



# An eco-friendly approach for toughening of polylactic acid from itaconic acid based elastomer

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## Abstract

Sustainable and biocompatible novel lactic acid based bioelastomer (LBPE) was synthesized by polycondensation process which has been confirmed by FTIR and <sup>1</sup>H NMR. Owing to the resemblances in the lactate structures of polylactic acid (PLA) and LBPE, the synthesized LBPE bioelastomers can act as an excellent PLA toughener in presence of free radical initiator dicumyl peroxide (DCP). The mechanical, morphological and thermal were investigated. Chemical crosslinks endow the LBPE with relatively high elasticity and environmental stability which ultimately enhances the mechanical properties of PLA matrix.

**Keywords** Polylactic acid · Lactic acid · Bioelastomer · Toughness · Crosslinked

## Introduction

It is inevitable to draw a great deal of attention towards renewable, eco-friendly plastics, which can contend with conventional plastics, as current lifestyle has encouraged more consumption of plastic every year. Consequently, leading to the production of large extent of waste. Polylactic acid (PLA) has attained lot of alertness in both scientific and commercial sector [1]. Owing to its low toughness and poor elongation at break, PLA has been deprived for wide range of applications. Therefore, many modification routes have been intended to improve PLA toughness. Blending is considered as the most common and cost-effective method among various modifications such as plasticization and copolymerization [2]. However, toughening PLA through blending with resources which are fully biobased is a challenging task. Various researches have been done to toughen PLA, by using biobased and biodegradable polymers. However, in order to improve the impact strength and elongation at break of PLA, the most efficient method is blending with elastomeric polymers, particularly when PLA and

elastomeric polymers exhibits good interfacial adhesion among themselves [3–5].

In our previous study, biobased elastomer synthesized from itaconic acid (IA), sebacic acid (SA), butanediol (BDO), and 1,3 propane diol (PDO) (BBPE) and its blend with PLA has contributed in improving the toughness characteristics of the matrix. Also, PLA/BBPE blends displayed higher thermal stability and lesser water absorption tendency. [6] In the current chapter, attempt has been made to utilize monomer lactic acid (LA) as one of the reagent in addition to IA, SA and BDO to synthesize biobased elastomer as a toughening agent for PLA. Lactic acid based linear and crosslinked bioelastomers attributes to good elasticity, low glass transition temperature ( $T_g$ ) and high mechanical properties. Lactic acid is mainly included to limit the crystallisation of synthesized elastomer. To prepare an amorphous LA based elastomers, the following three procedures were followed to inhibit the crystallization: (a) the four biobased monomers LA, BDO, SA, and IA, were used altogether to decline the geometric regularity of the macromolecular chains; (b) introduction of LA units to the aforementioned monomer can hinders the mobility of the polymer chains; (c) the chemical crosslinking can further restrain chain mobility and regularity. So IA obtained from renewable resources and consisting pendent double bonds was employed for the synthesis of biobased elastomer. BDO, LA, and IA are industrially manufactured by fermentation whereas, sebacic acid can be obtained from castor oil. However, there is not much research on the preparation of lactic acid based biobased elastomers and its blend with PLA. In this study, the effects of varied composition of synthesized lactic acid based

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bioelastomer (LBPE) in enhancing the mechanical, thermal and morphological properties of PLA, were investigated. LBPE was synthesized from the renewable resources based monomers. Itaconic acid is used as a versatile building block for the synthesis of renewable resource based elastomers [7]. Active sites for free radicals to crosslink were obtained from the pendent unsaturated groups of monomer itaconic acid moiety and furthermore, PLA/LBPE blends (PLE) changes from a rigid plastic to flexible and elastomeric material. Consequently, the blends were investigated for mechanical, thermal and morphological properties. Also the biodegradability behavior of the blends has been studied.

## Experimental

### Materials

PLA (4042 D with  $M_w = 1,65,000$  g/mol) was purchased from M/s Nature Works LLC, USA. Itaconic acid (IA) (purity 99%), DCP, Sebacic acid (SA), Tetraisopropyl orthotitanate (TTIP) and p-methoxy phenol (PMP) were procured from M/s Tokyo Chemical Industry, Tokyo. 1,4-Butanediol (BDO)(99% purity) and L-lactic acid (LA) (98% purity) were supplied from M/s Sigma Aldrich, Hyderabad, India.

### Synthesis of the LBPE

The LBPE was obtained through three phase polymerisation method [8, 9]. The 40 mol% of lactic acid was used in this reaction. The reaction mixture with molar ratios of carboxyls/diols as 1: 1.1 and molar ratio of carboxyl/IA as 1:9 were poured into the 250 ml three necked flask equipped with water and oil separator, a condenser tube, mechanical stirrer and were heated at 130 °C for 1 h under  $N_2$  atmosphere. As an inhibitor, PMP (0.05 wt% relative to all reactants) was used in the reaction. The reaction experiences esterification at 180 °C for another 2 h. Subsequently, TTIP as a catalyst (0.1 wt% relative to all reactants) was added during the condensation process performed for about 6-8 h, by steadily rising the temperature to 220 °C under vacuum, until the Weissenberg effect was observed. The synthesized LBPE was further used without any purification. The synthetic reactions of LBPE bioelastomer was indicated in Scheme 1.

### Preparation of PLE blends

PLA and LBPE were dried in an oven at 60 °C for 24 h before blending. The PLA/LBPE blends were melt blended in a batch mixer (M/s Haake Rheomix 600, Germany) at a temperature of 175 °C and the speed of 80 rpm for a mixing time of 10 min. The PLE blends with varied compositions 100/0, 90/10, 85/15, 80/20 and 75/25 were prepared. Initially, PLA and LBPE were

premixed in the batch mixer for about 5 min, followed by the addition of DCP (0.2phr). Till the torque becomes stagnant (about 5 min), the dynamic crosslinking was continued.

The prepared samples were cooled to room temperature, granulated and kept at 60 °C for 2 h. Consequently, specimens were fabricated for various analysis by micro injection jet (M/s DSM 15 mL xplore, Netherlands). The molding was done at a process temperature of 175 °C and with a screw speed of 50 rpm. The mould was retained at 35 °C temperature and the molding was employed at an injection pressure of 145 psi. The formulations of PLA/LBPE blends for the varied ratios 90/10, 85/15, 80/20 and 75/25 are denoted as PLE-10, PLE-15, PLE-20, and PLE-25 respectively.

### Characterization

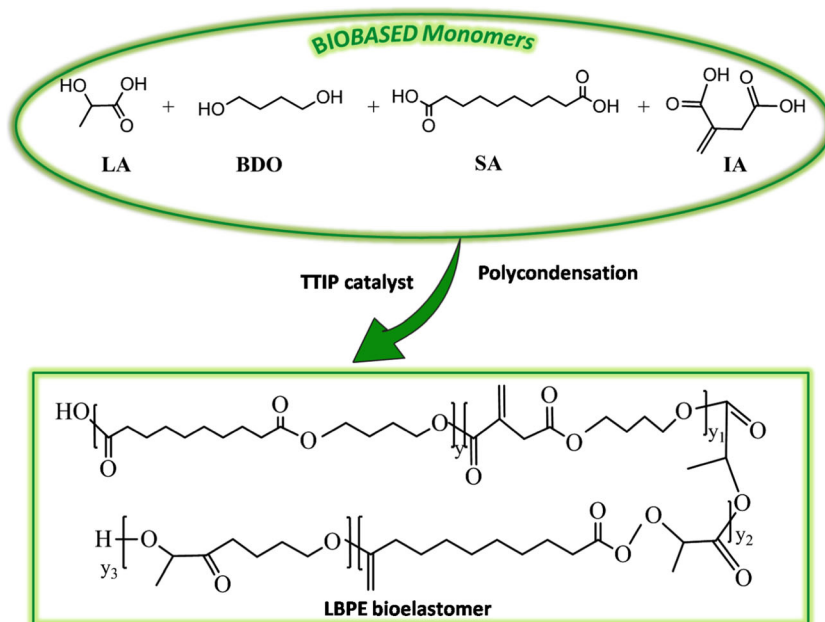
Fourier transform infrared spectroscopy (FTIR) analysis of the synthesized LBPE sample was recorded using M/s ThermoNicolet 6700 FTIR spectrometer, Thermofisher, USA. The FTIR spectra were done in the region 500 to 4000  $cm^{-1}$  with the resolution of 4  $cm^{-1}$ . The  $^1H$  NMR spectra was obtained on a 400 MHz Bruker AVANCE III nuclear magnetic resonance (NMR) spectrometer M/s Bruker, Switzerland with  $CDCl_3$  as a solvent.

Wide angle X-ray Diffractometer (Shimadzu XRD-700 L, X-Pert MPD, Japan) fitted with graphite monochromatic operated at 40 kV and 30 mA was used to assess the WAXD patterns of the PLE blends. PLE blends was dissolved in chloroform and then stirred and refluxed for 2 days to collect the vulcanized part at the bottom. The sediment material was annealed at 110 °C for crystallization of PLA and then compared to the virgin PLA.

The average molecular weight and polydispersity index of the synthesized polymer were analyzed by a Waters Corporation GPC, that is fitted with a 515 HPLC pump, 2489 UV visible detector and a refractive index detector. As a solvent tetrahydrofuran was used while, standard for the calibration is polystyrene.

Universal Testing Machine (M/s Instron 3382, UK) was used to analyze the tensile strength, tensile modulus and elongation at break (EB). Dumb-bell shaped specimens were prepared with dimensions of  $165 \times 12.7 \times 3$  mm and tensile tests were performed at a crosshead speed of 5 mm/min with a gauge length of 100 mm and with a load cell of 10 KN in accordance to ASTM D 638. The notched impact strength of the samples with dimensions of  $63.5 \times 12.7 \times 3$  mm was done according to ASTM D 256 in an impact tester (M/s Tinius Olsen, USA).

Hardness (Shore D) of the PLA and PLE blends was analyzed by using durometer as per ASTM D-2240 standard. For all the blends, the Shore D value was calculated by taking an average of ten measurements at various sites of the same sample.

**Scheme 1** The synthetic reactions of LBPE bioelastomer

The morphology of the neat PLA and PLE blends were depicted using scanning electron microscopy (SEM) EVO MA 15 (M/s Carl Zeiss, SMT Ltd., Germany). The impact fractured samples were employed for the analysis and the test surface was gold coated prior to testing.

Differential scanning calorimetry (DSC Q20, M/s TA instruments, USA) was assigned to analyze the thermal analysis of PLA and PLE-20 blend. About 5-10 mg of samples was heated from  $-80$  to  $250$  °C at a heating rate of  $10$  °C/min for a first heating scan, then the samples were cooled to  $-80$  °C at a cooling rate of  $20$  °C/min, held at  $-80$  °C for 5 min, and then again heated from  $-80$  to  $250$  °C at a heating rate of  $10$  °C/min. The glass transition temperature ( $T_g$ ), crystallization temperature ( $T_{cc}$ ), melting temperature ( $T_m$ ) and maximum degree of crystallinity ( $\chi_{max}$ ) were observed from the second heating scan. The degree of crystallinity of PLA and its blends during heating was estimated from the below given equation, where  $\Delta H_m$  is the melting enthalpy of sample in J/g and  $\Delta H_{m^0}$  is the melting enthalpy of 100% crystalline PLA (93 J/g).

$$\chi_{max} = \frac{\Delta H_m}{w\Delta H_{m^0}} \times 100\%$$

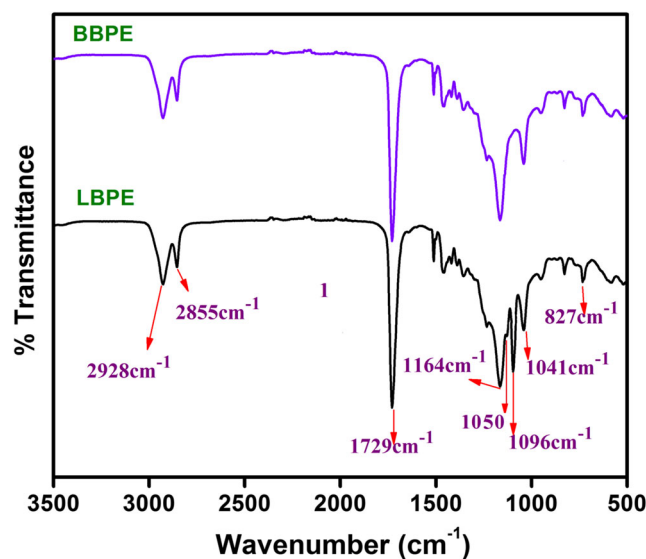
## Results and discussion

### Characterization of LBPE bioelastomer

Figure 1 depicts the FTIR absorption spectra of synthesized LBPE and BBPE. The FTIR spectra of LBPE and BBPE elastomers show an identical absorption peak, except an additional peak at  $1096$   $\text{cm}^{-1}$  and  $1050$   $\text{cm}^{-1}$ , which demonstrates the C-O groups and C-CH<sub>3</sub> symmetrical stretching peak respectively of the lactate groups. The symmetrical and

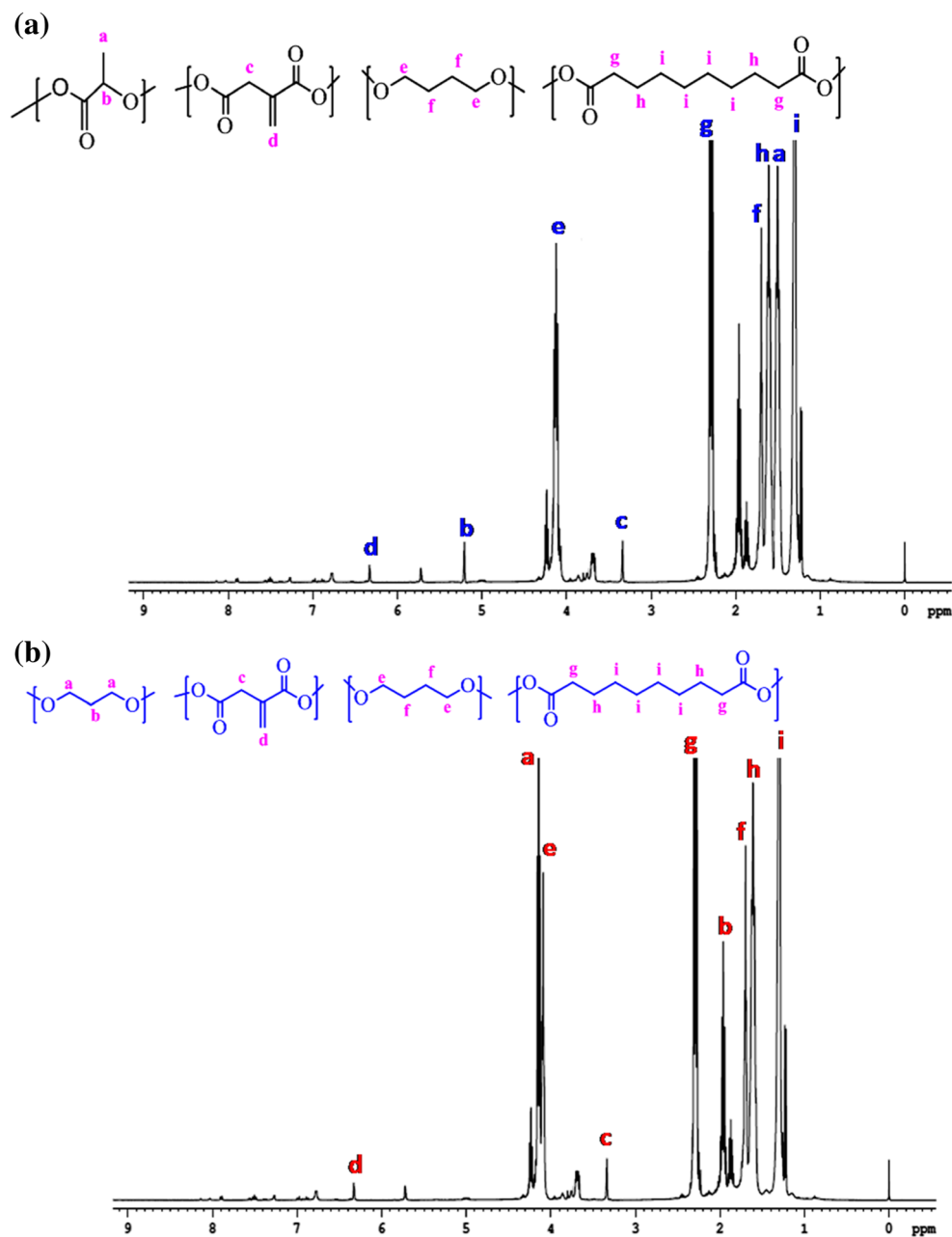
antisymmetrical stretching peak of  $-\text{CH}_2$  group was verified by absorption peaks at  $2928$   $\text{cm}^{-1}$  and  $2854$   $\text{cm}^{-1}$  respectively. The ester bonds presence was confirmed by the strong peak at  $1729$   $\text{cm}^{-1}$  which is associated to  $-\text{C}=\text{O}$  stretching vibration. The O=C-O-C symmetrical stretching peak of ester linkage was observed at  $1164$   $\text{cm}^{-1}$ . The peak in the region  $1041$   $\text{cm}^{-1}$  is assigned to  $-\text{C}-\text{O}$  stretch of 1,4-Butanediol and 1,3-Propanediol. The transmittance at  $827$   $\text{cm}^{-1}$  in the spectra contributes to C=C stretching peak of itaconate esters. Thus, the FTIR investigation reveals the successful introduction of lactate groups into the macromolecular polymer chains of synthesized LBPE polyester [6].

Figure 2 represents the  $^1\text{H}$  NMR spectra of LBPE and BBPE elastomers, where all the characteristic signals of



**Fig. 1** FTIR spectra of BBPE and LBPE copolyesters

**Fig. 2**  $^1\text{H}$  NMR spectra of the synthesized BBPE and LBPE

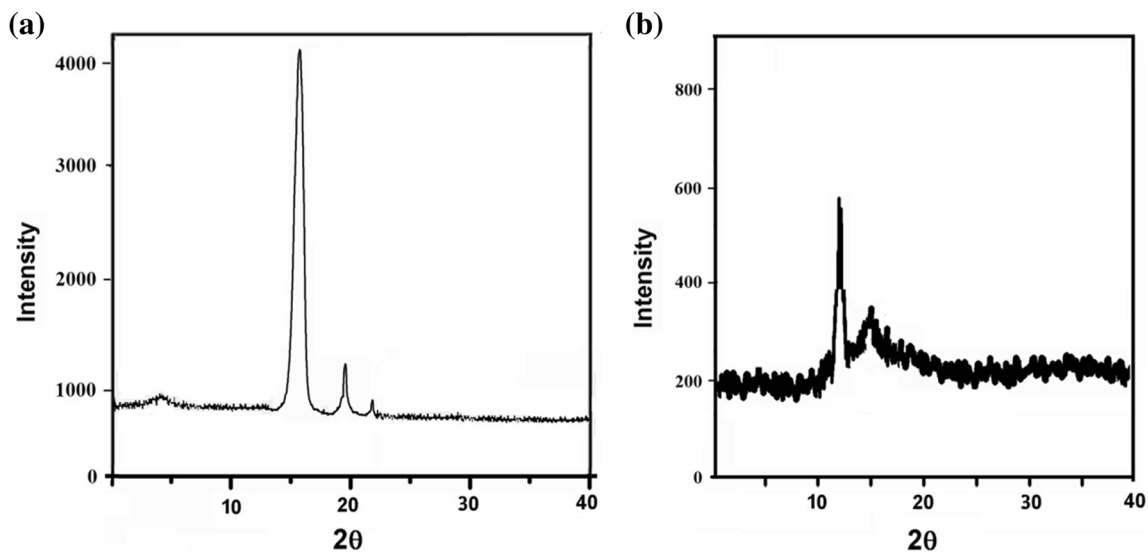


the monomer units are verified. Particularly, the signals at 6.35, 5.72 and 3.73 ppm, which is attributed to pendant unsaturated group and  $-\text{CH}_2$  group of IA, indicating that even after high temperature polycondensation process, the unsaturation is visible, attributed to the inhibition of PMP. The sebacic acids  $-\text{CH}_2$  group peaks are found at 1.3, 1.62 and 2.29 ppm while, doublet and singlet at 4.09 ppm, 1.71 ppm respectively, verifies the presence of BDO group. The chemical shifts at 1.88 ppm and 4.22 ppm clearly depicts the PDO group in bioelastomer. Additionally, characteristic protons of  $-\text{CH}$  and  $-\text{CH}_3$  groups of LA can be noted at 5.2 ppm and 1.5 ppm respectively for LBPE elastomers. All these

peaks reveal the successful incorporation of the different repeating units of monomers into the LBPE elastomer.

### Highly toughened polylactide with LBPE elastomer

Figure 3 demonstrates the WAXD patterns of (a) virgin PLA and (b) crosslinked part of PLE blend. Annealed virgin PLA depicts a sharp diffraction peak at  $2\theta$  value of  $17.50^\circ$ , related to the (110) and/or (200) planes of  $\alpha$  form PLA crystals [10]. The specific diffraction peak was also observed in the crosslinked portion of PLE blend. This behavior can be explained due to the facts that no self-cross-linking of PLA occurred during dynamic vulcanization and the free PLA was



**Fig. 3** WAXD patterns of (a) virgin PLA and (b) crosslinked part of PLE blend after annealing at 110 °C for 12 h

removed completely by dissolving in chloroform. The specific PLA diffraction peaks in the crosslinked part could be attributed due to the formation of LBPE-g-PLA, which had PLA chains grafted onto the crosslinked LBPE surfaces and was located at the interface between dispersed LBPE phase and PLA matrix to enhance their compatibilities.

Table 1 summarizes the impact and tensile properties of neat PLA and PLE blends. PLA's conversion from its original brittle behaviour into ductile nature can be observed with the incorporation of LBPE elastomer. The impact strength shows an enhancement as LBPE content increases. The maximum notched impact strength reaches upto 81.5 J/m for 20 wt% of LBPE, i.e. an increment of about three fold than neat PLA. This depicts the homogeneous dispersion of crosslinked LBPE particles in the PLA matrix as represented in Scheme 2. Further, raising the LBPE content to 25%, causes decrease in impact strength to 74 J/m, which is credited to the alteration of LBPE crosslinking in the PLA matrix [11].

However incorporation of LBPE to the tune of 10 to 25 wt% within PLA matrix results in decrease in the tensile strength and modulus. The tensile strength of PLA decreased to 36% whereas the modulus to 18% with the incorporation of LBPE. This behavior is probably due to the elastomeric effect of LBPE within the virgin material. Also it is assumed that the presence of soft elastomeric phase in the blend matrix reduces

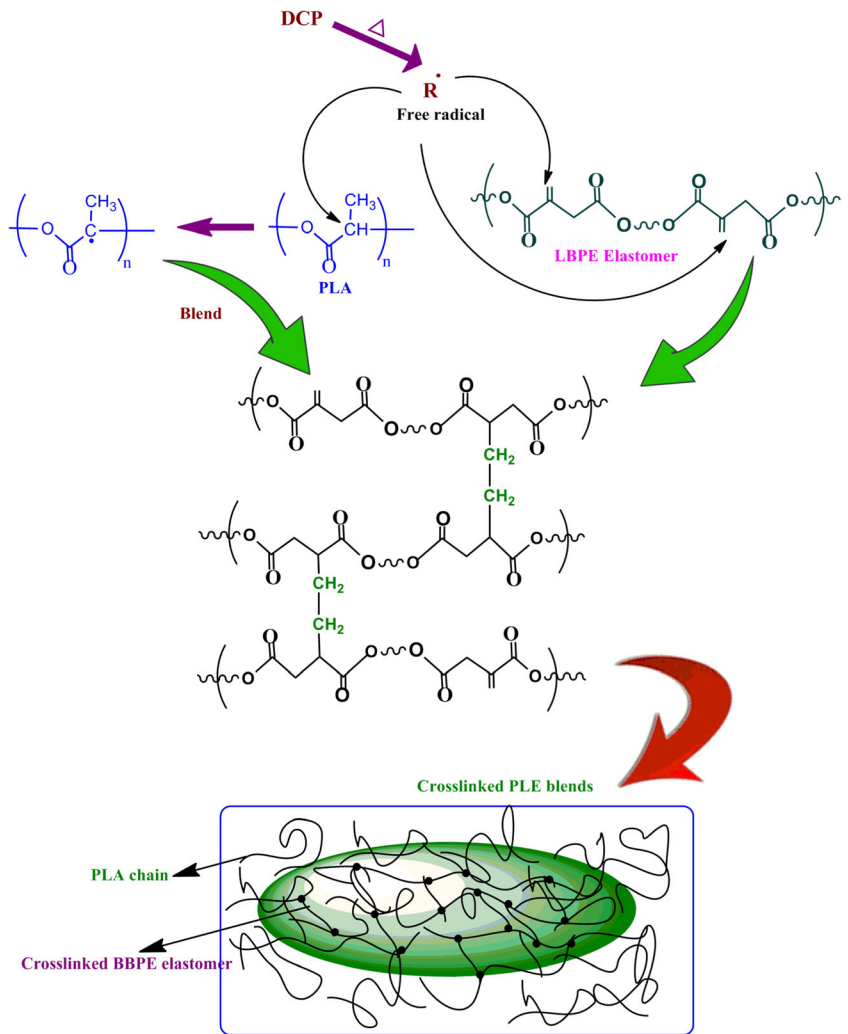
the crystallinity of PLA which has been confirmed from the DSC studies represented in the later sections of the article.

A similar decrease in the hardness of the PLE blends from 86 to 60 respectively at variable content of LBPE was observed. This signifies that LBPE content plays a crucial role in influencing hardness behavior of the blend. Virgin PLA exhibits its hardness above the Shore A hardness and because of the elastomeric effects of LBPE, the hardness retards as its content was increased from 0 to 25%. In addition to this, PLE-20 shows the maximum elongation at break of 45% that is about 19 fold increase as compared to virgin PLA, which attributes to good dispersed distribution of crosslinked LBPE elastomeric particles in the PLA matrix, as LBPE and LA contain similar ester and lactate groups, implying good compatibility between them as represented in Scheme 2. Whereas, PLE-25 demonstrated a decreasing elongation at break with enhancing LBPE content, this might be the consequence of the phase separation and agglomeration of both the materials at higher LBPE amount. Thus from the test results reported in Table 1, it may be noted that the virgin material undergoes a brittle to ductile transition with the increase in the LBPE content from 0 to 20 wt%, beyond which phase inversion mechanism could be observed. Further, comparing the mechanical test results of PBE and PLE blends, it is observed that the later shows an improved toughness characteristic.

**Table 1** Mechanical properties of PLA with different blending ratios of PLA/LBPE

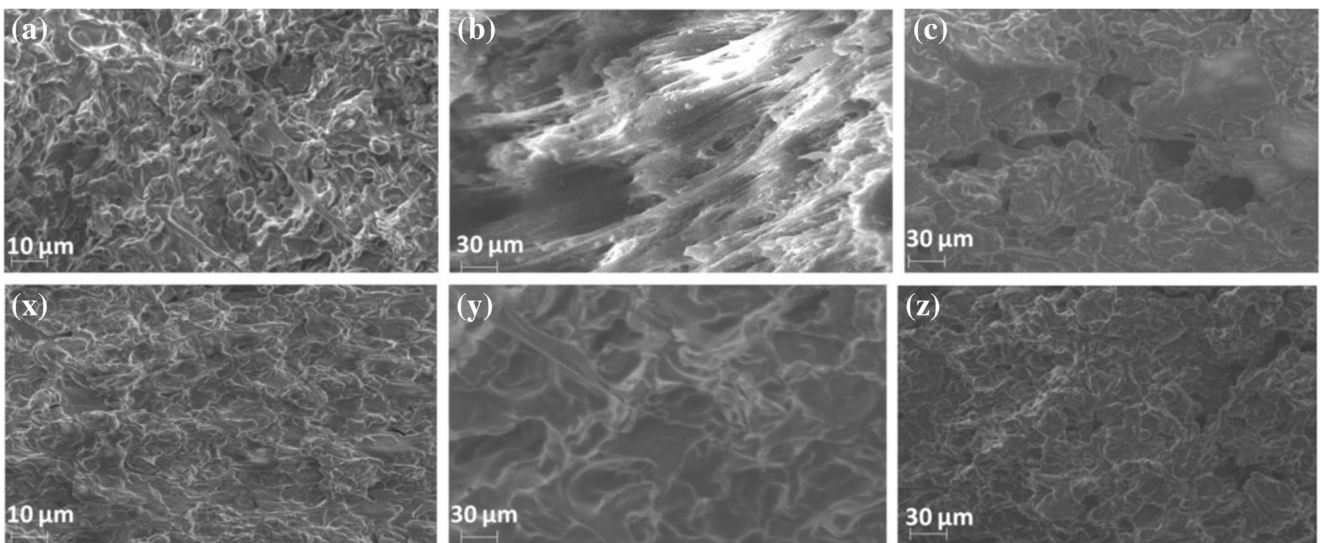
Samples	Tensile strength (MPa)	Elongation at break (%)	Tensile Modulus (MPa)	Impact strength (J/m)	Hardness (Shore A)
PLA	56 ± 3	2.3 ± 0.1	1958 ± 20	25 ± 2	–
PLE- 10	50 ± 0.5	11 ± 0.6	1900 ± 15	38 ± 2	86
PLE -15	44 ± 1.7	25 ± 1.2	1837 ± 9	62 ± 1	78
PLE- 20	40 ± 2.4	45 ± 1.3	1752 ± 13	81.5 ± 1	65
PLE -25	36 ± 0.5	35 ± 0.4	1596 ± 10	74 ± 0.5	60

**Scheme 2** The schematic depiction of crosslinked PLE blend formation in presence of DCP



This behavior is possibly because LBPE and PLA contain similar ester and lactate groups, thus implying good

compatibility between the two. Since the PLE-20 blend prepared at a ratio of PLA:LBPE of 80:20 shows optimum impact



**Fig. 4** SEM images of Tensile fractured surface of (a) PLE-15 (b) PLE-20 (c) PLE-25 and Impact fractured surface of (x) PLE-15 (y) PLE-20 and (z) PLE-25

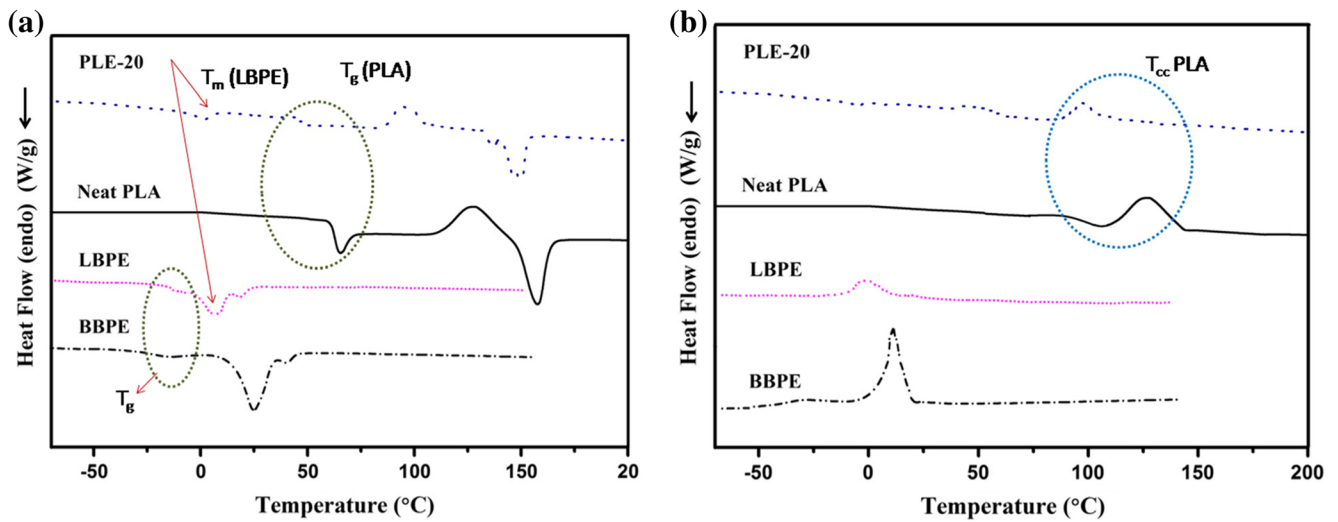


Fig. 5 DSC thermograms of BBPE, LBPE elastomer, neat PLA, and PLE-20 blend

property, this composition has been taken for further characterization studies.

**Scanning electron microscopy (SEM) of PLA and PLE-20 blend**

The SEM micrographs of impact and tensile fractured surfaces were further analyzed to assess the toughening and crosslinking effects of PLA and PLE blends as shown in Fig. 4a-c and (x-z) respectively. The plain surface of neat PLA was reported elsewhere [6] however, a distorted rough surface was noted for PLA and its blends matrix, signifying the modification from brittle fracture to ductile fracture. The ductile manner was observed for tensile test specimen, with whitening in the area of maximum deformation with the formation of micro-cracks which are bridged by polymer fibrils. The number of crazes increases in presence of LBPE due to the micro elastomeric regions in its matrix, which averts the abrupt failure by absorbing the energy of deformation. Since, crazing probably occurs in the regions of high deformational stress, i.e., the region under the neck of tensile specimens were noted in the SEM. Fibrils on the surface of the PBE-20 tensile fractured surface (Fig. 4b) confirms that matrix had undergone great level of elastic deformation before failure. Besides the initiation of cracks, voids were noticed with elongation. This demonstrates the fact that the elastomer was pulled out thus

indicating the excellent interfacial adhesion between PLA and LBPE matrix resulting to the toughening of PLA [11, 12]. Brittle nature of the impact fractured SEM micrographs of PLA was verified, [6] due to the presence of smooth surface, while, SEM of PLE-20 (Fig. 4y) demonstrates a similar rough surface along with the presence of cavities suggesting its ductile fracture as observed in case of PBE-20 blend. Also there was existence of crazes or shear yielding during the tensile test, which confirms the toughening mechanism in PLE-20 blend. The impact fractured sample of PLE-20 blend displayed a rough morphology indicating absorption of more impact energy. Further, it is also evident from Fig. 4(c) and (z) that the PLE-25 blend depicts phase separation with wider gaps thus revealing phase separation [13].

**Thermal properties**

Figure 5a, b represents the DSC heating and cooling curves respectively of neat PLA and PLE-20 blend with comprehensive data in Table 2. PLE-20 blend displays four transition peaks while heating; the LBPE endothermic melting peak ( $T_m$ ), glass transition temperature peak ( $T_g$ ) of PLA, exothermic crystallization peak of PLA ( $T_{cc}$ ) and endothermic melting peak of PLA ( $T_m$ ). In comparison to BBPE, LBPE elastomer shows increased  $T_g$  and decreased melting temperature ( $T_m$ ).

**Table 2** Thermal properties of PLA and PLBE blends

Sample	Bioelastomer			PLA				
	$T_g$ (°C)	$T_m$ (°C)	$^a T_{cc}$ (°C)	$T_g$ (°C)	$^a T_{cc}$ (°C)	$T_m$ (°C)	$\Delta H_m$ (Jg <sup>-1</sup> )	$\chi_{max}$ (%)
PLA	–	–	–	57	128.1	157.8	20	21.5
PLE- 20	-1	23.04	–	48	94	150.4	8.5	11.45
LBPE	-9	7	-3	–	–	–	–	–
BBPE	-20	26	10	–	–	–	–	–

<sup>a</sup>  $T_{cc}$  – cold crystallization peak measured from DSC cooling curves

The steady rise in  $T_g$  of LBPE was noted, due to the presence of side chain methyl group leading to suppress the mobility of the elastomeric matrix. Thereby, making it more flexible. With the introduction of LBPE to PLA in PLE blend, the  $T_g$  of the PLA reduces from 57 °C to 48 °C. In contrast, the  $T_g$  of LBPE in the PLE-20 blend raises to -1 °C from initial -9 °C. The migration of PLA and LBPE elastomers  $T_g$  towards each other corroborates the improved compatibility between PLA and LBPE matrix [11, 14]. Besides, the inclusion of LBPE into PLA matrix declines the  $T_c$  and melting enthalpy ( $\Delta H_m$ ) of the PLA component, as the presence of LA units as well as crosslinking leads to disturbance in the regular chain and inhibits the crystallization of PLE-20 blends. The degree of crystallinity ( $\chi_{max}$ ) of the PLE-20 blend declines to 11.45% from the 21.5% of the neat PLA. Additionally, the melting temperature ( $T_m$ ) of LBPE in the PLE-20 blend retards in comparison to pure LBPE elastomer, which signifies the existence of crosslinked LBPE in the PLA matrix. As a result, it is summarized that LBPE restricts the mobility of PLA matrix, which leads to decreased crystallinity of PLA. Furthermore, the shifting of both the  $T_g$ 's related to LBPE and PLA towards each other and widening of the transition area, affirms the compatibility and interaction between them.

## Conclusions

PLA was toughened by melt blending it with a renewable resource based aliphatic copolyester elastomer in presence of free radical initiator DCP. Mechanical properties, DSC and SEM exhibits an improved performance for PLA/LBPE blends fabricated at a ratio of 80:20. Subsequently, PLE-20 blend shows the suppressed crystallinity of the PLA in presence of LBPE elastomer. By deviating the elastomer LBPE ratio, the PLE blends can be tuned from brittle to ductile and flexible polymers. Blend with 20 wt% of LBPE elastomer content, reveals that impact strength and elongation at break improves to 81.5 J/m and 45% respectively, in contrast to those of 25 J/m and 2.3% for neat PLA respectively. So, at an optimal elastomeric content of LBPE, PBE blends can be the potential material for transforming the brittle PLA into flexible and ductile form without altering its biocompatibility.

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