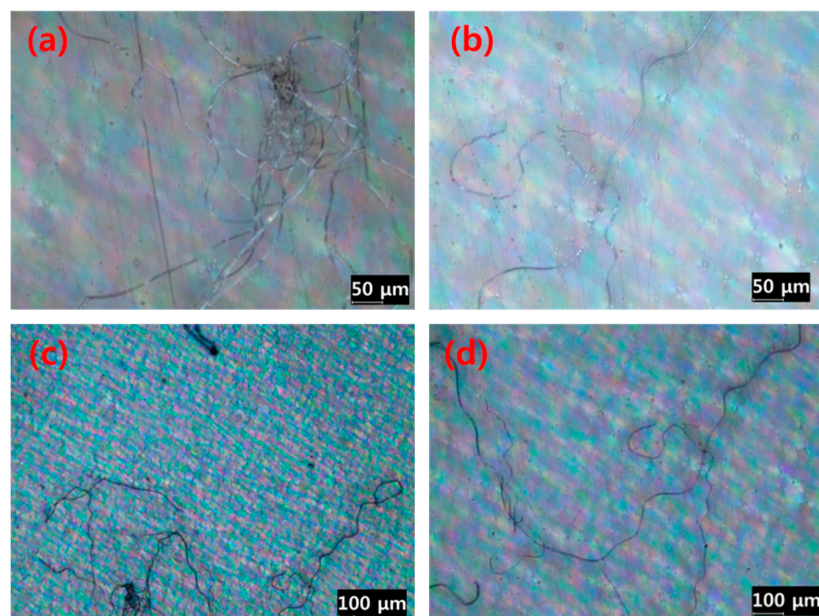


Figure 8. Optical images of PBz/Epoxy/PCLA50 film at different magnifications.

4.6. Hydrophobicity of PBz/Epoxy/PCLA Films

The water interface angle (WIA) of PBz/Epoxy and PBz/Epoxy/PCLA composites was investigated to unravel their water-repellent characteristics. Utilizing a Kyowa goniometer, the WIA was meticulously analyzed using water as the probing liquid, offering a comprehensive understanding of the hydrophobic behavior exhibited by these films, whose images are displayed in Figure 9. The findings of the study unveiled an intriguing trend: both PBz/Epoxy and PBz/Epoxy/PCLA composites demonstrated pronounced hydrophobicity, showcasing contact angle values of 89° for PBz/Epoxy, 101° for PBz/Epoxy/PCLA10, 114° for PBz/Epoxy/PCLA30, and 106° for PBz/Epoxy/PCLA50. Particularly noteworthy was the PBz/Epoxy/PCLA30 composite film, which exhibited the highest contact angle of 114° (Figure 9c), effectively transcending the threshold into the realm of superhydrophobicity. This exceptional water-repellent characteristic can be attributed to the presence of elongated alkyl chains intricately embedded within the molecular structure of the polymer [40,41]. These extended chains act as formidable barriers, impeding the interaction with water molecules and endowing the surface with remarkable water-repellent properties. Significantly, PBz/Epoxy/PCLA, despite sharing a comparable alkyl chain length with PBz/Epoxy and incorporating an unsaturated unit, also demonstrated a striking contact angle of 114° . This observation suggests that the influence of alkyl chain length on hydrophobicity outweighs the impact of unsaturation within the polymer matrix. However, in comparison to other polybenzoxazines, PBz/Epoxy/PCLA50 lacks the presence of extended aliphatic chains crucial for maximizing hydrophobicity. This implies the pivotal role played by extended alkyl chains in augmenting the water-repellent attributes of PBz/Epoxy and PBz/Epoxy/PCLA composite films. While unsaturation may exert some influence, its significance appears relatively minor when juxtaposed against chain length [42–44]. Further endeavors aimed at fine-tuning the chain length within these composite materials hold the promise of yielding even more superior water-repellent materials.

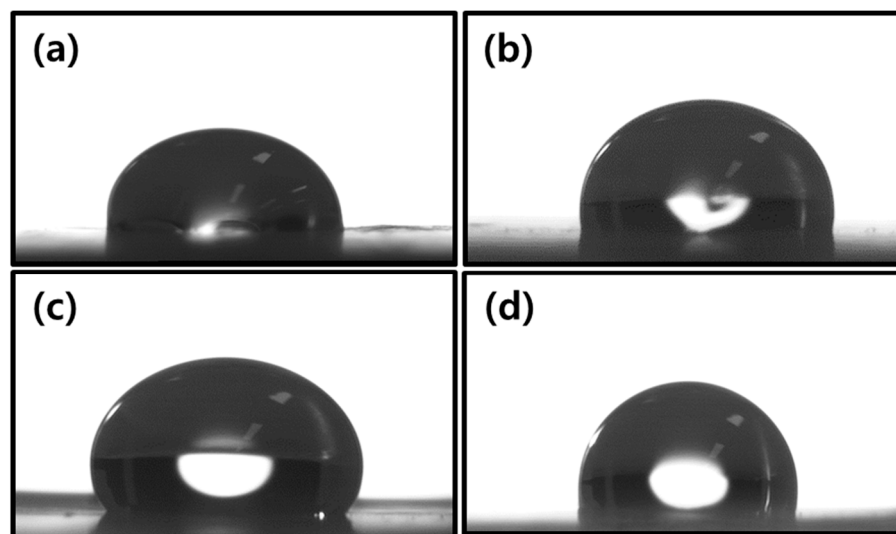


Figure 9. Water contact angle images of (a) PBz/Epoxy, (b) PBz/Epoxy/PCLA10, (c) PBz/Epoxy/PCLA30 and (d) PBz/Epoxy/PCLA50 films.

4.7. Thermal Stability of PBz/Epoxy/PCLA Composite Films

The impact of incorporating caprolactam into polybenzoxazine/epoxy resin composite was explored by analyzing their thermal stability and decomposition behavior. Thermogravimetric analysis (TGA) was employed to evaluate these effects, and the thermograms are displayed in Figure 10, with detailed data summarized in Table 1. The key finding is a remarkable improvement in thermal stability observed with increasing CPLA content within the PBz/Epoxy/PCLA composites. This translates to a significant positive shift in their degradation temperatures compared to pristine PBz/Epoxy film. The initial degradation temperature (T_i) exhibits a noteworthy rise for all the PBz/Epoxy/PCLA films when measured against PBz/Epoxy alone. Specifically, T_i increases from 258 °C (PBz/Epoxy) to 273 °C (PBz/Epoxy/PCLA10); for PBz/Epoxy/PCLA30 and PBz/Epoxy/PCLA50, this rises further to 296 and 284 °C, respectively. This trend is mirrored for the degradation temperatures at 5 and 10% weight loss (T_5 and T_{10}), which also demonstrates a rise towards higher temperatures. The incorporation of CPLA plays a crucial role in enhancing the thermal properties of PBz/Epoxy film. This phenomenon can be attributed to the well-established propensity of CPLA, epoxy, and PBz to engage in π - π stacking interactions. These interactions foster robust interfacial interactions between CPLA and PBz at the supramolecular level. Furthermore, PBz/Epoxy/PCLA composites possess a network structure with a high degree of cross-linking, which effectively restricts the mobility of chain segments within the material. Additionally, a network of hydrogen bonds is established within the composites, contributing to their superior stability compared to pristine PBz [45–47]. The combined effects of these factors lead to a commendable increase in char yield at 800 °C. The char yield progressively increases from 36.2% for PBz/Epoxy to 38.4, 46.7, and 42.3% for the PBz/Epoxy/PCLA composites containing 10, 30, and 50 wt.% CPLA, respectively.

Table 1. TGA data obtained from TGA thermograms.

S.No.	Samples	T_i (°C)	T_5 (°C)	T_{10} (°C)	CY (%)	LOI
1.	PBz/epoxy	258	336	394	36.2	31.9
2.	PBz/epoxy/CPLA10	273	358	407	38.4	32.8
3.	PBz/epoxy/CPLA30	296	383	438	46.7	36.2
4.	PBz/epoxy/CPLA50	284	362	419	42.3	34.4

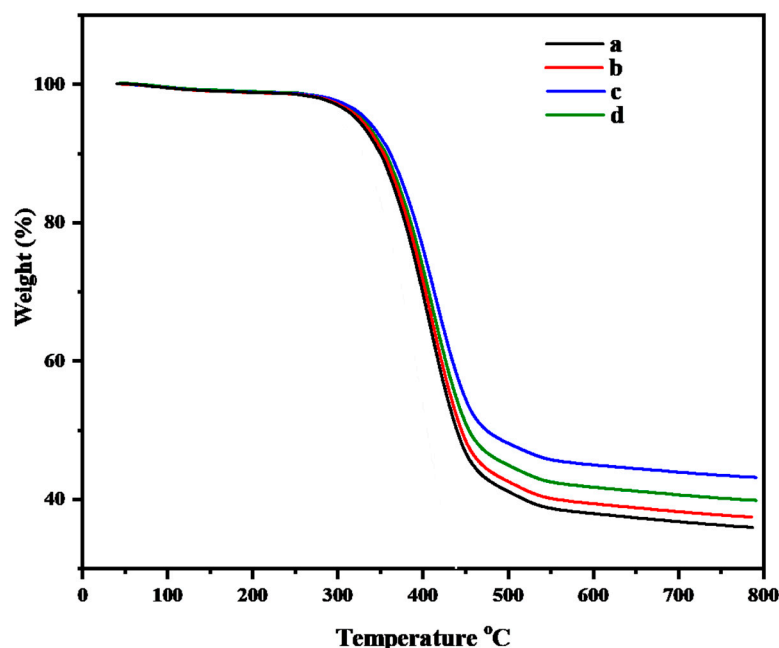


Figure 10. TGA thermograms of (a) PBz/Epoxy, (b) PBz/Epoxy/PCLA10, (c) PBz/Epoxy/PCLA30 and (d) PBz/Epoxy/PCLA50 films.

4.8. Flame Retardancy of PBz/Epoxy/PCLA Composite Films

The assessment of flame-retardant properties in PBz/Epoxy and PBz/Epoxy/PCLA films is crucial for determining their suitability in various applications. One method to evaluate these properties is through the measurement of the limiting oxygen index (LOI), a parameter often derived from char yield data obtained via thermogravimetric analysis (TGA) at 800 °C. LOI values were calculated utilizing the van Krevelen and Hoftyzer equation [48]. Equation (1) provides insight into a material's ability to resist combustion. The equation is given below.

$$\text{LOI} = 17.5 + 0.4 \text{ CR} \quad (1)$$

where LOI is the limiting oxygen index and CR is the char yield obtained at 800 °C from TGA analysis. In evaluating the flame retardancy of these composites, it is imperative to consider the char residue (CR) obtained from TGA analysis as it directly influences the LOI value. Typically, polymeric materials with LOI values exceeding 26 are deemed excellent flame retardants. The incorporation of PBz into the matrices significantly enhances char residue formation, consequently elevating LOI values. For PBz/Epoxy and PBz/Epoxy/PCLA films, the observed higher LOI values can be attributed to the substantial residual char content present in these blends. Remarkably, the PBz/Epoxy film exhibits a notable LOI value of 31.9, signifying superior flame-retardant behavior compared to pure polybenzoxazine matrices. By adjusting the proportion of benzoxazine within the Benzoxazine/Epoxy/CPLA blend, the char yield and subsequently the LOI value can be manipulated based on the weight percentage concentration of PBz, epoxy, and CPLA. Notably, the PBz/Epoxy/PCLA30 composite film demonstrates superior flame-retardant properties compared to other films, likely owing to its cross-linked network structure enriched with heteroatoms. The observed LOI values exceeding the threshold of 26 affirm the self-extinguishing and flame-retardant characteristics of these materials. It is concluded that the flame-retardant properties of PBz/Epoxy and PBz/Epoxy/PCLA composites are closely linked to the char residue formation, with higher LOI values indicative of enhanced flame retardancy. These findings underscore the potential of these composites for applications requiring stringent fire safety standards. Further research into optimizing the blend composition could lead to the development of even more effective flame-retardant materials.

5. Summary and Conclusions

The effect of the addition of caprolactam on improving the properties of PBz/Epoxy has been studied and investigated in detail. PBz/Epoxy/PCLA films were produced directly from a bar coating, followed by subsequent drying and curing at higher temperatures. The properties of the composite film, PBz/Epoxy/PCLA, were compared with the hybrid film, prepared from polybenzoxazine and epoxy resin. As evidenced by DSC analysis, the compatibility between the three components, i.e., benzoxazine, epoxy, and caprolactam, which is an important criterion for film formation, has been proved. A single exotherm observed for the Bzo/Epoxy and Bzo/Epoxy/caprolactam blends confirmed the miscibility between them. Additionally, the processing window of the Bzo/Epoxy blend has been widened by the incorporation of caprolactam and increasing the content of caprolactam. Optical images of PBz/Epoxy/PCLA50 film display thread-like structures distributed throughout the PBz/Epoxy matrix. In some regions, these threads are agglomerated and from few point junctions. The crucial effect of different concentrations of caprolactam on the PBz/Epoxy film was revealed by SEM analysis, which found that the smooth morphology of PBz/Epoxy film was completely altered by the incorporation of caprolactam, especially leading to an agglomerated surface at a higher content of caprolactam. These morphological changes are reflected in the thermal properties of PBz/Epoxy/PCLA films, where the synergistic effect could be observed in PBz/Epoxy/PCLA30 and diminishes with increased content of caprolactam in PBz/Epoxy/PCLA50. These polymer films prepared from PBz/Epoxy/PCLA with formability and enhanced thermal properties can be used as matrix resins for advanced composite applications requiring excellent thermal and flame-retardant properties.

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