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ORIGINAL PAPER

Effects of Diisocyanate and Polymeric Epoxidized Chain Extenders on the Properties of Recycled Poly(Lactic Acid)

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Abstract Increasing demand in the use of poly(lactic acid) (PLA) leads to a debate about using potential foodstuffs for plastic production and a moral issue when starvation problem is taken into account. One of the solutions is recycling of PLA; however, recycling results in property losses during melt processing due to low thermal stability of PLA. This study focuses on using chain extenders to offset thermal degradation of recycled PLA. The effects of a diisocyanate and a polymeric epoxidized chain extender on the properties of the recycled poly(lactic acid) were investigated. In order to mimic the recycling process, PLA was subjected to thermo-mechanical degradation using a laboratory scale compounder. Chain extender type, loading and mixing time were investigated. On-line rheology and intrinsic viscosity measurements of PLA before and after chain extension confirmed that the molecular weight increased. Dynamic mechanical analysis, rheology and tensile tests revealed that the chain extenders led to a significant increase in modulus, strength and melt-viscosity. It was found that diisocyanate had slightly higher and faster chain extension reactivity than polymeric extender. Differential scanning calorimetry results showed an increase in the crystallization temperature due to the branched and extended chain structure.

Keywords Poly(lactic acid) · Chain extension · Recycling · Mechanical properties · Rheology · Morphology

Introduction

Recently, biodegradable polymers have attracted much attention in the plastics industry due to the environmental concerns and limited fossil resources. The most popular biodegradable polymers are linear aliphatic polyesters such as poly(lactic acid) (PLA), poly(epsilon-caprolactone) (PCL), poly(butylene adipate terephthalate) (PBAT) and polyhydroxybutyrate (PHB) [1–3]. Among these biopolymers, PLA, a commercially available linear aliphatic thermoplastic polyester is produced from renewable resources such as corn, potato and sugarcane. PLA is generally synthesized by ring-opening polymerization of lactide, which is produced from lactic acid, a fermentation product of sugar feed stocks [4]. Commercial PLA grades are commonly found in copolymers of poly(L-lactide) and poly(D-lactide) enantiomers. The ratio of L- and D-enantiomers influences the properties of PLA, such as melting temperature, optical clarity, mechanical properties and crystallinity [5–7].

PLA resin can be processed as conventional polymers using injection moulding and extrusion methods. Due to good processability and relatively lower price compared to the other biodegradable polymers, PLA is an alternative to conventional polymers in commodity applications, such as packaging [8, 9]. Despite all these advantages, the increasing volumes of PLA production have led to a debate about using potential foodstuffs (such as corn or sugar cane) to make plastic as there are still starving children on the earth. This concern enforces the scientists and the

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bioplastic producers to recycle PLA to a point at which PLA cannot be used as a plastic material [10]. On the other hand, low thermal stability of PLA leads to a significant decrease in physical properties with recycling [11]. Hydrolytic chain scission and unzipping reactions during thermo-mechanical processing result in molecular weight reduction of PLA [12].

Several researchers investigated the effects of recycling on the properties of PLA. Zenkiewicz et al. focused on the characterization of multi-extruded PLA. They processed PLA up to 10 times and it was indicated that the mechanical properties were deteriorated with increasing extrusion cycles. In addition, the thermal stability of PLA slightly decreased [13]. Badia et al. [14] investigated the effect of recycling on the morphological, thermal and mechanical properties of amorphous PLA. It was found that the properties deteriorated with reprocessing due to the thermo-mechanical degradation. The molecular weight reduction was found to be the responsible factor in this observation. Pillin et al. studied the effects of thermo-mechanical cycles on the properties of PLA. It was found that the tensile modulus remained constant with the thermo-mechanical cycles, whilst stress and strain at break, hardness and rheological properties decreased. This was attributed to the larger decrease in the molecular weight due to many complex degradation processes [15].

In order to overcome property deterioration of PLA in the melt processing, use of chain extenders is reported to be an efficient method [11]. Chain extension is the reaction of functional molecules with the carboxyl or hydroxyl end groups of PLA chains. Chain extenders usually increase molecular weight of PLA by entering between two chain ends. Bifunctional chain extenders can react with two end groups, which lead to a linear structure, whilst the multifunctional chain extenders with more than two functionalities result in branched or cross-linked structures [16, 17]. In this regard there are many works on the use of chain extender during reprocessing of PET, a linear, aromatic polyester having carboxyl and hydroxyl end groups as similar to PLA [18–26]. Some of the chain extenders used in these studies are 1,6-diisocyanatohexane, 1,4-butanediol diglycidyl ether, poly(phenyl isocyanate-co-formaldehyde), pyromellitic dianhydride (PMDA), diepoxides, epoxydized acrylic copolymers, 1,4-phenylene bisoxazoline, phatalic anhydride [18, 20, 21, 24, 25]. A few publications mentioned the use of chain extenders to lessen thermal degradation of pristine PLA and PLA/organoclay nanocomposites during melt processing [11, 27–29].

Najafi et al. investigated the effects of tris(nonyl phenyl)phosphite (TNPP), polycarbodiimide (PCDI) and a commercial epoxidized acrylic copolymer (Joncryl® ADR-4368) to control thermal degradation. They found that Joncryl® ADR-4368 was the most efficient chain extender among the others [27]. Meng et al. compared the effect of three different chain extenders, such as PMDA, hexamethylene diisocynate (HDI) and Joncryl. Joncryl. HDI showed higher chain extension reactivity as compared to PMDA; whereas Joncryl was shown to be the more effective one. The chain extender HDI is a bifunctional molecule therefore yielded mostly linear structures. In contrast, since Joncryl is a multi-functional reactive polymer, the molecular structure of the PLA changed from linear to a branched or cross-linked structure, depending on Joncryl loading level and processing temperature, as confirmed by H-NMR analysis. Joncryl also showed a remarkable thermal stabilization effect on PLA/organically modified clay nanocomposites containing up 6 wt% of the organoclay [11]. Najafi et al. studied the effect of the chain extender and processing conditions on the properties of the PLA/organoclay nanocomposites. The results showed that the Joncryl-based nanocomposites enhanced the degree of clay dispersion and exhibited a significantly reduced permeability as compared to others. The mechanical properties were also investigated. The increased molecular weight in Joncryl based nanocomposites caused a significant increase in the modulus, draw-ability and toughness of the samples [28]. Corre et al. used an epoxide additive (Joncryl® ADR-4368) in order to melt strengthen the pristine PLA with the objective to enlarge its process-ability window. The rheological investigations highlighted the enhancement of the melt properties by using the chain extender [29].

It was seen in the literature that there are studies on the reactive extrusion of recycled PET using chain extenders [18–26] and the chain extension of pristine PLA and PLA/organoclay nanocomposites [11, 27–29]. However, to our knowledge the effect of chain extenders on the properties of "recycled PLA" has not been investigated. In this study, the effects of a commercial multi-epoxide chain extender (Joncryl ADR-4368) and an isocyanate based chain extender (1,4-phenylene diisocynate) on the rheological, mechanical, thermal and morphological properties of recycled poly(lactic acid) (PLA) were investigated. The concentration of chain extender and the residence time in the reactive processing were taken as the parameters.

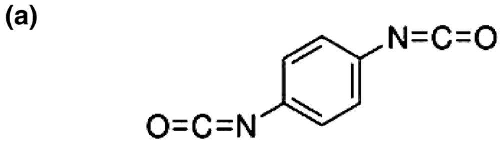
Experimental

Materials

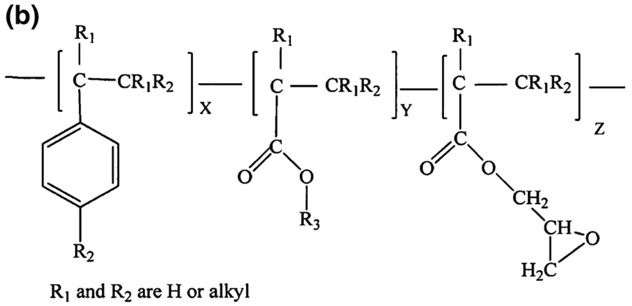
Injection-molding grade PLA was purchased from Natureplast (France). It has density of 1.24 g/mL and MFI range of 5–7 g/10 min at 190 °C. The two chain extenders used in this study were 1,4-phenylene diisocynate (PDI, Sigma-Aldrich) and Joncryl® ADR-4368 (BASF, Germany). PDI, a bifunctional aromatic isocyanate, is a white solid at room temperature and has a melting point of 96 °C and a boiling point of 260 °C. It should be noted that personal safety precautions such as splash goggles, chemical resistant gloves and impervious clothes must be taken in the use of PDI since PDI is irritant to skin, eyes and lungs. Joncryl$^{®}$ADR 4368, a commercial multi-epoxy functional acrylic copolymer, has density of 1.08 g/mL at 25 °C, molecular weight of 6800 g/mol, epoxy equivalent weight of 285 g/mol, functionality of 9 and glass transition temperature (T_g) of 54 °C. The structures of chain extenders are shown in Fig. 1a, b.

Sample Preparation

Melt compounding was carried out using a laboratory twin-screw compounder (Xplore Instruments 15 cc Micro-compounder) that allows both batch and continuous mixing. Prior to processing, PLA was dried in a vacuum oven at 60 °C for 12 h. The chain extenders were used as received. Firstly, PLA was melt-processed for 4 min at a barrel temperature of 200 °C and screw speed of 100 rpm. This PLA sample was abbreviated as rPLA. The aim of this initial thermo-mechanical stage was to mimic the reprocessing or recycling of PLA. In this period, it was expected to decrease in molecular weight of PLA and hence a deterioration in the physical properties. Thereafter, 1 and 3 wt% of chain extenders were added to this melt and compounded for different periods of time such that 1, 2 and 4 min. At the end of mixing time, polymer was extruded from the compounder and subsequently injection moulded into standard test shapes with an Xplore Instruments 12 cc laboratory injection molding machine. The injection moulding was carried out under 9 bars with the mould and the melt temperatures of 25 and 200 °C, respectively. The control sample was prepared by injection molding of the pristine PLA pellets.



1,4 phenylene diisocynate



Joncryl$^{®}$ADR 4368

Fig. 1 The chemical structures of chain extenders

In order to characterize rheological properties of the samples, disks of 25 mm diameter and 1.5 mm thickness were prepared by compression molding at 200 °C using a pressure of 15 MPa during 4 min.

Characterization

Intrinsic viscosities of the samples were determined in chloroform at 30 °C using an Ubbelohde capillary viscometer. The viscometer was immersed in a thermostatic water bath to keep the temperature constant throughout the test. The viscosity measurements were done at different concentration levels from 0.08 to 0.5 (mg/L). To ensure accuracy of the results, the measurements were repeated five times for each concentration. The intrinsic viscosity was then calculated by linearly extrapolating the reduced viscosity to a zero concentration.

Tensile test was conducted according to ISO 527 standard, using a computer controlled Lloyd Instruments-LRX Plus model universal testing machine. Yield strength and elongation at break were determined using 5 dumbbell-shaped samples for each composition at 5 mm/min cross-head speed.

Dynamic mechanical analysis (DMA) was conducted to investigate the temperature dependent dynamic mechanical properties of the samples by using a Metravib 01 dB DMA50 instrument. The heating rate was set at 1 °C/min with 1 Hz frequency in tension mode. Temperature range was 30–120 °C.

Rheological analyses were carried out using a strain-controlled ARES rheometer (Rheometric Scientific Inc., USA) with 25 mm parallel plate flow geometry, at 200 °C. The strain amplitude was set at 0.01 %. Frequency sweep tests were performed over a frequency range of 0.1–100 rad/s.

Differential scanning calorimetry (DSC) analyses were carried out under nitrogen atmosphere using a Mettler Toledo DSC1 Star System. The samples of approximately 5 mg were placed in the aluminium pans and heated from 25 to 180 °C at a heating rate of 10 °C/min, and then cooled down to 25 °C at a cooling rate of 10 °C/min. A second heating scan was also recorded at a heating rate of 10 °C/min to 180 °C. The second heating run was used to assess Tg, Tm and ΔHm.

The morphologies of the samples were analysed by using a scanning electron microscope (SEM, JEOL 6060). Prior to analysis, sample surfaces were coated with gold.

Results and Discussion

Possible Interactions Between PLA and Chain Extenders

Figure 2 represents the chain extension of PLA with diisocynate. The reaction with the hydroxyl group is faster and leads to the formation of a stable carbamate (1 in Fig. 2a), while the reaction with carboxyl end groups of PLA provides unstable O-acylcarbamates (3 in Fig. 2b), which decompose to amides with loss of CO_2. At higher concentrations of isocyanates, the allophanates (2) and ureas (5) are formed in a branched structure.

Chain extension mechanism of PLA with Joncryl is shown in Fig. 3. The chain extension reaction involves epoxy ring-opening of the chain extender and results in the formation of covalent bonds due to hydroxyl side groups [12]. It should be noted that the reactivity of isocynates with hydroxyl groups is greater than that of epoxides.

On-line Rheology by Vertical Force Measurement

The barrel of the micro-compounder used in the experiments was positioned on a lever, where the barrel was allowed to swivel around a stationary axis, and was counter balanced by a load-cell at the other end. A 10 kN load cell was used to measure force. The measured force was the vertical force exerted by the barrel opposing the pushing forces imposed by the screws toward the bottom, while the polymer melt was pumped through the recirculation channel or die. For a given polymer, when the screw speed and the barrel temperature were fixed, the vertical force measured by the load cell represented the melt viscosity of the polymer. In this study, the vertical force measurements were conducted as preliminary experiments to enable the comparison of the melt viscosity of the materials at different compositions. The vertical force data were recorded at 5 s interval, after filling the barrel with a constant amount of the polymer. In addition, vertical force is an indication of the melt viscosity that can be used to compare the rheological characteristics of the melts and cannot be directly converted into the viscosity units due the complex geometrical shape of the compounder [30]. In this study, vertical force measurements were used to monitor process induced degradation and chain extension of the PLA samples during melt compounding.

Figure 4 shows the vertical force profiles of the samples during melt compounding. It should be noted that the vertical force profile of pristine-PLA was used as control for comparison. It can be seen from the figure that the vertical force reached to a maximum (line-A) when the PLA pellets were fed into the compounder (in the first 30 s). This increase can be attributed to the increasing volume fraction of the polymer in the barrel. After this peak, the vertical force, in other words the melt viscosity gradually decreased due to the degradation of the PLA [31–33]. When t = 240 s, the chain extenders at 3 wt% loading were fed into the compounder.

In the case of PDI, after nearly 30 s of induction period, vertical force started to increase very sharply. During induction-period, solid chain extender heated, melted and then reacted with the polymer. The sudden increase in the viscosity confirmed chain extension reactions that resulted in an increase in the melt viscosity. After this peak point, the vertical force started to decrease. This behaviour can be attributed to the rapid consumption of PDI in the system due to the higher reactivity. However in the case of Joncryl, the vertical force steadily increased after 60 s from the induction period. Longer induction time of Joncryl can be attributed to branched structure of the samples. It can also be observed that the vertical force did not decrease after the addition of Joncryl. This indicated a slower reaction of PLA with Joncryl than PDI. As the preliminary

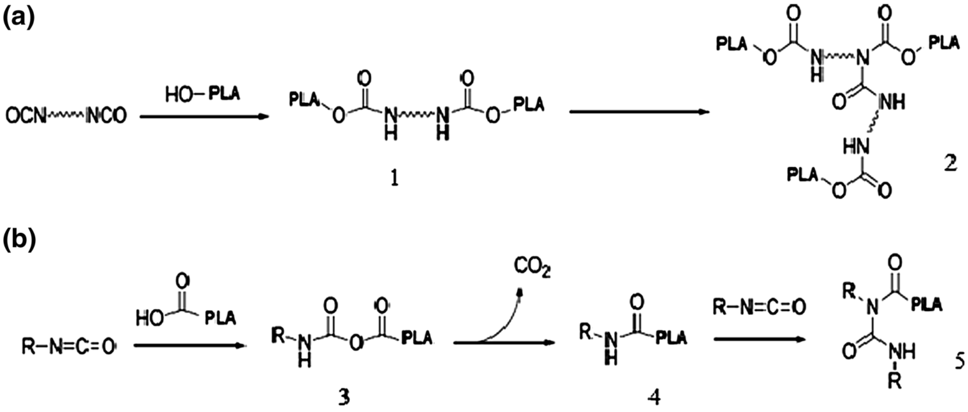
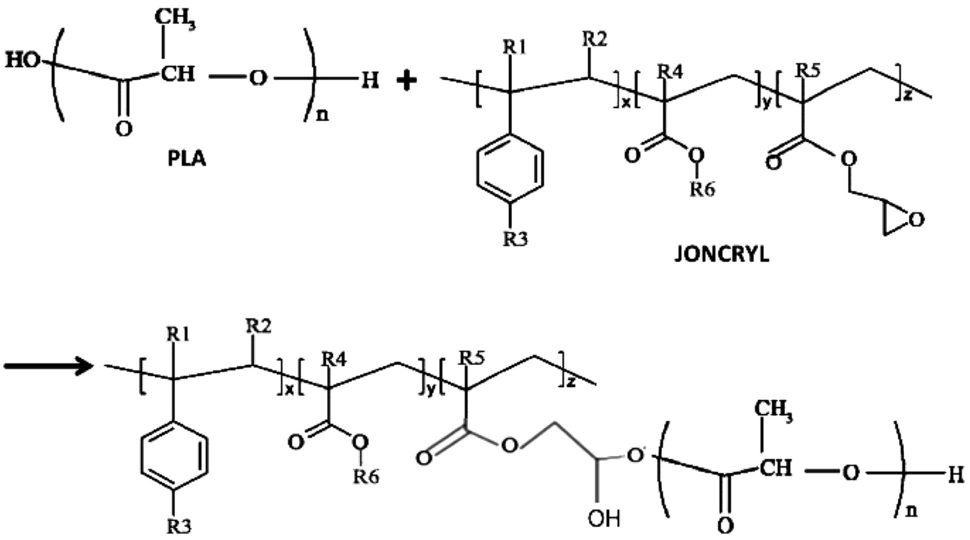


Fig. 2 Chain extension mechanism of PLA with a diisocyanate: **a** reaction with hydroxyl ends groups, **b** reaction with carboxylic acid end groups

Fig. 3 Chain extension mechanism of PLA with Joncryl [12]



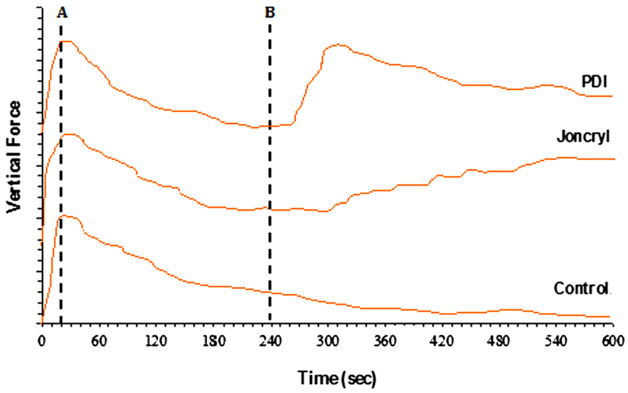


Fig. 4 Vertical force profiles of PLA at 3 % chain extender loadings (i.e. PDI or Joncryl). (The *line-A* represents the end of filling period, and *line-B* represents the time when the chain extenders were added. It should be noted that the control is the neat PLA)

experiments, the vertical force measurements showed first impression about reactivity of chain extenders.

Intrinsic Viscosity (IV) Measurements

Figure 5 shows the variation in the intrinsic viscosity of the samples in terms of reaction time, type and loading of chain extenders. The intrinsic viscosity of PLA decreased from 1.4 to 1.2 indicating a reduction in the molecular weight due to thermal and hydrolytic degradation reactions in the melt processing [31–33].

The incorporation of the chain extenders increased the viscosity of PLA without reaction time, type and loading of chain extender. The results showed that the highest loading (3 wt%) was more effective for both chain extender types. It is also important to note from the samples at 3 wt% PDI and Joncryl loadings that PLA-PDI processed for 1 min and PLA-Joncryl processed for 4 min showed higher viscosities than prisitine-PLA. The intrinsic viscosity of the samples containing Joncryl increased with reaction time, whilst PDI showed a decreasing trend over the reaction time which was also shown in the vertical force measurements. This

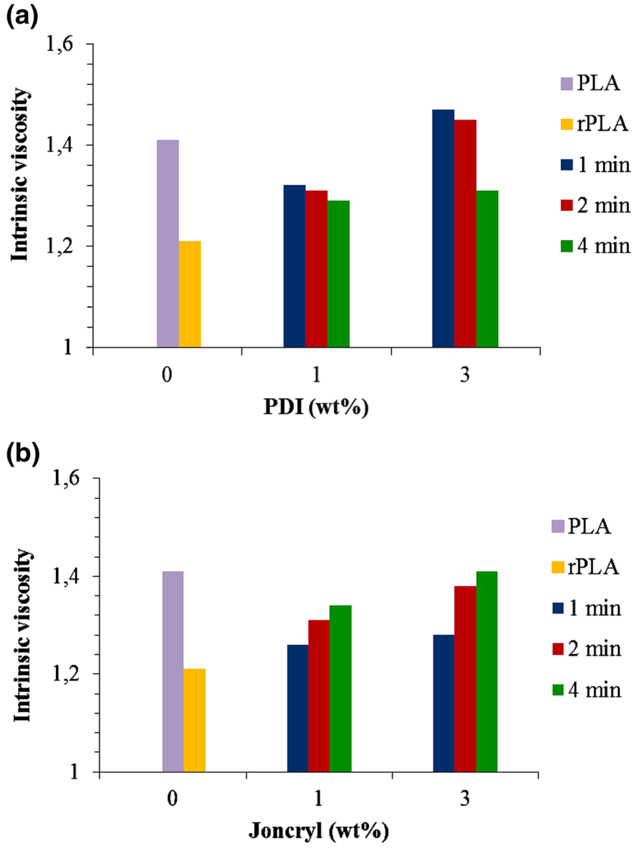


Fig. 5 Variation of intrinsic viscosity of PLA, rPLA and modified PLA with respect to reaction time and chain extender content: **a** PDI and **b** Joncryl

can be explained that PDI reacted with polymer rapidly and was consumed in a short time (approximately 1 min). In the absence of PDI at longer processing times, thermo-mechanical effects resulted in chain scission and thus lower molecular weight. However, the viscosity of the samples containing Joncryl increased with reaction time suggesting that the multifunctional structure of Joncryl led the samples to remain reaction media for longer times.

Tensile Properties

Yield strength of the samples were shown in Fig. 6a, b. The results indicated that yield strength of PLA decreased nearly 4 MPa compared to pristine-PLA due process induced degradation. The incorporation of chain extenders offset thermal degradation and therefore increased the yield strength of PLA. From the results, it was also concluded that yield strength of the samples containing Joncryl increased with the reaction time, whilst PLA-PDI systems showed a decreasing trend in the yield strength with processing time. These results indicated consistency with intrinsic viscosity data, since molecular weight and yield strength are closely related to each other.

As shown in Fig. 7a, b that elongation at break decreased after processing due to chain scission of PLA. PDI slightly increased the deformability of the samples in tensile test independent from the reaction time and loading; whereas Joncryl remarkably increased the elongation at break at longer reaction times. When the chain extender loading was taken into account, neither PDI nor Joncryl showed significant differences at 1 and 3 % loadings.

Dynamic Mechanical Analysis (DMA)

Variation of the storage modulus (E') with respect to temperature is shown in Fig. 8a, b. It can be observed from the figure that the storage modulus curve has a plateau region for pristine-PLA, so called glassy region, before the glass transition temperature. A significant decrease in the modulus can be observed at around the glass transition temperature of the pristine-PLA. The modulus of rPLA at the lower temperature plateau region was found to be lower than the pristine-PLA. In addition, the onset temperature of modulus drop was observed at relatively lower values. This can be attributed to the lower molecular weight and glass transition temperature of rPLA due to the presence of oligomeric chains that may act as a plasticizer.

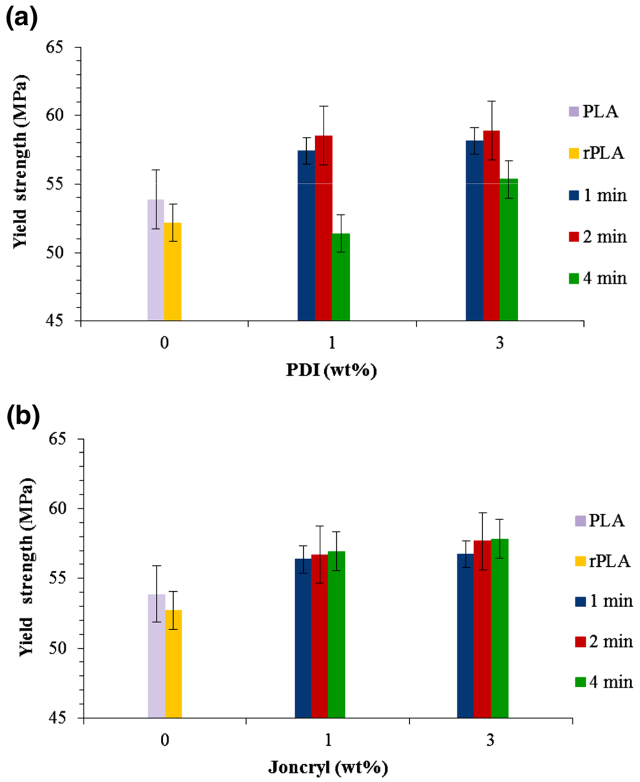


Fig. 6 Variation of yield strength of PLA, rPLA and modified PLA with respect to reaction time and chain extender content: **a** PDI and **b** Joncryl

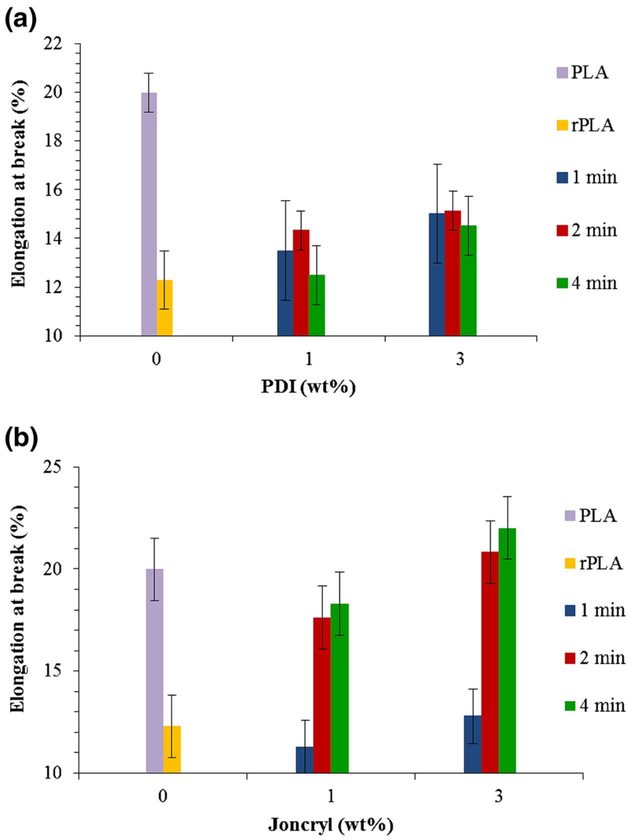
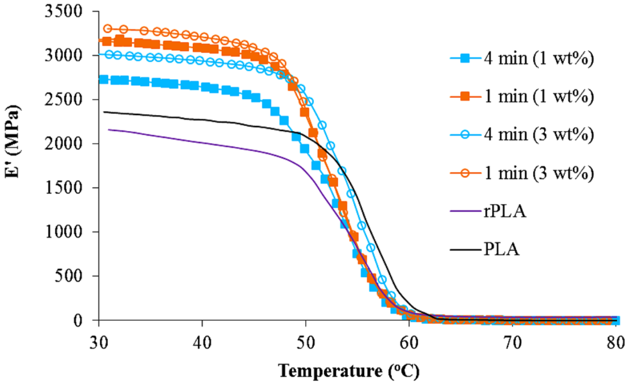
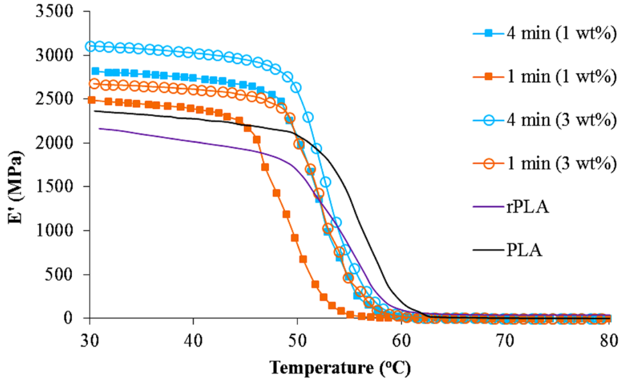


Fig. 7 Variation of elongation at break of PLA, rPLA and modified PLA with respect to reaction time and chain extender content: **a** PDI and **b** Joncryl

PDI-PLA systems exhibited higher storage modulus compared to the pristine-PLA and rPLA in the glassy region. The polar groups of PDI (isocyanates) and Joncryl (acrylates, epoxides) may increase the polarity of the PLA chains. The polar groups of the chain extenders may increase the hydrogen capability of the samples. Since glassy modulus of polymers is governed by molecular interactions such as van der Waals hydrogen bonds, the increased hydrogen bonding capability may improve the glassy modulus as a result of the chain extension. In addition, the increasing molecular weight as a result of chain extension and/or branching can also play a minor role in glassy modulus due to the increased chain entanglement density [34]. From the overall results, the highest modulus was observed in the sample at 3 wt% PDI loading, compounded for 1 min due to having the highest molecular weight, as already discussed in the intrinsic viscosity section. Joncryl-PLA systems exhibited higher storage modulus in the glassy region compared to PLA and rPLA and the sample at 3 wt% loading processed for 4 min had the highest value which showed a good agreement with the intrinsic viscosity data.



(a) PDI



(b) Joncryl

Fig. 8 Variation of storage modulus versus temperature for PLA, rPLA and modified PLA with respect to reaction time and chain extender content: **a** PDI and **b** Joncryl

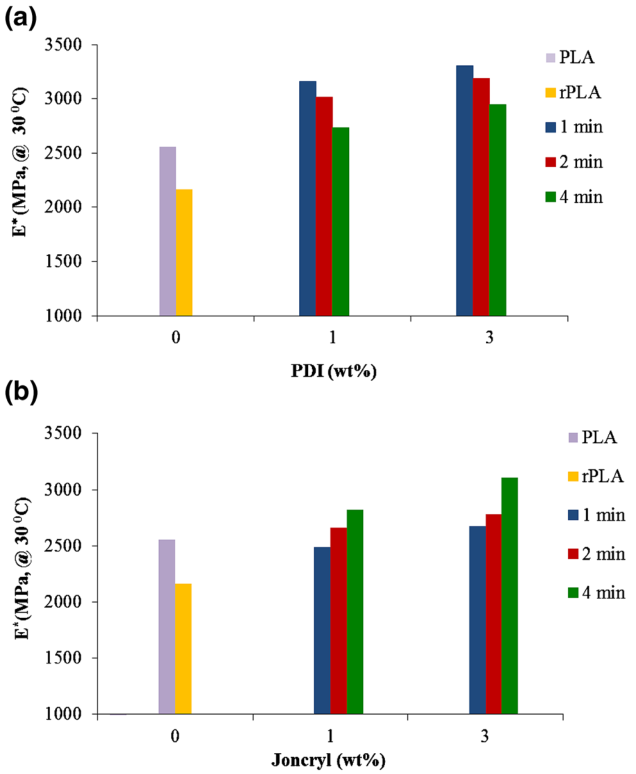


Fig. 9 Complex modulus (E*) at 30 °C for PLA, rPLA and modified PLA with **a** PDI, **b** Joncryl

Complex modulus of the samples at 30 °C reported in Fig. 9a, b. All chain extended samples showed higher complex modulus than the reprocessed PLA. Significant increment in the complex modulus of PLA-chain extender systems can be explained by chain extension and/or branching [35, 36]. The complex modulus of the PLA-chain extender systems over time showed consistency with intrinsic viscosity and tensile test data.

Rheological Properties

The storage modulus and complex viscosity of samples were assessed in the frequency sweep tests. In general, the polymers show different viscoelastic features during the frequency sweep tests. Low frequencies allow time to polymer for oscillation and responding therefore viscous properties become more dominant, while the elastic properties are dominant at higher frequencies [37]. Figure 10 shows the storage modulus as a function of frequency for rPLA and the samples containing 3 wt% chain extender. As a function of elastic properties, storage modulus increased with the frequency. It can be seen that storage modulus of Joncryl increased with reaction time, whereas PDI showed a decreasing trend due to the different reactivity of the chain extenders. As shown in Fig. 10b, Joncryl led to a stepper plot that can be explained by long chain branching [27].

Figure 11 shows that the curves of PLA and PLA containing PDI were overlapped due to linear chain structure of the samples. PLA-Joncryl system presented lower loss angle values at all frequencies with a different plot. These observations indicated different structures of the PLA-chain extender systems and can be concluded that PDI resulted in a linear structure, whereas Joncryl led to a branched structure PLA [27, 38].

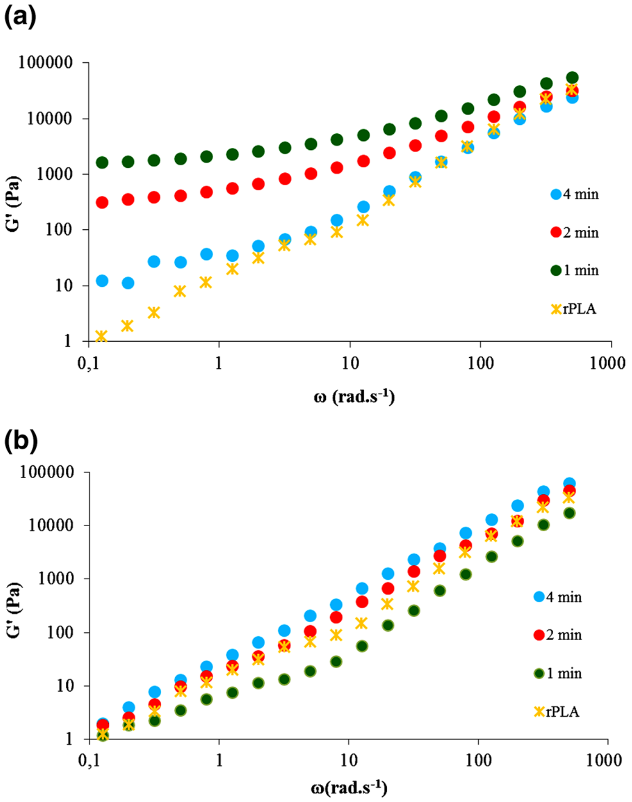


Fig. 10 Storage modulus as a function of frequency for rPLA and modified PLA with **a** PDI (3 wt%) and **b** Joncryl (3 wt%)

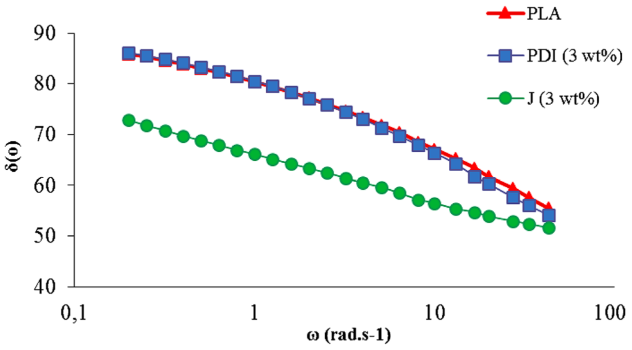


Fig. 11 Loss angle as a function of frequency for pristine PLA and modified PLA at 3 wt% chain extender loadings mixed for 2 min (J: Joncryl)

The decreasing trend of complex viscosity with increasing frequency is commonly referred as shear-thinning behavior and believed to arise from the stretching of the entangled state of polymer chains to the oriented state when the applied shear rate is higher than a certain critical

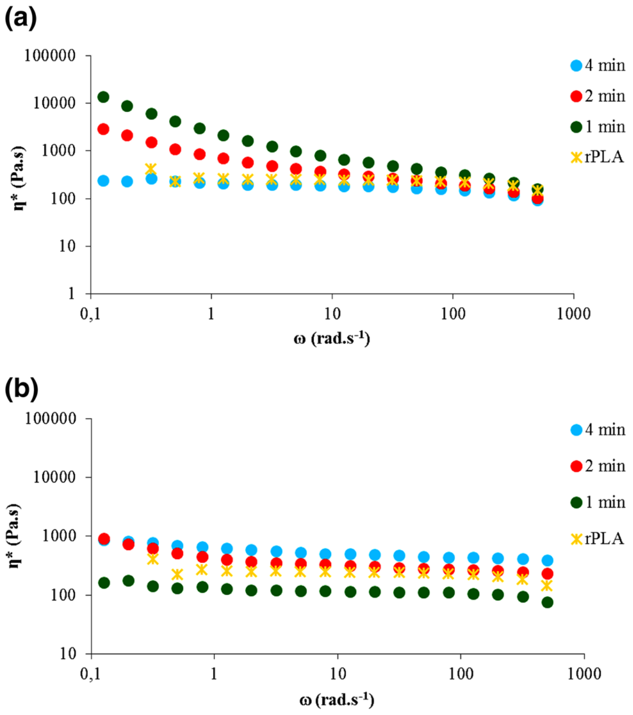
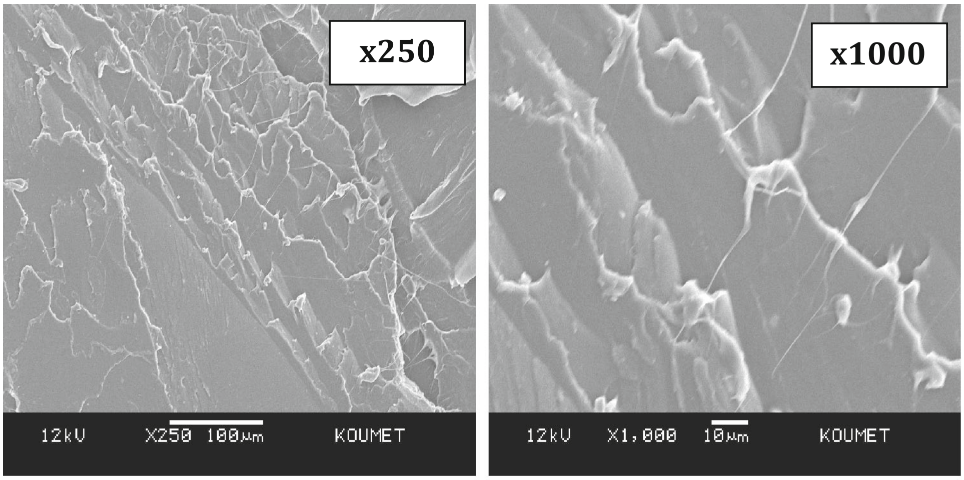


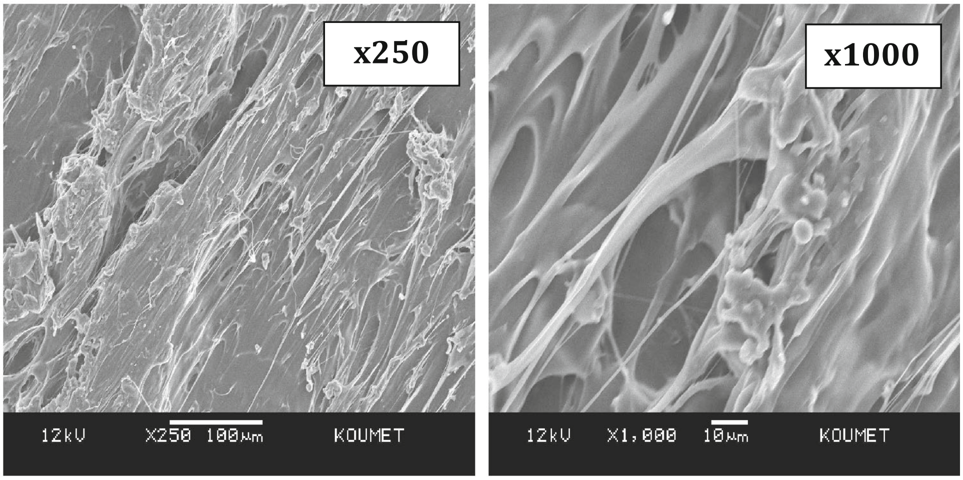
Fig. 12 Complex viscosity functions of frequency for rPLA and modified PLA with **a** PDI (3 wt%) and **b** Joncryl (3 wt%)

Table 1 Thermal properties of the samples

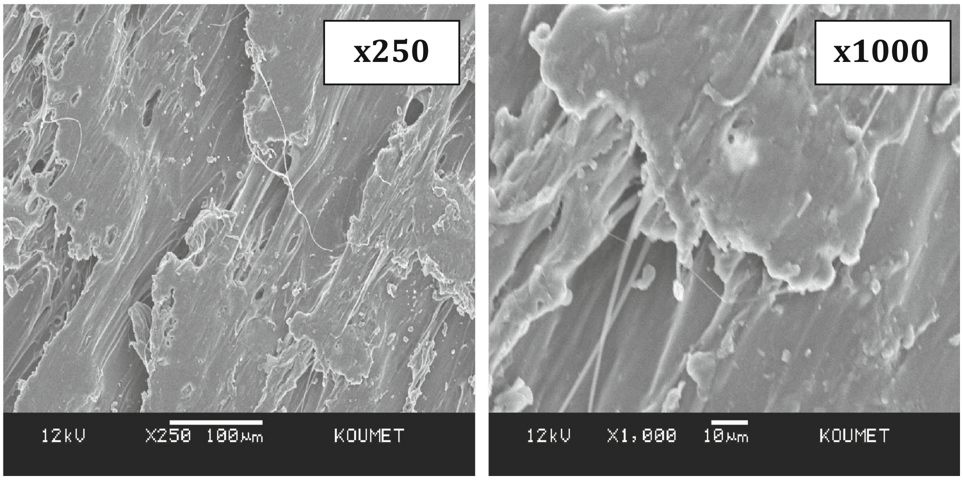
		Thermal transitions (°C)		
		T_g	T_{cc}	T_m
Chain Extender/Wt%	rPLA	59.7	117.8	148.6
PDI				
1 %	4 min	59.5	118.3	147.4
	2 min	59.7	118.9	148.2
	1 min	58.5	119.0	148.3
3 %	4 min	59.4	120.8	149.0
	2 min	60.2	121.3	149.8
	1 min	60.0	121.4	149.3
Joncryl				
1 %	4 min	59.5	119.4	148.1
	2 min	59.6	119.7	148.3
	1 min	59.3	118.5	148.4
3 %	4 min	59.7	123.4	149.0
	2 min	59.7	123.3	148.9
	1 min	59.4	122.7	147.6



(a) rPLA



(b) 3% PDI (1 min mixing)



(c) 3% Joncryl (4 min mixing)

Fig. 13 SEM micrographs of tensile fractured surfaces of rPLA and chain extended PLA samples

value. However, shear thinning behavior usually can not be observed for long chain branched polymers due to lower orientation [37, 39]. As seen in Fig. 12, PDI indicated shear-thinning behavior, while Joncryl did not show due to the chain branching. As a general trend, the complex viscosity of the samples containing Joncryl increased with the reaction time, whilst PDI decreased. This finding is in good agreement with the intrinsic viscosity, tensile test and DMA results.

Differential Scanning Calorimetry (DSC)

The thermal transition temperatures of the samples obtained from DSC analysis were summarized in Table 1. The glass transition (T_g) and melting temperature (T_m) of the samples did not significantly change suggesting that chain extension or matrix degradation did not influence the melting behaviour of the samples. Similar to that, the samples at 1 wt% chain extender loading did not show a remarkable change in the cold crystallization (T_{cc}) temperature regardless of chain extender type and mixing time. However, higher chain extender loading (3 wt%) retarded the cold crystallization behaviour of the samples and reflected larger crystallization temperatures. This can be atrributed to more kinetic energy requirement of the extended and/or branched PLA for crystal formation.

Fracture Morphology

Figure 13a–c represents the tensile fracture morphology of rPLA and chain extended PLA samples. The fracture surface of rPLA showed deep concavities and hackles due to multiple craze formation. It can also be observed from this sample that the fracture surface was smoother and more brittle than the other samples. The fracture surfaces of the samples containing PDI and Joncryl showed more plastic deformation, whereas rPLA indicated a less plastic deformation. The fractured surfaces of PLA-chain extender samples were covered with uneven fibrils, layers, and a number of microvoids. Therefore, this could be categorized as ductile fracture [40], because the fibrils presented on the fracture surface. Moreover, the fractures that were resulted in the fibrils less than 1 micron long can be considered as the brittle fracture [41]. These findings pointed that the brittle nature of rPLA shifted to ductile structure when molecular weight increased by chain extension during reprocessing or recycling.

Conclusion

The effects of a commercial multi-epoxide chain extender (Joncryl ADR-4368) and an isocyanate based chain extender (1,4-phenylene diisocynate) on the rheological, mechanical, thermal and morphological properties of recycled poly(lactic acid) (PLA) were investigated. On-line rheology measurements enabled to monitor thermal degradation and chain extension during melt processing. As expected, viscosity of PLA decreased during processing due to several external factors such as thermal degradation, oxidation and hydrolysis. The addition of the chain extenders led to increase in viscosity with recoupling of chain end groups. In the case of PDI, the viscosity of PLA showed a faster increase than Joncryl due to multifunctional structure of Joncryl. Intrinsic viscosity measurements, dynamic mechanical analysis, rheological and tensile test results revealed that the addition of the chain extenders compensated the degradation and increased the molecular weight of the samples. For both chain extender types, higher loading (3 wt%) was found to be the most efficient. The results also showed that the longest reaction time (4 min) for Joncryl exhibited the highest viscosity, modulus and strength values, while these were obtained at the shortest reaction time (1 min) for PDI. Cold crystallization temperature of PLA/chain extender systems increased with chain extender loading for both types suggesting that extended PLA chains need more kinetic energy for crystallization due to extended and/or branched chain structure. Fracture morphology of the samples showed that brittle structure of rPLA changed into the ductile structure due to molecular weight increase by chain extension.

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References

1. Nampoothiri KM, Nair NR, John RP (2010) Bioresour Technol 101:8493
2. Gumus S, Ozkoc G, Aytac A (2012) J Appl Polym Sci 123:2837
3. Rasal RM, Janorkar AV, Hirt E (2010) Prog Polym Sci 35:338
4. Lunt J (1998) Polym Degrad Stab 59:142
5. Lim LT, Auras R, Rubino MJ (2008) Prog Polym Sci 33:820
6. Bastioli C (2005) Handbook of biodegradable polymers. Rapra Technology, Shropshire
7. Carrasco F, Pagès P, Gámez-Pérez J, Santana OO, Maspoch ML (2010) Polym Degrad Stab 95:116
8. Signori F, Coltelli MB, Bronco S (2009) Polym Degrad Stab 94:74
9. Garlotta D (2001) J Polym Environ 9:63
10. Vink ETH, Rabago KR, Glassner DA, Gruber PR (2003) Polym Degrad Stab 80:403
11. Meng Q, Heuzey MC, Carreau PJ (2012) Polym Degrad Stab 97:2010
12. Al-Itry R, Lamnawar KS, Maazouz A (2012) Polym Degrad Stab 97:1898
13. Zenkiewicz M, Richert J, Rytlewsky P, Moraczewski K, Stepczynska M, Karasiewicz T (2009) Polym Testing 28:412
14. Badia JD, Strömberg E, Karlsson S, Ribes-Greus A (2012) Polym Degrad Stab 97:670
15. Pillin I, Montrelay N, Bourmaud A, Grohens Y (2008) Polym Degrad Stab 93:321
16. Pilla S, Kramschuster A, Yang L, Lee J, Gong S, Turng LS (2009) Mater Sci Eng 29:1258
17. Corre YM, Maazouz A, Duchet J, Reignier J (2011) J Supercrit Fluids 58:177

18. Raffa P, Coltelli MB, Savi S, Bianchi S, Castelvetro V (2012) React Funct Polym 72:50
19. Villalobos M, Awojulu A, Greeley T, Turco G, Deeter G (2006) Energy 31:3227
20. Awaja F, Pavel D (2005) Eur Polym J 41:2614
21. Incarnato L, Scarfato P, Maio LD, Acierno D (2000) Polymer 41:6825
22. Haralabakopoulos AA, Tsiourvas D, Paleos CM (1998) J Appl Polym Sci 71:2121
23. Daver F, Gupta RA, Kosior EN (2008) J Mater Process Technol 204:397
24. Karayannidis GP, Psalida EA (2000) J Appl Polym Sci 77:2206
25. Bikiaris DN, Karayannidis GP (1996) J Polym Sci, Part A: Polym Chem 34:1337
26. Awaja F, Daver F, Kosior EN (2004) Polym Eng Sci 44:1579
27. Najafi N, Heuzey MC, Carreau PJ, Adams PM (2012) Polym Degrad Stab 97:554
28. Najafi N, Heuzey MC, Carreau PJ (2012) Compos Sci Technol 72:608
29. Corre YM, Duchet JM, Reignier J, Maazouz A (2011) Rheol Acta 50:613
30. Karagoz S, Ozkoc G (2013) Polym Eng Sci 53:2183
31. Taubner V, Shishoo R (2001) J Appl Polym Sci 79:2128
32. Hyon SH, Jamshidi K, Ikada Y (1998) Polym Int 46:196
33. Wachsen O, Platkowski K, Reichert KH (1997) Polym Degrad Stab 57:87
34. Oommen Z, Groeninckx G, Thomas SJ (2000) J Polym Sci B Polym Phys 38:525
35. Liu J, Lou L, Yua W, Liao R, Li R (2010) Polymer 51:5186
36. Grosvenor MP, Staniforth JN (1996) Int J Pharm 135:103
37. C. D. Han, Rheology and Processing of Polymeric Materials Volume 1: Polymer rheology (Oxford University Press, New York, 2007)
38. Al-Itry R, Lamnawar K, Maazouz A (2014) Eur Polym J 58:90
39. Macosko CW (1994) Rheology: principles, measurements and applications. Wiley, New York
40. Jeevitha D, Amarnath K (2013) Colloid Surf B 101:126
41. Yew GH, Yusof MAM, Ishak MZA, Ishiaku US (2005) Polym Degrad Stab 90:488