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RESEARCH ARTICLE

Mechanical recycling simulation of polylactide using a chain extender

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Abstract

This work studied the commercial chain extender effectiveness on the mechanical recycling simulation of a pristine PLA using a single-screw extruder. We processed the material by two extrusion cycles to simulate a recycling process. In the second extrusion, part of the material was processed with chain extender and we evaluated its molecular weight, thermal degradation, melt flow index (MFI), thermal transitions, and mechanical properties. The molecular weight for the extruded neat PLA decreased and the MFI and crystallinity degree increased while the mechanical properties worsened. The onset thermal degradation occurred at lower temperature for the processed material. With the introduction of the chain extender, there was a recovery of properties with the increase in the polymer molecular weight, decrease in the MFI and crystallinity degree, and an improvement in both thermal stability and mechanical properties in relation to recycled PLA without this component.

KEYWORDS

biopolymers, extrusion, mechanical properties, recycling, thermal properties

1 | INTRODUCTION

The plastic industry is aware of the environmental issues as the petroleum-based plastics come from fossil resources and demand thousands of years to degrade. For this reason, there are many researches aiming to develop plastics from renewable resources with better properties. Poly(lactic acid) (PLA) is a bio-based plastic produced from lactic acid (LA) derived from corn or sugarcane.^[1,2] In comparison with other polymers, PLA production generates less net greenhouse gas (GHG) emission. Considering the corn growing, the net CO₂ uptake from the atmosphere and harnessed in the polymer is 1.83 kg CO₂ eq/kg PLA, while CO₂ emitted in PLA production leads to a net greenhouse gas (GHG) emission of 0.6 kg CO₂ eq/kg PLA^[3] in the entire process. This value is about four times less than the polyethylene terephthalate (PET) production, responsible for a net GHG emission of 2.2 kg CO₂ eq/kg PET.^[3]

However, bio-based polymers are not necessarily sustainable as it depends on how the material is discarded at the end of its usable life.^[4] PLA is biodegradable only under industrial composting conditions and unable to degrade in home composting.^[5] Due to the strict conditions of degradation, it is important to look for another waste reuse options as mechanical or chemical recycling.^[6–8]

According to ISO 15270-2008,^[9] mechanical recycling is the process in which plastics wastes are converted into products or secondary raw materials without significantly changing the material chemical structure. There are some necessary operations before the recycling process as decontamination of the waste polymer (pre-treatment), plastic identification to allow its separation and size reduction (grinding or shredding).^[9] The most common way to recycle a polymer is by extrusion.^[7]

PLA recycling is very sensible to the process conditions with expressive increase on the melt flow index, decrease

on the thermal stability and worsening on the mechanical properties after successive PLA extrusion process.^[6,8,10,11] Few works in the literature presented the use of a compound to improve the PLA properties during the recycling. Pillin et al.^[11] used the quinone stabilizer in mechanical recycling by injection molding to preserve the PLA molecular weight. Another good alternative to improve the recycled PLA properties could be the use of a chain extender. This compound is able to re-link chains of degraded polymers through the formation of a bridge between its functional groups and the degraded chain ends,^[12] increasing the polymer molecular weight and improving their properties.

Joncryl is a family of commercial chain extender, and some grades have been already used to improve the recycled PET properties.^[12–14] This chain extender is a multifunctional epoxy compound that can react with nucleophilic end groups -OH and -COOH of PLA, producing a polymer with high molecular weight.^[15]

Besides recycling process, Joncryl was also incorporated in pristine and unprocessed PLA, using a twin-screw extruder, according to previous works.^[16–18] The use of Joncryl in PLA was also reported for clay dispersion improvement in nanocomposites,^[19] for blend compatibilization,^[20] for an enhancement of PLA–ZnO nanocomposites properties,^[21] and in polymerization of LA using a chain extender.^[22] Usually, prior works used the twin-screw extruder or internal mixer for samples preparation by melting processing.

As presented above, previous published works have reported the use of chain extenders for pristine PLA, while this work aims to study the real effectiveness of the chain extender on the PLA recycling. Besides, our contribution is to reproduce the most common recycling condition, using a cheaper equipment, a single-screw extruder instead of a twin-screw machine.

2 | MATERIALS AND METHODS

In this study, we used polylactide (PLA) 4042D (NatureWorks®, USA). It has 4–8% of D-isomer and density of 1.24 g/cm³. In one of the mechanical recycling simulation steps, a commercial chain extender Joncryl ADR-4368, supplied by BASF, was incorporated (0.6 % weight) into the PLA.

2.1 | Recycling procedure

PLA pellets were dried for 12 hr at 80°C before processing. After, it was processed twice by extrusion in a single-screw extruder with a length/diameter ratio of 34 and diameter of 30 mm (Wortex Máquinas e Equipamentos Ltda, Brazil). The temperature of each zone is shown in Table 1. The screw rotation was 10 rpm. The extruded polymer was cooled in water and granulated. This material was divided into two

TABLE 1 Standard temperature profile

Feed throat	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6
45°C	180°C	190°C	200°C	200°C	190°C

parts, and before the second extrusion, we incorporated 0.6% by weight of the chain extender in one of them. We kept the same extrusion conditions for all steps.

To evaluate mechanical properties, samples were molded in an injection molding machine Thermo Scientific HAAKE Minijet II. The cylinder temperature was fixed at 188°C, the mold temperature was set at 47°C, the injection pressure was kept at 300 bars, and the back pressure was fixed at 200 bars. Before injection, we dried the pellets for 12 hr at 80°C. Specimens were injected to perform the Izod test and the tensile test, in which we used the type V, according to ASTM D638-10.^[23]

2.2 | PLA characterization

Molecular weight was monitored by Gel permeation chromatography (GPC) in a Viscotek GPC Max with refractive index detector VE3580 at 40°C using tetrahydrofuran (THF) as solvent. The calibration was conducted using polystyrene samples.

Melt flow index (MFI) data were obtained based on ASTM D1238-13^[24] in a MI-3 equipment manufactured by DSM–Instrumentação Científica Ltda. The temperature used was 190°C, and the weight was 2.16 kg.

TGA analyses were obtained in accordance with ASTM E2550-11^[25] in SDT 2960 Simultaneous DTA-TGA equipment from TA instruments. Samples of 5 mg were heated from room temperature to 600°C at 10°C/min using nitrogen gas flow rate of 40 mL/min

We conducted differential scanning calorimetry (DSC) analyses for extruded samples using DSC-2920 Modulated DSC equipment from TA Instruments. The thermal schedule was as follows: first cooling at 0°C for 5 min; first heating from 0 to 210°C, heating rate of 10°C/min, for 5 min at 210°C; second cooling from 210 to 0°C, heating rate of 5°C/min, for 5 min at 0°C; second heating from 0 to 210°C, heating rate of 10°C/min. We performed all tests under nitrogen atmosphere.

To evaluate the mechanical behavior, the tensile tests were performed in a MTS Alliance RT/5 equipment with a 1000 N load cell, according to ASTM D638-10,^[23] using injected specimens type V. The speed test was 1 mm/min. In addition, we conducted the Izod tests in accordance with ASTM D256-10,^[26] using an impact pendulum EMIC model AIC 1 of 2.7 J. The results obtained in the tensile test and Izod test were submitted to the Student's t test, considering a significance level of 0.05, to evaluate these properties variation with the extrusion number and the addition of a chain extender.

3 | RESULTS AND DISCUSSIONS

Table 2 shows the results of MFI and GPC analyses. We can observe in Figure 1 that the MFI increases and varies linearly with the number of extrusion. The same behavior was also observed in the literature by Zenkiewicz et al. and Wang et al.^[6,27] The increase in extrusion cycles enhances polymer degradation and decreases viscosity. During the extrusion, the melt is exposed to shear and elongational deformations for a long time and the residence time is an important parameter that is more influenced by the throughput of polymer than by the extruder screw speed.^[27] The second extrusion can be considered as mechanical recycling simulation where the PLA is exposed to an extra residence time and submitted to an increased shear and elongational deformations. PLA extruded twice shows a MFI of 34 g/10 min, an increase of almost 62% in comparison with PLA extruded once, which presents a MFI of 21 g/10 min. It is important to point out that the type of extruder can influence polymer degradation as well. The shear stress applied by a counter-rotating extruder is typically greater than the single-screw extruder, considering residence times close for both, what means that different results could be found depending of the screw configuration.^[28]

The increase in PLA extrusions leads to molecular degradation and decreases the number-average molecular weight (M_n) as well as the weight-average molecular weight (M_w). Figure 2 shows that M_n and M_w decrease with the number of extrusions as a second-degree polynomial.

PLA extruded twice decreases the M_n almost 21% and M_w 14% in comparison with PLA extruded once. However, the use of the chain extender recovers the polymer molecular weight. The sample extruded with Joncryl decreases MFI almost 68% in comparison with PLA processed twice and also presents M_n and M_w very close to the unprocessed PLA. The increase in shear viscosity was also related for rheological properties measurements and was attributed to the chain extension and/or chain branching, which creates more entanglements by longer and heavier chains.^[16]

The decrease in MFI observed here is comparable to reported for stereocomplex PLA in the presence of 1% of Joncryl.^[29] The effectiveness of the Joncryl ADR 4368 was confirmed for PLA recycling as both molecular weight and

MFI recovered the same values of the pristine material. These are important results considering the existing competition between the chain extension and the thermal and shear degradation during the processing.^[29]

Due to the thermal and shear degradation, the chain size of PLA extruded twice is lower than PLA processed once, which produces little chains with more chain ends, such as carboxyl and/or hydroxyl. These chain ends cause transesterification and backbiting reactions that induce random degradation and unzipping depolymerization.^[11] In turn, the chain extender acts to re-link chains of the degraded PLA through the formation of a bridge between its epoxy functional groups and the carboxyl and/or the hydroxyl groups of PLA.^[12,15]

PLA polydispersity index (PDI) increases significantly with the extrusion number as we can see in Table 2, due to its degradation. The PLA thermal degradation velocity is greater when the temperature is higher than 180°C, which causes the decrease in M_n .^[27,30] According to Yu et al.,^[30] the enhance or drop of the processing temperature influences the number-average molecular weight and the PDI. During the extrusion process, some chains are degraded to short length and others do not degrade, remaining as long chains. In mechanical recycling, the thermal degradation is worse as the polymer is submitted to more thermal and shear stress in comparison with the first extrusion. This causes even more random scission of bonds and more amount of shorter chain length.

The molecular weight distribution curves of the samples are shown in Figure 3. As we can see, these curves move to the left with extrusion number. This happens due to the chain thermal degradation during the extrusion process, which causes the formation of smaller molecules, in relation to unprocessed PLA.

The PDI of PLA extruded twice with Joncryl increases 24% in relation to PDI of PLA extruded twice. Furthermore, in Figure 3, it is shown that the enlargement of PLA extruded with Joncryl molecular weight distribution curve. This leads to a formation of a significant amount of larger size chains, according to the right side of the curve, in comparison with unprocessed PLA. Joncryl increases the weight fraction of molecules with higher molecular weight, which contributes to PDI increase. Some authors suggest that Joncryl raises the presence of branches at PLA chain to recover the chain size, which increases the polymer molecular weight.^[16,31,32]

TABLE 2 Results of GPC and melt flow index.

Extrusion number	M_n (g/mol)	M_w (g/mol)	PDI	Melt flow index (g/10 min)	Degradation parameter (k)
Unprocessed PLA	111,000	183,000	1.6	8 ± 1	–
PLA extruded once	80,000	132,000	1.7	21 ± 1	1.39
PLA extruded twice	63,000	114,000	1.8	34 ± 2	1.76
PLA extruded twice with Joncryl	88,000	197,000	2.2	11 ± 1	1.26

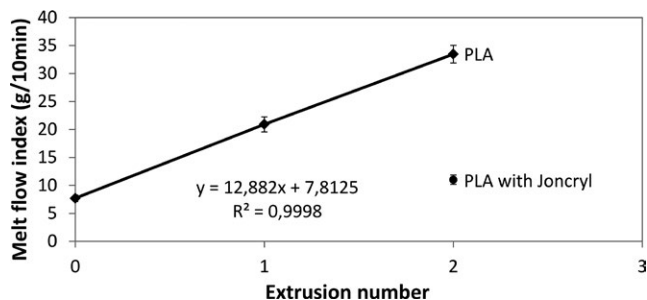


FIGURE 1 Melt flow index at 190°C as a function of two extrusion cycles [Colour figure can be viewed at wileyonlinelibrary.com]

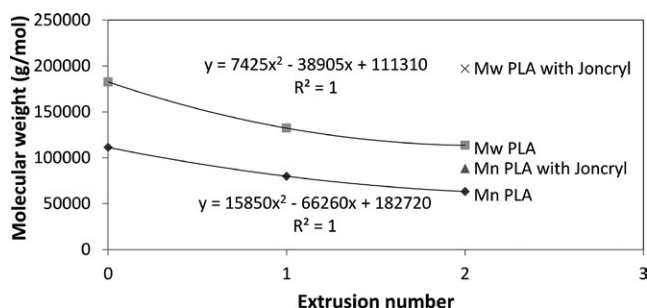


FIGURE 2 Molecular weight (M_n and M_w) of PLA as a function of two extrusion cycles [Colour figure can be viewed at wileyonlinelibrary.com]

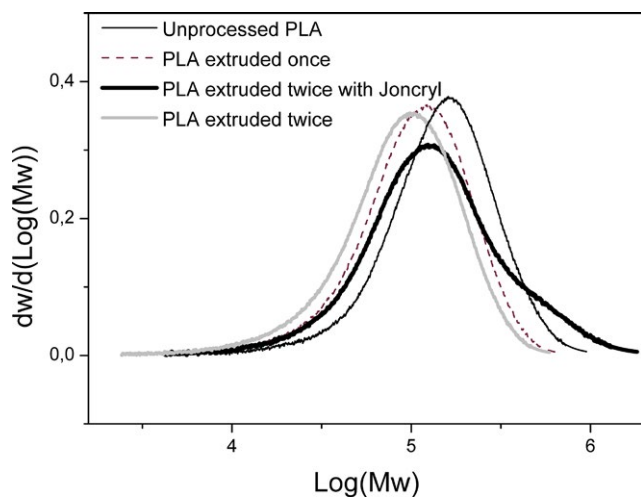


FIGURE 3 GPC curves of PLA processed

Degradation parameter (k) is defined as a ratio between M_n of raw material and M_n of processed material.^[33] The chain extender effect can be also confirmed by k . The PLA extruded twice presented the greatest degradation parameter (1.76), and the sample processed with Joncryl showed the lowest degradation parameter (1.26), vide Table 2.

To evaluate the average number of chains that underwent a process of scission as a function of unprocessed

PLA molecular weight (MWi), we used the method of the chain scission distribution function (CSDF),^[34] as shown in Figure 4. As we can see, PLA extruded once presents an increase in CSDF for very low molecular weight region and very high molecular weight region. For intermediate molecular weight values, there is no slope region, which means that chain scissions are independent of initial molecular weight.^[35] PLA extruded twice exhibits a different behavior due to the decrease in CSDF with initial molecular weight, but an increase in CSDF can be noticed for very high molecular weight. The chain extender presence in PLA extruded twice causes a decrease in CSDF with initial molecular weight and this curve presents a negative slope. There is a part of the PLA extruded twice with Joncryl CSDF curve that crosses the zero line and goes into the negative region due to the formation of much branched molecules with high molecular weight.

The PLA thermal degradation consists of random main-chain scission and unzipping depolymerization reactions. The scission reaction occurs via hydrolysis, oxidative degradation, cis-elimination and also via intramolecular and intermolecular transesterification. This process is increased by active chain-end groups, residual catalysts, residual monomers and other impurities. Thus, the PLA melt processing at high temperatures results in undesirable molecular weight reduction and weight loss.^[1,36]

PLA thermal stability after melt processing was studied by TGA. Table 3 shows the results of TGA analyses, and Figure 5 shows the TGA profile of unprocessed PLA. T_{onset} represents the material thermal stability. All the samples exhibited the same TGA profile.

The first extrusion decreases 2°C in T_{onset} in relation to unprocessed PLA, while the second extrusion reduces 5°C. PLA degradation is caused by the presence of little polymer chains, which means a large number of chain ends per mass.

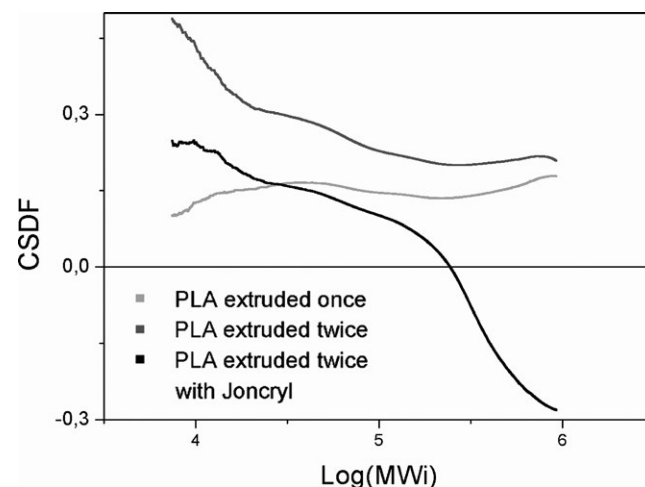
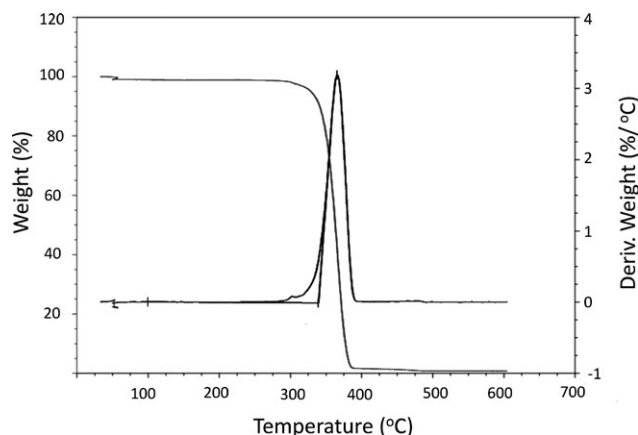


FIGURE 4 Chain scission distribution function (CSDF) of PLA after two extrusions

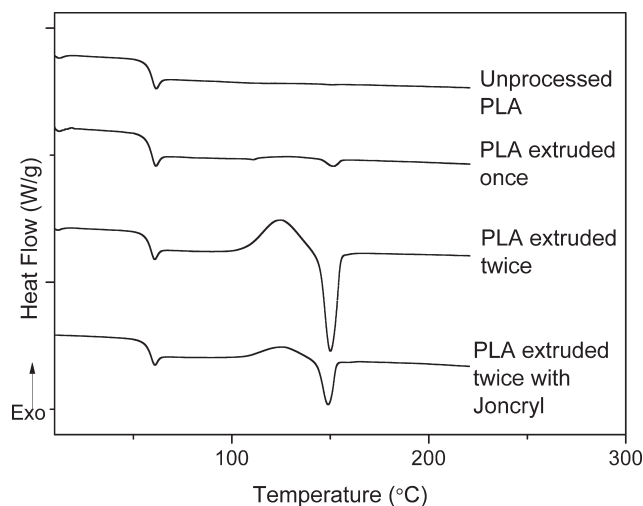
TABLE 3 Temperatures obtained at TGA test.

Sample	T_{onset} (°C)	T_{peak} (°C)
Unprocessed PLA	348	365
PLA extruded once	346	365
PLA extruded twice	343	361
PLA extruded twice with Joncryl	347	365

**FIGURE 5** TGA profile of unprocessed PLA [Colour figure can be viewed at [wileyonlinelibrary.com](#)]

These chain ends promote depolymerization by intramolecular transesterification in temperature extent from 270 to 360°C.^[15] In mechanical recycling by extrusion, the thermal degradation is even worse than the first extrusion and it is increased by enhancing the number of extrusion processing.^[6] The presence of Joncryl in the PLA extruded twice increased T_{onset} of 4°C in relation to PLA extruded twice without chain extender. Joncryl reacts with the chain ends, which reduces the available carboxyl and hydroxyl groups and avoids the depolymerization and intramolecular transesterification. Table 3 also presents the peak temperature (T_{peak}), which does not vary with the extrusion number.

The DSC profiles at second heating are presented in Figure 6. PLA may be amorphous or semicrystalline depending on its stereochemical structure and thermal history.^[11] As we can see in Figure 6, PLA 4042D is mainly amorphous with prior thermal treatments at a cooling rate of 5°C/min. Table 4 shows the results for the second heating of the DSC analyses. The glass transition temperature (T_g) is not modified by the

**FIGURE 6** DSC profiles of second heating [Colour figure can be viewed at [wileyonlinelibrary.com](#)]

number of extrusions. However, cold crystallization temperature (T_{cc}) and melting temperature (T_m) of the extruded PLA slightly decrease. Other researchers also obtained the same results.^[6] According to Saeidlou et al.,^[37] T_g can be influenced by molecular weight and optical isomers, as D-lactide formation and T_m are more influenced by molecular weight than T_g . For low M_n values, T_m increases due to the molecular weight increase until it reaches an asymptotical value at $M_n > 100$ kg/mol and T_{cc} decreases with T_m .^[37] This finding describes T_m behavior for the first and second extrusions. M_n , T_{cc} and T_m of PLA extruded twice decreased in comparison with PLA extruded once. The little decrease in T_m for PLA extruded twice with Joncryl suggests that the chain extender can cause chain branching and imperfect crystals.

The PLA degree of crystallinity (X_c) was calculated using the equation 1 and results of the second heating.

$$X_c(\%) = \left(\frac{\Delta H_m}{\Delta H_m^0} \right) \times 100 \quad (1)$$

Where ΔH_m is heat of melting and ΔH_m^0 is the ideal melting enthalpy ($\Delta H_m^0 = 93.6$ J/g).^[38]

The cold crystallization enthalpy was not considered in PLA degree of crystallinity because the overall crystallinity was the objective of the study, that is, the highest level of crystallinity that the material could achieve. The results were

TABLE 4 Results of DSC analyses of second heating.

Type of processing	T_g (°C)	T_{cc} (°C)	T_m (°C)	ΔH_{cc} (J/g)	ΔH_m (J/g)	X_c (%)
Unprocessed PLA	60	–	–	0.0	0.0	0
PLA extruded once	60	129	152	1.9	0.9	1
PLA extruded twice	59	125	150	20.5	20.7	22
PLA extruded twice with Joncryl	59	126	149	8.4	7.9	8

analyzed using second heating data to eliminate the polymer thermal history. As PLA presents mainly cold crystallization, it was highly amorphous under the cooling conditions used for DSC analysis. All crystallization processes may occur in second heating, and enthalpy of melting represents the energy required to melt these crystallites.

In some cases, as we can see in Figure 6, the samples show the enthalpy of cold crystallization (ΔH_{cc}) greater than enthalpy of melting (ΔH_m). The ΔH_{cc} is higher than ΔH_m due to undefined separation processes of cold crystallization and melting, which results in a partial superposition of the relevant peaks.^[6] We observed that PLA extruded twice presents higher degree of crystallinity (X_c) than PLA extruded once. As discussed above, multiprocessing causes thermal and shear degradation of the chains, and these smaller molecules present an easier arrangement, which increases the polymer

crystallinity. PLA extruded with Joncryl shows a lower X_c than PLA extruded twice as expected, as the molecular weight is higher and possibly chain branching may be present.

The PLA recycling mechanical properties are shown in Figure 7. According to Student's t test, the Izod impact (Figure 7a) does not vary with the extrusion number as well as with the chain extender presence. This happens because PLA is below its T_g at room temperature, which creates chains without enough energy to acquire mobility and the polymer presents low ability to absorb impact energy.^[39]

Figure 7(b-d) presents the tensile tests results. The first extrusion does not change the tensile strength (Figure 7b) in relation to unprocessed PLA as well as comparing PLA extruded twice with and without a chain extender; this property does not vary, considering the Student's t test. A significant variation in tensile strength occurs in PLA extruded twice in

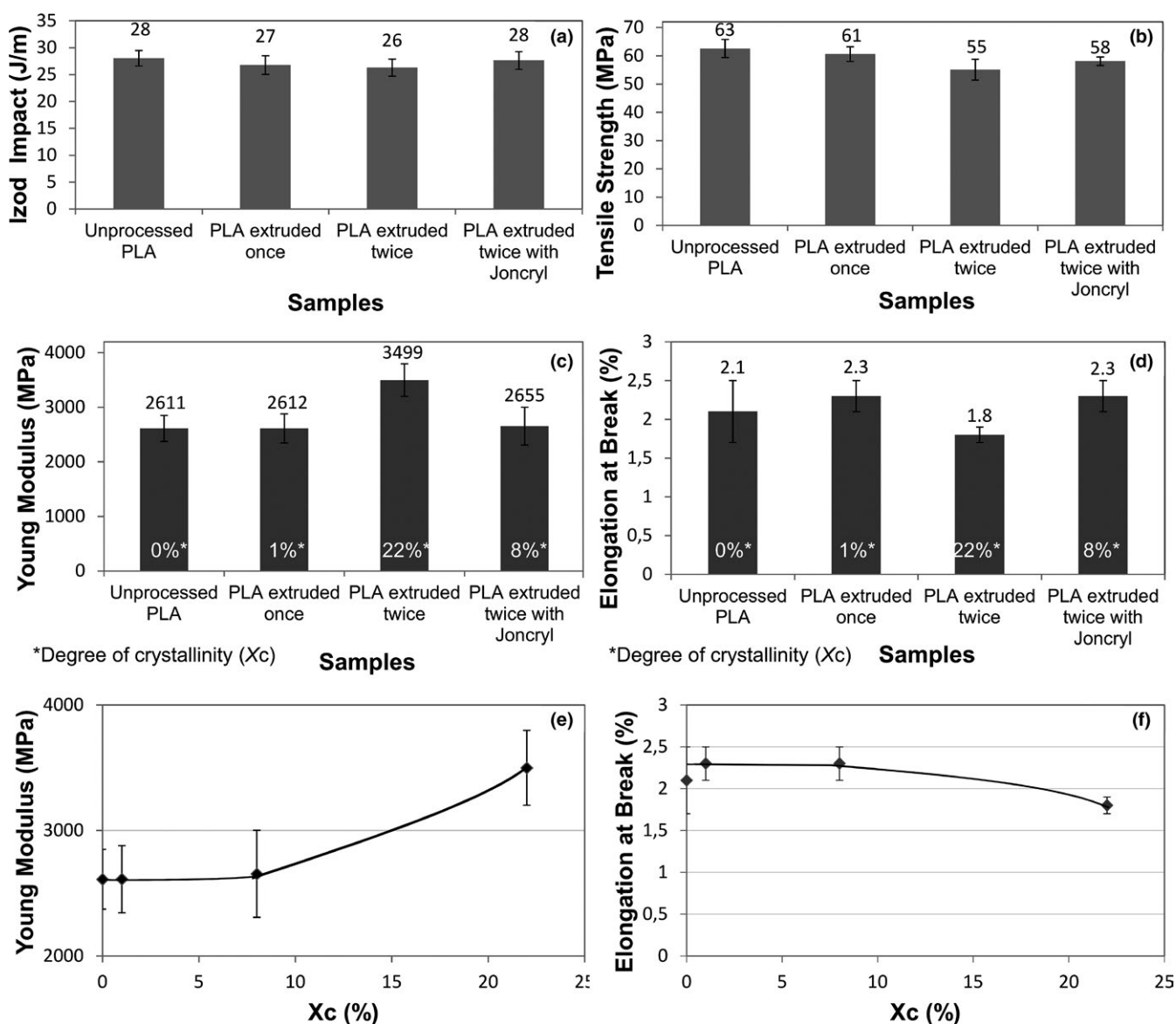


FIGURE 7 Mechanical properties: (a) impact resistance; (b) tensile strength; (c) Young's modulus; (d) elongation to break and mechanical properties of PLA as a function of X_c ; (e) Young's modulus; (f) elongation at break [Colour figure can be viewed at wileyonlinelibrary.com]

comparison with PLA extruded once. The second processing leads to an enhanced molecular degradation, which generates smaller molecules and raises the polydispersity index (vide Figure 3). The chain extender presence increases some molecules size, despite there are molecules that remain small, which causes an increase in polydispersity index. This molecular size variation causes a decrease in PLA extruded twice tensile strength with and without Joncryl in relation to PLA extruded once.

The first processing does not modify the Young's modulus (Figure 7c) in comparison with unprocessed PLA, which is in agreement with other authors.^[6,11] However, PLA extruded twice presents a considerable increase in Young's modulus in relation to PLA extruded once. PLA extruded twice presents a remarkable decrease in elongation at break (Figure 7d) in comparison with PLA extruded once and unprocessed PLA. Although PLA has T_g above the room temperature and its amorphous phase is fragile, it is interesting to correlate the mechanical properties to the crystallinity degree (X_c). Young's modulus (Figure 7e) and elongation at break (Figure 7f) do not vary with X_c until it reaches 8% of crystallinity. Above this value, the Young's modulus increases and elongation at break decreases with X_c . These results are in agreement to annealed samples, which the enhanced crystallinity causes an increase in Young's modulus and a decrease in elongation at break.^[10]

4 | CONCLUSIONS

The recycling process reproduced in a single-screw extruder showed that PLA was affected by thermal degradation during the extrusion, leading to a decrease in molecular weight (M_n and M_w), which caused an increase in melting flow index and crystallinity degree. The presence of Joncryl was able to recover the molecular weight although it caused an increase on the polydispersity, showing a change on the chain structure. These effects could be described by the chain scission distribution function (CSDF). The thermal properties presented slightly variation in agreement to this structure changing. The degree of crystallinity decreased with molecular weight and was responsible for Young's modulus and elongation at break results. The effectiveness of the Joncryl ADR 4368 was confirmed for PLA recycling using a usual single-screw extruder, as observed for the molecular weight, MFI and mechanical properties that recovered the values of the unprocessed material.

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