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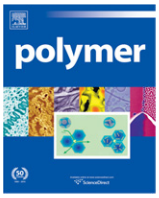

Degradable blends of semi-crystalline and amorphous branched poly(caprolactone): Effect of microstructure on blend properties

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The blend properties of semi-crystalline and amorphous polycaprolactone (PCL) are shown here for the first time. The amorphous polycaprolactone (PCLB) having 20% branches was made by radical-ring-opening polymerization of 2-methylene-1,3-dioxepane. The presence of branches led to non-crystallinity in PCLB. The blends were made in solution in entire concentration range and showed some very interesting properties in terms of synergistic effect on crystallinity leading to the increased crystallinity of PCL and induced crystallinity of amorphous PCLB, minima in the % elongation and maxima in spherulite size depending upon the ratio of amorphous and crystalline part. There was a drastic increase in the compostability as compared to pure PCL on adding even low % of amorphous PCLB in the blends without affecting the thermal stability. The addition of PCLB also affected the transparency and it increased exponentially from about 8% at 650 nm for PCL to about 45% for a blend with composition PCL:PCLB 30:70.

1. Introduction

Poly(ε-caprolactone) (PCL) is a highly investigated biodegradable polymer in terms of its synthesis and properties evaluation. The importance and relevance of (bio)degradable polymers, for example PCL, are due to the potential applications in various medical and non-medical fields like agriculture, medicine, pharmacy, biomedical and also as environmentally friendly materials in packaging industry [1]. Poly(ε-caprolactone) (PCL) is a semi-crystalline polymer with a melting point of 59–64 °C and a glass transition temperature of −60 °C and has a set of mechanical, optical, thermal and degradable properties [2,3] which make it suitable for some of these applications but make it unsuitable for many other applications. In general, tuning of properties is required for any specific application. In case of PCL, it is generally carried out either by copolymerization or by blending. Copolymerization of ε-caprolactone with many other cyclic monomers like β-butyrolactone, valerolactone, glycolide, L-lactide, ethylene carbonate, dioxepan-2-one etc. is known for modification of physical properties and degradability [4–11]. A lot of literature is also available regarding property modification by blending with poly(vinyl chloride) (PVC), polycarbonate, polystyrene, poly(methyl methacrylate) etc. [12–15]. Eastmond [16] provided a review of blends of polycaprolactone PCL. PCL like many other aliphatic polyesters is not flexible and also lacks high use temperature because of low glass transition and melting temperatures. Studies related to blending of PCL with other polymers are mainly directed towards these problems besides understanding the basics of blending with crystalline and amorphous polymers. For example, Yoshiyuki et al. tried to blend PCL with cellulose alkyl esters with an aim to improve the glass transition temperature [17]. Blending of PCL with poly(vinyl alcohol) has been carried out in solution by David et al. [12] Interestingly, this specific blend showed specific physical interactions between the two components as supported by various analytic techniques. Compatible blends of PCL and poly(vinyl chloride) PVC are reported by Stein et al. and showed no crystallinity above 60% of PVC in the blends i.e. blends were compatible and amorphous [14,18].

Transparent amorphous/low crystalline degradable polyesters could be of commercial interest for packaging industry. The literature shows that PCL can have reduced crystallinity by blending with other polymers like PVC but this would sacrifice important property of PCL i.e. degradability. After degradation of the PCL part, the non-degradable part like PVC will remain as such. The same problem remains in blends of PCL with olefinic polymers like polyethylene and polypropylene. Therefore, blends of PCL with other degradable polymers are of commercial interest from degradability point-of-view. Recently, there was an interesting work from Lertworasirikul et al. [19] regarding preparation of flexible and transparent polylactides by crystallization manipulation. They blended semi-crystalline L-polylactide (L-PLA) with

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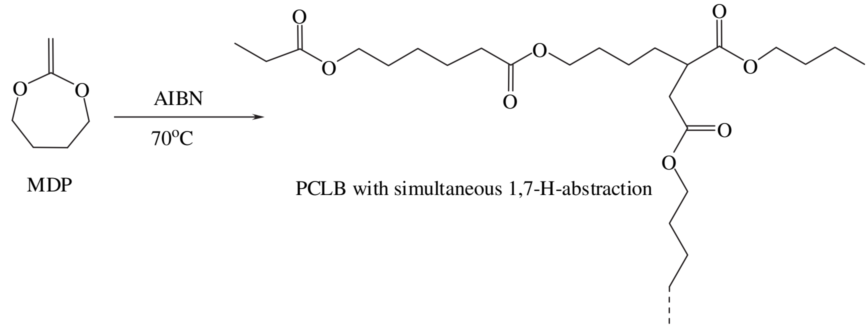


Scheme 1. Reaction scheme for the radical-ring-opening polymerization of 2-methylene-1,3-dioxepane (MDP) giving branched polycaprolactone (PCLB).

amorphous DL-PLA. This was done to manipulate crystallization keeping the degradable chemical repeat units the same.

In general, aliphatic polyesters like PCL and PLA are made by ring-opening polymerization of cyclic esters like caprolactone and lactide using metallic, anionic or cationic catalysts [20–24]. Different synthetic routes to polycaprolactone are summarized in a recent review article by Labet et al. [25]. Other conventional method of making aliphatic polyesters is by condensation polymerization. In our group, we carry out radical-ring-opening polymerization (RROP) of cyclic ketene acetals to make aliphatic polyesters. For example, RROP of 2-methylene-1,3-dioxepane (MDP) using radical initiator like 2,2′-azobisisobutyronitrile (AIBN) gives polycaprolactone with some amount of branches depending upon the reaction temperature. The resulting PCL therefore, is amorphous unlike the conventional semi-crystalline PCL made by ROP of cyclic esters. We have used this chemistry extensively with an aim to provide degradability to vinyl polymers like poly(methyl methacrylate), polystyrene, poly(*N*,*N*′-isopropylacrylamide), poly(vinyl acetate) etc. [26–31]. There is no other method to get high molecular weight amorphous PCL directly after synthesis. Amorphous PCL combined with semi-crystalline PCL could generate some interesting properties in terms of degradability, transparency and other properties.

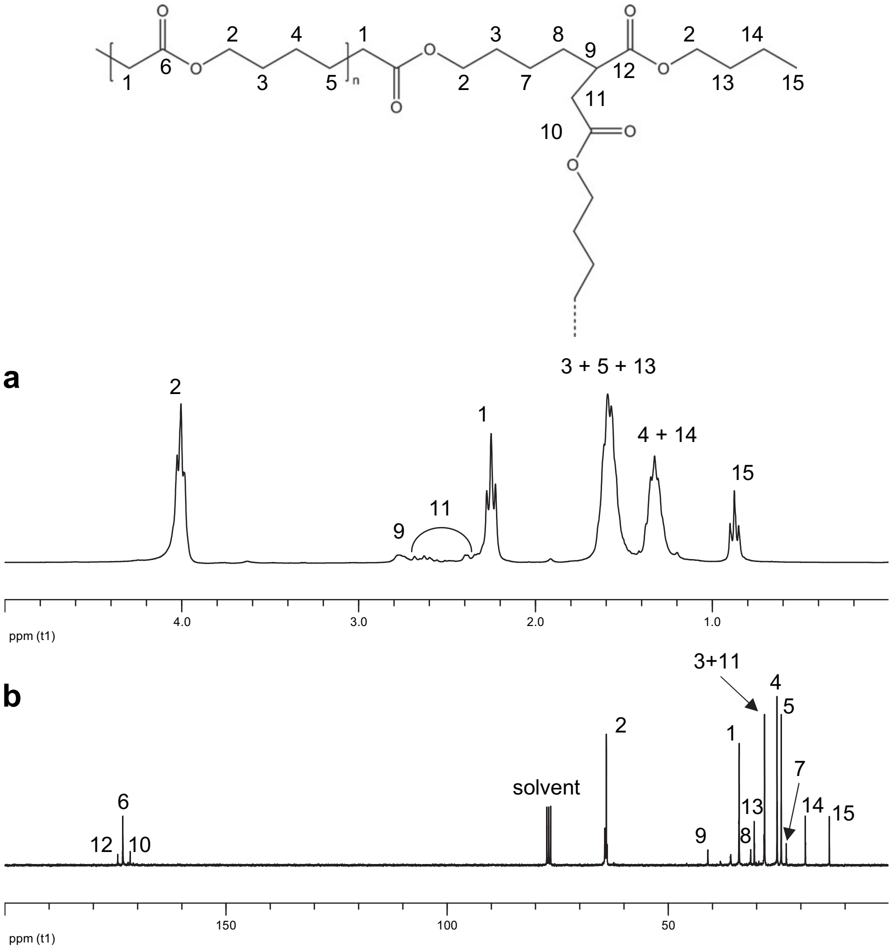


Fig. 1. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of polycaprolactone (PCLB) made by polymerization of 2-methylene-1,3-dioxepane (MDP) polymerized at 70 °C with 2,2′-azobisisobutyronitrile (AIBN).

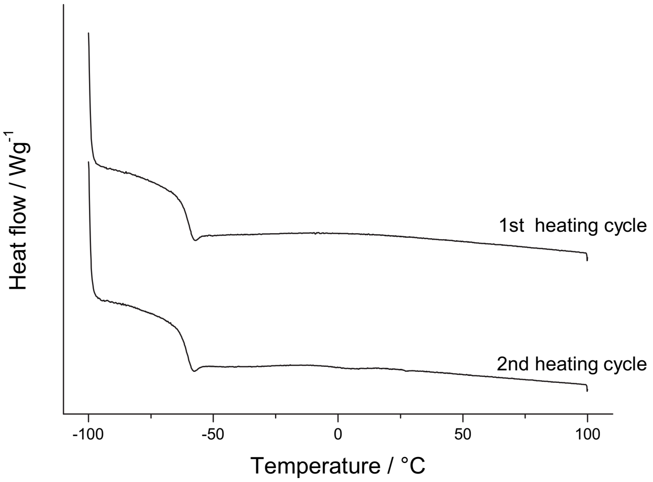


Fig. 2. DSC curves of PCLB showed a glass transition during the first and the second heating cycle at −60 °C, while no melting peak was observed.

Therefore, it would be of interest to study the effect of mixing amorphous PCL with crystalline PCL on the resulting mechanical, thermal and optical properties. It is also interesting to see how branched amorphous PCL with same degradable structural units as that of conventional PCL affects its crystallization behaviour. Is it possible to get degradable transparent PCL with optimum mechanical properties by blending amorphous and semi-crystalline PCL, is another important industrially relevant question? To answer these questions, we made a study of structural changes, crystallization behaviour and thermal properties change in blends of amorphous and semi-crystalline PCL covering the entire concentration range.

2. Experimental

MDP was synthesized in laboratory according to the published procedure. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from methanol prior to use. PCL ($M_n = 42\,500$; Aldrich) was used as received.

^{1}H(400.13 MHz) and ^{13}C(100.21 MHz) NMR spectra were recorded on a Bruker DRX-400 spectrometer using tetramethylenesilane (TMS) as an internal standard. Mettler Thermal Analyser having 821 DSC module was used for thermal analysis of the polymers. DSC scans were recorded in nitrogen atmosphere (flow rate $= 80$ mL min^{-1}) at a heating rate of 10 °C min^{-1}. Thermal stability was determined by recording TG traces in nitrogen atmosphere (flow rate $= 50$ mL min^{-1}). A heating rate of 10 °C min^{-1} and a sample size of 10 ± 1 mg were used in each experiment.

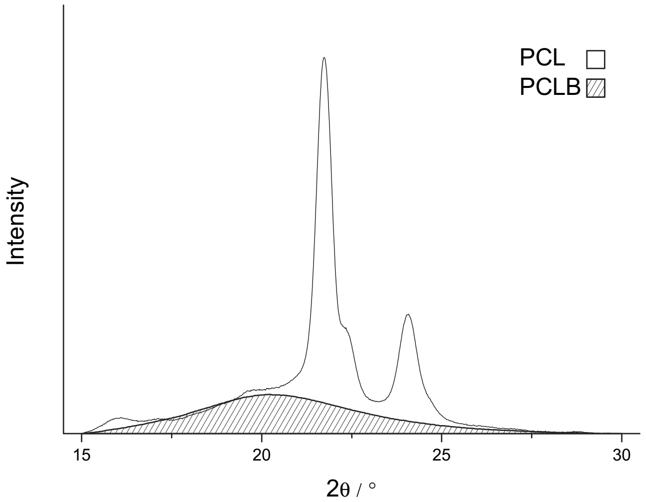
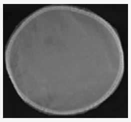
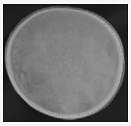
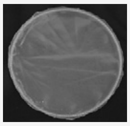
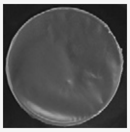
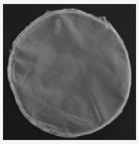
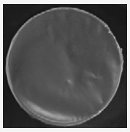
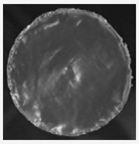
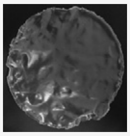


Fig. 3. XRD reflexes of PCL (Aldrich) due to the planes (110) and (200) at $2\theta = 21.4°$ and 23.8° in comparison to the halo of amorphous PCLB (patterned).

Table 1
Solution blending of polycaprolactone (PCL) and branched polycaprolactone (PCLB) in CHCl$_3$:blend compositions and the corresponding films.

Weight % PCLB in feed	Blend film
10.0	
20.0	
30.0	
40.0	
50.0	
60.0	
70.0	
80.0	
90.0	No film obtained

X-ray diffraction pattern of the polymer films (100 μm thick) was recorded with a Siemens goniometer D5000 using CuK_α-radiation

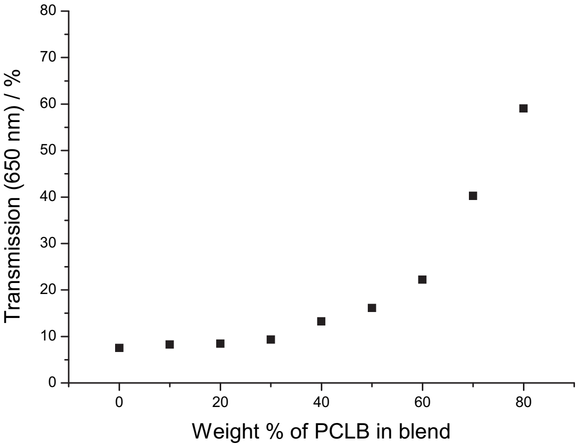


Fig. 4. Transmission of polycaprolactone (PCL):branched polycaprolactone (PCLB) blends (film thickness = 100 μm) at $\lambda = 650$ nm.

of $\lambda = 1.54$ Å. Digital photographs were taken on a Keyence VHX-100 microscope. A Zwick/Roell BT1-Fr0.5TN-D14 machine equipped with a 200 N KAF-TC load sensor was used to determine the mechanical properties of the polymer films. Bone-like specimens were punched out of the polymer with an average length of 3.9 cm and a width of 0.35 cm. The effective diameters were calculated by mass. The assumed value of the density was based on the crystallinity determined via DSC and the density of amorphous and crystalline PCL (1.094 g/mL and 1.187 g/mL, respectively [32]). A preload of 0.1 MPa and a subsequent traction speed of 50 mm/min were applied. 5 samples were measured for each composition.

Compostability of the blend films (diameter = 5.9 cm; thickness = 80 μm) was checked by burying them in compost at 45 °C. A mixture of mature compost derived from a aerobic composting plant was used. The test films are introduced into closed containers, for example, plastic boxes with intermediate aeration. The polymer films were checked physically at different time intervals for the cracks.

Homopolymerizations were carried out under Argon in pre-dried, Schlenk tubes using free radical initiator, AIBN, at 70 °C. In a typical bulk homopolymerization reaction, 15.0 mL (132.6 mmol) of MDP and 2 mol-% of initiator (AIBN) (435 mg (2.65 mmol)) were polymerized in an oil bath at 70 °C for 20 h. Post-polymerization, $CHCl_3$ was used as the dissolving medium, while *n*-hexane was the precipitating medium. For purification, the sample was re-dissolved in $CHCl_3$ and re-precipitated in *n*-hexane. Finally, the sample was dried under vacuum at 40 °C. The conversion was estimated by gravimetry and was found to be about 67%. The resulting material (PCLB) was characterized using NMR spectroscopic technique and the branching density was determined as reported in our previous work [29] and was found to be 20%. The molecular weight (M_n) of the polymer was 39 600 g/mol and the glass transition temperature (T_g) was −60 °C with no melting peak in DSC.

Solution blending of PCL and PCLB was carried out in chloroform. A 3.3 wt% solution of each PCL and PCLB in chloroform was mixed, stirred at room temperature (22 °C) and the blend films were made by solution casting in petri dishes. The petri dishes were covered with a perforated aluminium foil and led to slow solvent evaporation at room temperature for about 24 h. The blend films were further dried at room temperature for 2 days and then dried in vacuum for 24 h. Before starting measurements, the residual solvent was determined using thermogravimetric analyser and in case the films showed traces of solvent, were further dried till constant wt%.

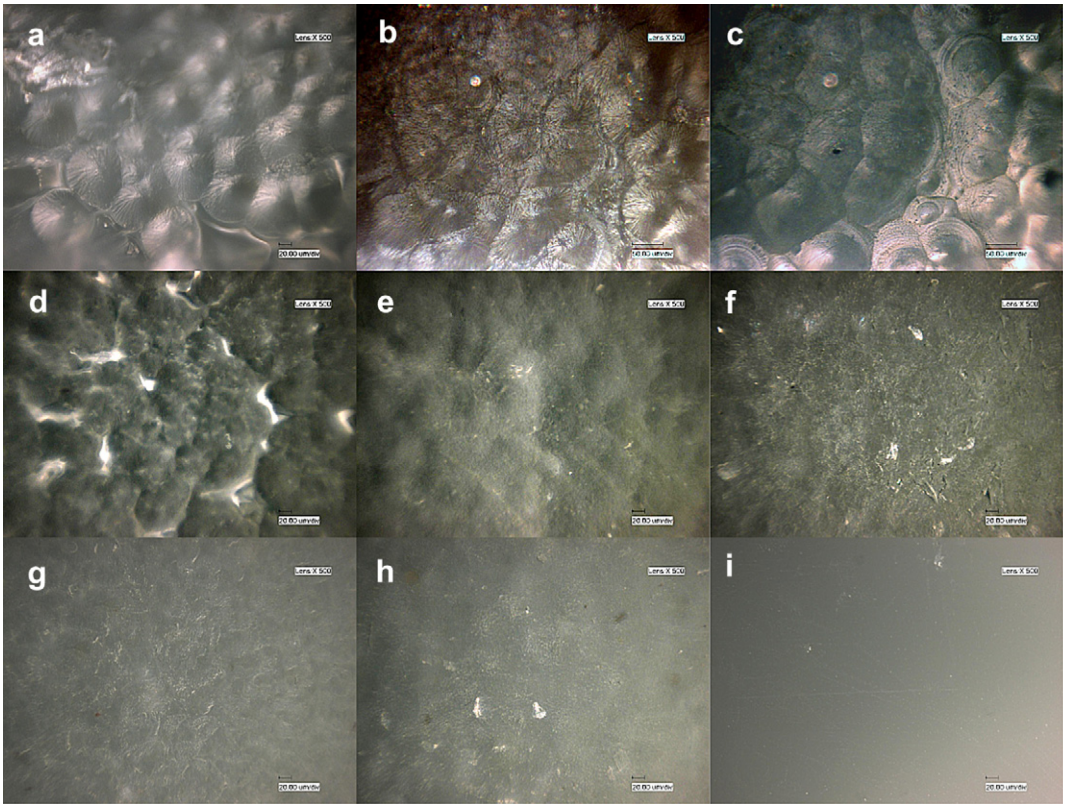


Fig. 5. Digital microscopic pictures of blend (PCL:PCLB) surfaces with wt% of PCL (a) 100% (b) 90% (c) 80% (d) 70% (e) 60% (f) 50% (g) 40% (h) 30% (i) 20%.

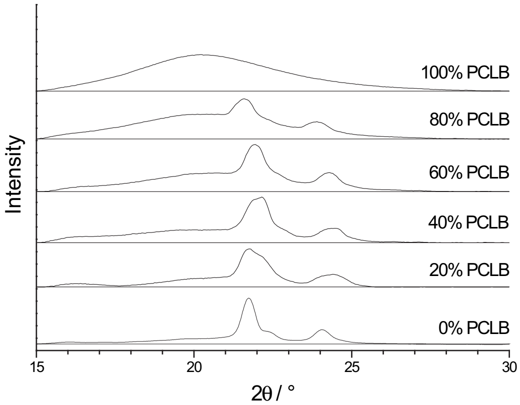


Fig. 6. XRD diffractograms of PCL:PCLB blends with different ratios.

3. Results and discussion

The radical-ring-opening polymerization (RROP) of MDP using AIBN as radical initiator at 70 °C gave PCL repeat unit structures with some branches (Scheme 1). The resulting material will be referred as PCLB throughout the work. The representative ^{1}H and ^{13}C NMR of the resulting polymer is shown in Fig. 1. The details of PCLB characterization (peak assignments) and the method for determination of the degree of branching are described in our previous publication [29]. The branched polycaprolactone PCLB showed about 20% branching in PCL structure. The polymer showed no melting peak and a clear peak for glass transition temperature at about −60 °C (Fig. 2). Also, in comparison to the XRD spectra of semi-crystalline PCL (obtained from Aldrich), our polymer (PCLB) obtained by radical-ring-opening polymerization of MDP showed no sign of crystallinity as shown in Fig. 3.

Blending of semi-crystalline PCL (Aldrich; $M_n = 42\,500$ g/mol) and amorphous PCLB ($M_n = 39\,600$ g/mol) was carried out in solution ($CHCl_3$ as solvent) using different wt% of the two components. The detailed method of blending is described in the experimental part. The films obtained are shown in Table 1.

Optical properties of blend films (about 100 μm thick) were measured using UV/Vis spectrophotometer by measuring transmission at $\lambda = 650$ nm. The results are shown in Fig. 4. PCL is a semi-crystalline polymer, which was turbid in film form and showed very low transmission (less than 10%). The transparency of PCL could be modified by changing the blend composition i.e. the ratio of PCL and PCLB. There was an exponential increase in the transparency with increased amount of amorphous component (PCLB) in the blends and reached about 45% for a blend having 70 wt% PCLB from about 8% for only PCL.

The film surfaces were observed by digital microscope and the respective digital microscope pictures of blend films with increasing amount of amorphous PCLB component are shown in Fig. 5. The PCL film surface showed very clear spherulites. With increase in the amount of PCLB, the films became smooth i.e. above 60% of PCLB in the blends it was very difficult to assign clear crystalline regions, which gives a hint for the homogeneous distribution of the PCL inside of the amorphous matrix with increasing amount of PCLB. This hint gets further support from the observation of the missing necking behaviour for samples with high amount of PCLB which had not been observed if there was a phase separation. It is also interesting that on the outside the crystalline domains decrease with decreasing amount of PCL while in bulk the spherulites' size behaves completely different and these phenomena are discussed in the later part of this work.

Further XRD technique was used to get insight into the blend structure. The XRD study of the PCL/PCLB blend films (Fig. 6) revealed no additional diffraction profile distinct from those coming from the semi-crystalline PCL. The strong diffraction rings derived from the (110) and (200) planes of the orthorhombic PCL lattice could be readily observed at $2\theta = 21.4°$ and 23.8° respectively, in the WAXD patterns of all the blends. With increasing amount of PCLB in the blends the two crystalline peaks of PCL became a little broad with overlapping amorphous region of PCLB. It is not possible to determine quantitatively the degree of crystallinity due to overlapping peaks from XRD diffractograms.

In an attempt to get quantitative data regarding the degree of crystallinity of the blends, differential scanning calorimetric measurements were carried out. All blends showed a single glass transition temperature around −60 °C and a melting peak at 60 ± 2 °C with no significant change in the melting temperature with blend composition (Fig. 7). However, a decrease in the area under the melting peak was obtained.

As expected, a decrease in melting enthalpy/g of the blend (Fig. 8) was obtained with decreasing amount of semi-crystalline PCL in the blends. % crystallinity was calculated based on the known melting enthalpy of 100% crystalline PCL (melting enthalpy of 136 J/g for 100% crystalline PCL is taken from the literature) [32]. The % crystallinity based on melting enthalpy/g of blend decreased continuously (Fig. 8) with increasing amount of amorphous PCLB in the blends but still the blends with very high amount of PCLB i.e. having 90 wt% of PCL were crystalline. These results are in accordance with XRD results.

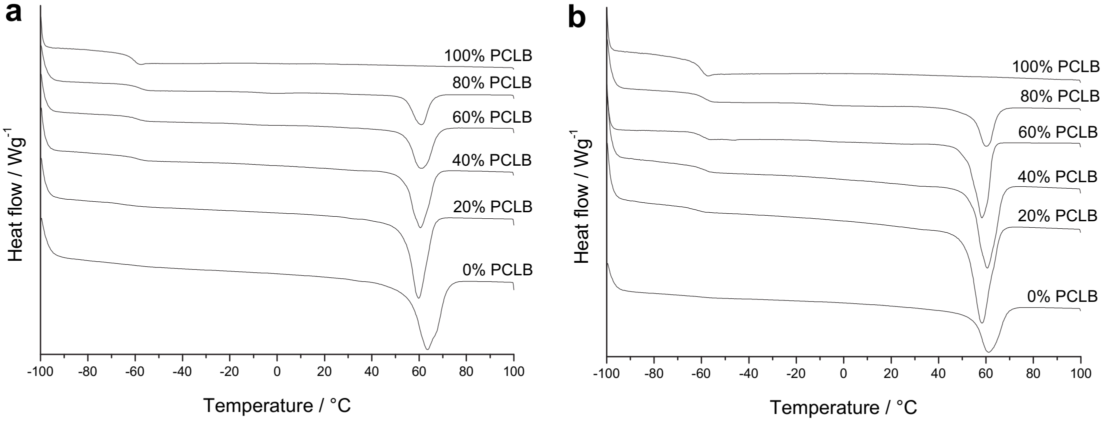


Fig. 7. DSC curves of samples with different PCLB content; (a) first heating cycle, (b) second heating cycle.

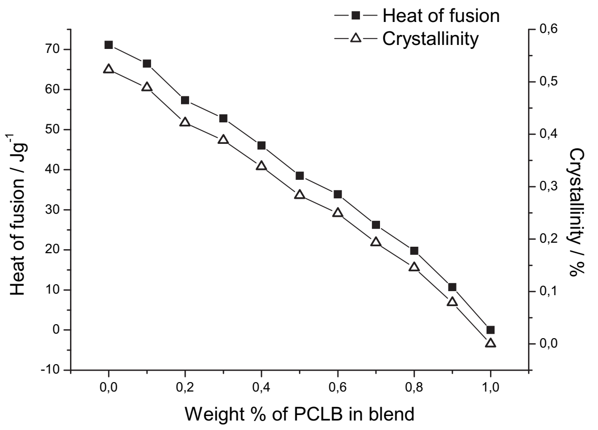


Fig. 8. Linear decrease of melting enthalpy per gram of blend (square), total % crystallinity (% crystallinity/g blend) with increasing amount of amorphous component PCLB in the blends (triangle).

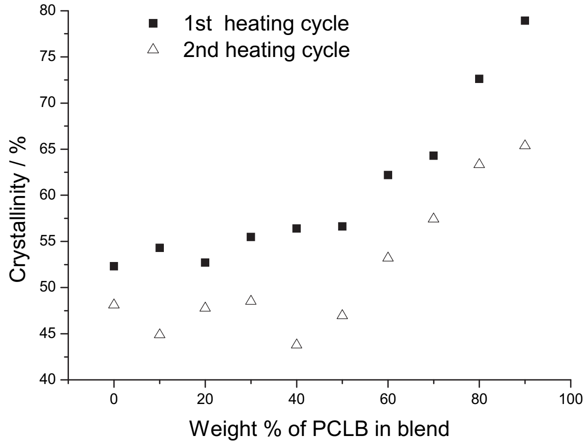


Fig. 9. Increased % crystallinity/g PCL at high amounts of PCLB gives hint of interactions between PCL and PCLB during first heating cycle (squares) as well as second heating cycle (triangles).

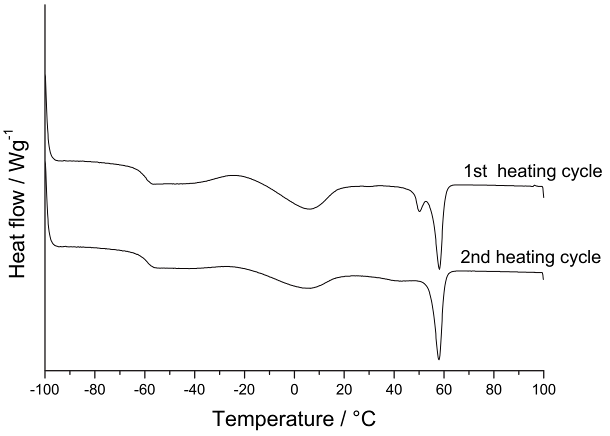


Fig. 10. DSC curve shows appearance of a new endothermic transition at 4 °C during first heating cycle and second heating cycle.

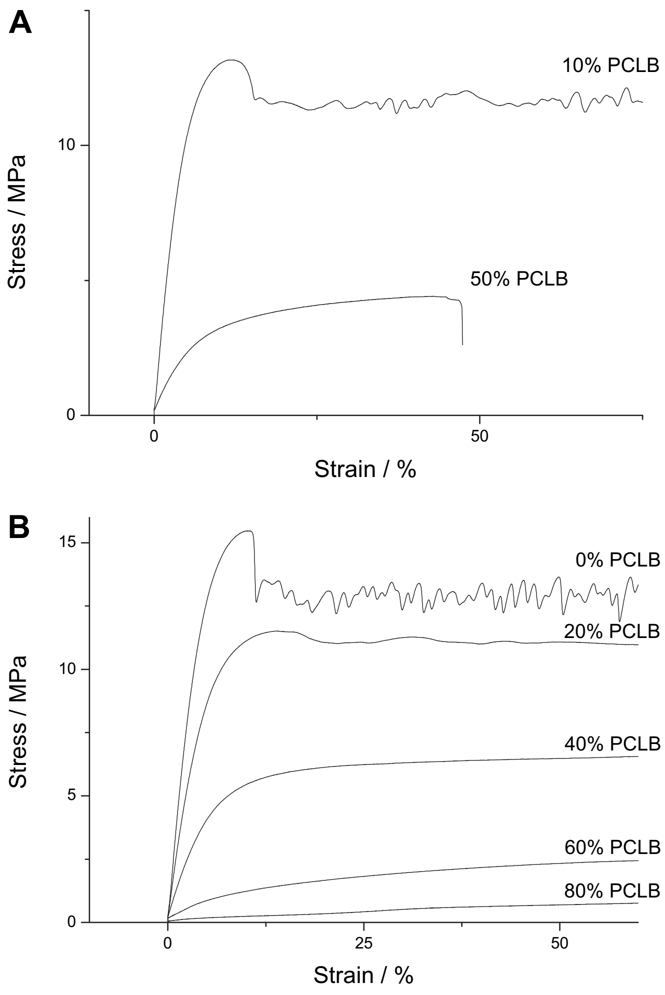


Fig. 11. Stress–strain curves of blends of different compositions.

An interesting observation is made while calculating the % crystallinity based on melting enthalpy/g PCL component (as PCL is the crystalline part in the blends). The % crystallinity based on melting enthalpy/g of PCL did not change significantly till about 50 wt% of the amorphous component PCLB keeping in view the instrumental/measurement error involved, but afterwards showed a sudden increase in the % crystallinity/g PCL and after that there was a continuous increase with increasing amount of amorphous PCLB in the blends (Fig. 9). This is an interesting and peculiar phenomenon observed for this blend pair of semi-crystalline and amorphous polycaprolactone. Laredo et al. [33] observed increased crystallinity of PCL from 42 to 56% in the blends of polycaprolactone and amorphous poly(DL-lactide) for one particular composition i.e. when PCL content is 80%. On the other hand the crystallinity of amorphous PDLLA is also shown to increase from 2 to 7% for blends with 60 and 80% of PDLLA content. Although no experimental proof was provided, the reason given was the nucleating effect of PDLLA on PCL and plasticizing effect of PCL on PDLLA for crystallization. In our system, continuous increased crystallinity gives a hint of interactions between amorphous PCLB and semi-crystalline PCL with increased amounts of PCLB in the blends influencing crystallization in a significant way. The increased % crystallinity/g PCL could be due to either increased crystallization of the PCL component or induced crystallization in the amorphous PCLB component or a combination of the two.

The blend films with about 90 wt% of amorphous PCLB component showed some peculiar behaviour in DSC curves (Fig. 10), which was different from other blend compositions. A new broad endothermic transition was seen at temperature around 3–5 °C in both first and second heating cycles. Also two melting

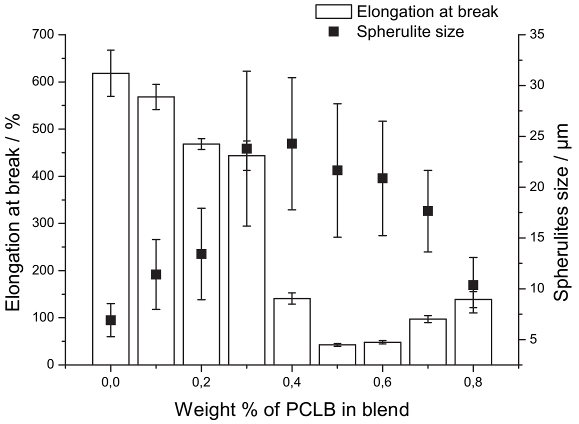


Fig. 12. Minima in elongation at break with blend composition (white bars) in comparison to the size of spherulites (black squares).

peaks were seen in the first heating cycle at peak temperatures 51 and 59 °C. The % crystallinity calculated using area under the peaks for both melting regions gave a value which was more than 100% crystallinity. This confirmed some induced crystallization of amorphous PCLB in blends. Because of similar chemical structure, the PCLB–PCL interactions are not expected to be much different from PCL–PCL interactions. With increased amount of PCLB, the semi-crystalline PCL would be in the matrix of PCLB and the interactions between PCLB and PCL could have a synergistic crystallization effect, leading to increased crystallization of PCL part and also inducing crystallization in PCLB part.

To confirm this fact experimentally, effect of molecular weight of PCLB on degree of crystallization was carried out keeping the degree of branching almost the same. The idea was that the low molecular weight PCLB should be able to diffuse more between the semi-crystalline PCL chains and was therefore expected to have better interactions thereby increasing crystallinity. In fact, it was confirmed experimentally and the low molecular weight PCLB ($M_n = 23\,300$ g/mol) with 17% branching showed tremendous increase in % crystallinity from 47 to 88% on changing the amount of PCLB from 30 to 90% as compared to the high molecular weight ($M_n = 39\,600$) PCLB with 20% degree of branching from 49 to 65%.

A decrease in tensile strength and modulus was obtained with an increase in amorphous PCLB component in the blends (Fig. 11). An interesting observation during mechanical testing was the significant decrease in the elongation at break with 40% and 50% of PCLB in the blends as compared to 100% PCL and later slight increase with further increase in the amount of PCLB in the blends i.e. observation of a minima in elongation at break with blend composition (Fig. 12).

This could be due to the fact that the blends with low % (10%) of PCLB having high total crystallinity, showed necking behaviour with stretching of crystalline region before break. In contrary the blends with increased % of amorphous PCLB (50%) showed no such behaviour Fig. 11. Further increase in the amount of PCLB from 50% towards 90% led to PCLB–PCL interactions as discussed above and led to an increase in the crystallinity therefore could lead to increase in % elongation again but showed no necking behaviour (Fig. 11b).

It is not only the % crystallinity but also the spherulite size and morphology that could affect this behaviour. The facts are further supported from careful observation of spherulite morphology. The blends under polarized microscope also showed a difference in the corresponding spherulite morphologies and size with different blend compositions. The PCL films showed very small spherulites which are more compact and volume filling. With increased amount of PCLB starting from 20% till about 60% there is a significant increase in the spherulite size as compared to pure PCL (almost five times increase). Further increase in the amount of PCLB to 80% led to decrease in the size of the spherulites (Fig. 13). Although, in general, lower spherulite size gave more elongation at break, it cannot be completely correlated just based on the size of spherulites. In fact, it is supposed to be a combination of spherulite size and % crystallinity that has affected the % elongation of the blends.

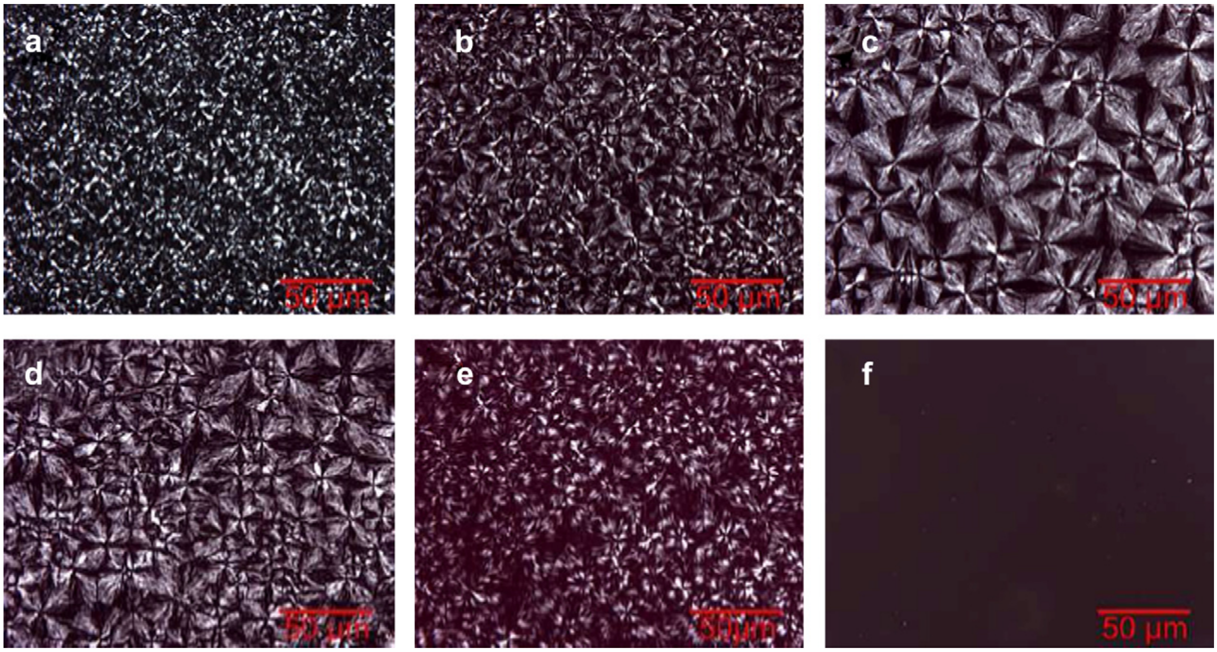


Fig. 13. The size of the spherulites changed significantly while increasing the PCLB amount in the blends and passed through a maximum at about 40% of PCLB; (a) 0% (b) 20% (c) 40% (d) 60% (e) 80% (f) 100%.

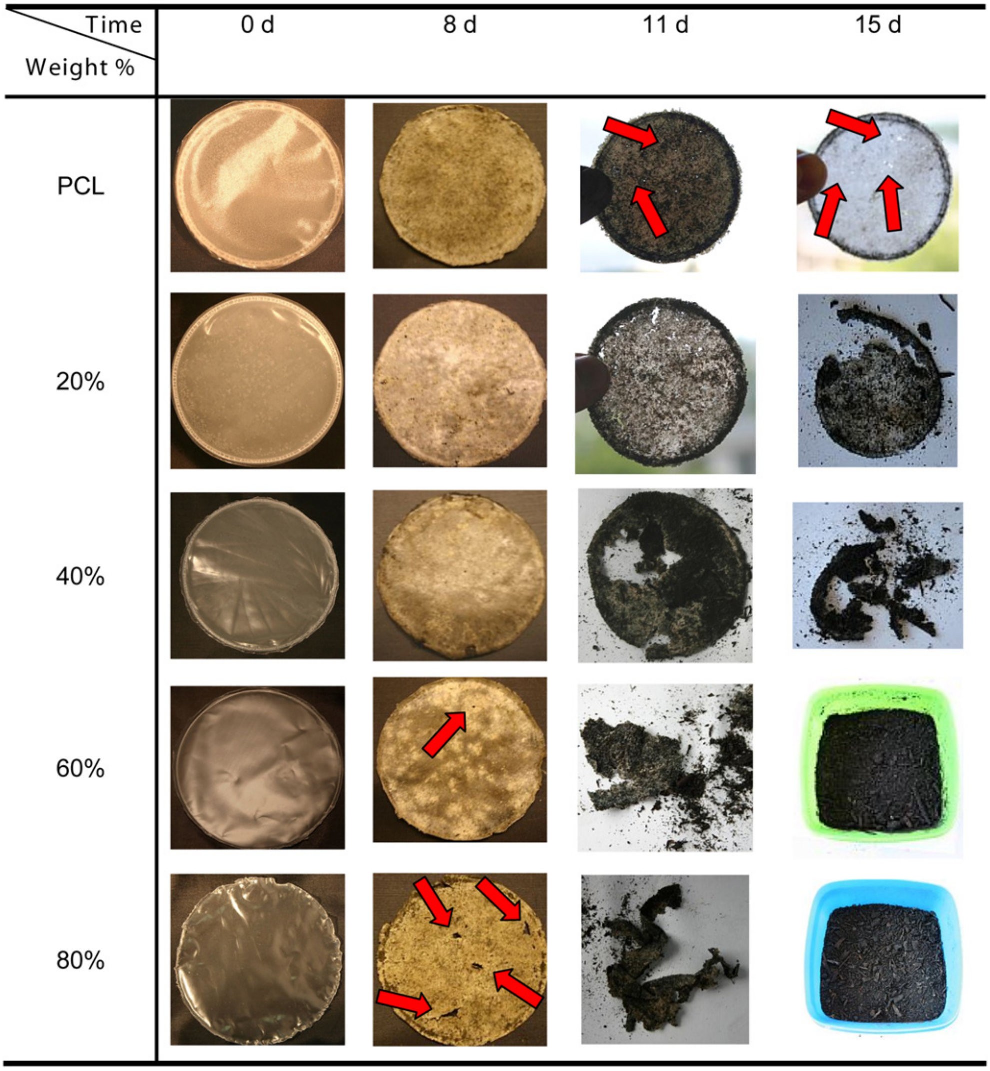


Fig. 14. An increased degradation rate at higher PCLB content was observed due to the reduced overall crystallinity.

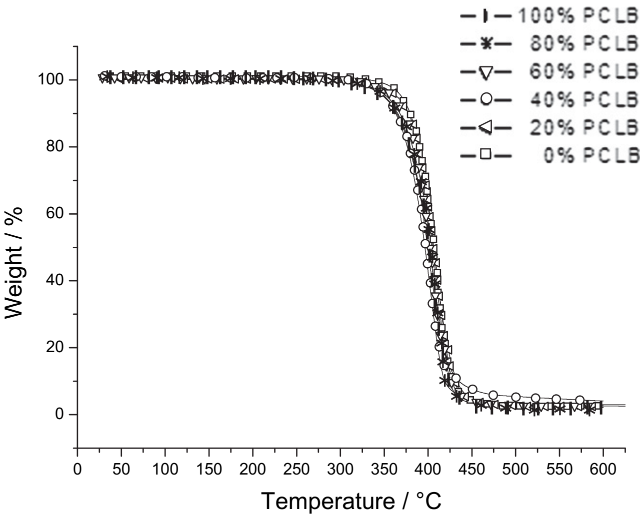


Fig. 15. Thermogravimetric analysis showed no effect of blend composition on thermal stability.

Compostability of the blend films (diameter = 5.9 cm; thickness = 80 μm) was checked by burying them in compost at 45 °C. The polymer films were checked physically at different time intervals for the cracks. It was very clear that there was an increase in the rate of degradation with increased amount of PCLB in the blends which could be due to the reduced overall crystallinity. PCL film which was taken as a blank showed some holes in the film as marked by arrows in Fig. 14 after 11 days and 15 days of burial. On contrary the blend films showed clear holes after 11 and 15 days and the blends with 60 and 80% of PCLB were completely degraded in 15 days (Fig. 14).

It was also of interest to check the thermal stability of blends. It was checked by thermogravimetric analysis and showed no effect of blend composition on thermal stability (Fig. 15).

4. Conclusions

Semi-crystalline PCL and amorphous PCLB made by RROP of MDP have similar chemical repeat unit structures and the solution blending of the two led to some interesting property change in PCL keeping its glass transition temperature and melting temperature almost the same. The amorphous polycaprolactone (PCLB) having

20% branches was made by radical-ring-opening polymerization of 2-methylene-1,3-dioxepane. The presence of branches led to non-crystallinity in PCLB. The blending enhanced the transparency and degradability in compost and further they can be tuned by changing the ratio of PCL and PCLB in the blends without affecting the thermal stability.

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