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Enhanced re-processability of poly (butylene adipate-co-terephthalate) (PBAT) via chain extension toward a more sustainable end-of-life

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Abstract

Poly (butylene adipate-co-terephthalate) (PBAT) is a biodegradable polymer recognized for its potential to reduce plastic waste due to its biodegradability and compostability. However, conventional end-of-life options for PBAT, such as composting and biodegradation, involve additional costs, require substantial space, and consume significant energy, which may not align with broader sustainability goals. Therefore, an alternative approach through recycling is highly desirable. This study investigates the recyclability of neat PBAT and Joncryl ADR 4468-modified PBAT with 0.5 wt% Joncryl, a multifunctional epoxy-based chain extender known to enhance the processing stability and properties of polymers. The research evaluates the tensile, flexural, thermal, and rheological properties of the materials after multiple injection molding cycles to provide comprehensive data on their performance under re-processing conditions. The results demonstrate that neat PBAT retains its tensile modulus with only a~ 6% reduction after seven cycles, while Joncryl-modified PBAT exhibits a 26% increase in modulus after five cycles, attributed to enhanced branching. Additionally, modified PBAT showed superior rheological stability and resistance to thermal degradation compared to unmodified PBAT. This study highlights the potential of mechanical recycling to extend the lifecycle of biodegradable polymers, reducing environmental impact and conserving resources.

Highlights

- 0.5% Joncryl enhances PBAT recyclability by preserving mechanical properties.
- Both PBAT and Joncryl-PBAT retain tensile strength, supporting recycling.
- Joncryl-PBAT resists degradation, showing stable modulus after reprocessing.
- Reprocessing raises crystallization temperature.
- Joncryl-PBAT maintains higher viscosity and modulus, resisting degradation.

KEYWORDS

injection molding, Joncryl, poly (butylene adipate-co-terephthalate) (PBAT), recycling, re-processing

1 | INTRODUCTION

The increasing awareness of environmental issues has driven the demand for sustainable materials in various industries. One such material is poly (butylene adipate-co-terephthalate) (PBAT), a biodegradable polymer widely recognized for its potential in reducing plastic waste due to its biodegradability and composability.[1,2] However, the conventional end-of-life options for PBAT, such as composting and biodegradation,[3–6] involve additional costs, require substantial space, and consume significant energy, which may not align with the broader goals of sustainability. Therefore, an alternative approach to managing PBAT waste through recycling is highly desirable.[7] Recycling, especially mechanical recycling, offers a promising route to extend the lifecycle of polymers, thereby reducing environmental impact and conserving resources. Mechanical recycling involves reprocessing waste materials into new products without altering their chemical structure.[8–10] This method has been extensively applied to various conventional plastics, yet its application to biodegradable polymers like PBAT has been relatively underexplored. This becomes more important since PBAT is derived from fossil fuel resources, therefore, recycling can also reduce the carbon footprints during the PBAT production process.

On the other hand, the recycling of polymer wastes including biodegradable polymers presents unique challenges due to their susceptibility to degradation during thermal and mechanical processing. Studies have shown that repeated processing cycles can significantly impact the mechanical and thermal properties of biodegradable polymers. For instance, Agüero et al. investigated the recyclability of poly (lactic acid) (PLA) and found that repeated injection led to a reduction in the mechanical properties of PLA. More specifically the impact strength of PLA decreased from 57.8 ± 3.7 at unprocessed PLA to 31.1 ± 1.9 $kJ.m^{-2}$ at sixth injection cycle of PLA.[9] Similarly, research by Badia et al.[11] on PLA indicated that multiple (five) injection processing cycles resulted in tensile properties, highlighting the material's sensitivity to thermal degradation. Their study showed that the tensile modulus dropped ~28% after the third injection cycle at the fifth cycle. This is while the impact resistance remained unchanged after the first 10% drop in the first injection cycle. Main et al.[12] also investigated the effect of five times extrusions on the properties of polyhydroxybutyrates (PHBs). It was shown that impact strength of the virgin PHB substantially reduced from nearly ~5 kJ/m^2 to somewhat near ~2.5 kJ/m^2 after five extrusion times. This was revealed to be due to decrease in molecular weight of the PHB during each cycle primarily stemmed from chain scission degradations.

PBAT, as a biodegradable polymer, shares these challenges. Studies specific to PBAT are limited, but analogous research on other biodegradable polymers suggests similar trends. Studies noticed that mechanical properties deteriorated with each recycling cycle, primarily due to chain scission and thermal degradation. These findings urge the need for strategies to enhance the recyclability of PBAT, ensuring that its mechanical integrity is maintained over multiple processing cycles, remembering that PBAT is a synthetic biodegradable polymer from fossil-based origins.[13] This again highlights the increased need for mechanical recycling of PBAT to conserve renewable resources.

In this context, our study investigates the recyclability of neat PBAT and PBAT modified with the addition of 0.5 wt% Joncryl. Joncryl, an epoxy-functionalized chain extender, is widely used to enhance the performance of various polymers, including PBAT.[14–19] The mechanism by which Joncryl enhances polymer properties involves its reactive epoxy groups, which can form covalent bonds with polymer chains, thus increasing molecular weight and reducing chain scission during processing. This modification has been shown to improve the mechanical and thermal stability of polymers under multiple processing conditions.

Significant research has been conducted on the effects of Joncryl on PLA, providing insights that can be extrapolated to PBAT. Both PLA and PBAT are aliphatic polyesters, meaning they contain ester linkages in their molecular backbone. These ester groups are susceptible to hydrolysis and thermal degradation during processing, which can lead to chain scission.[17,18] Tang et al.[17] and Costa et al.[18] demonstrated that adding chain extenders (Joncryl) could enhance the PBAT molar mass and slow down the loss of mechanical properties during weathering due to the crosslinked structures. Although the efficiencies of such chain extenders in delaying the weathering and enhancing properties are explored, the extend to which they can affect the properties during mechanical recycling and re-processing is not fully acknowledged.

In relation to recycling, Ramos-Hernández et al.[20] reported that the addition of Joncryl to PLA resulted in an improved tensile strength after two extrusion cycles, demonstrating the chain extender's effectiveness in mitigating the adverse effects of thermal processing. They reported that adding Joncryl has hindered the degradation of PLA chains. Similarly, Cosate de Andrade et al.[21] found that Joncryl-modified PLA exhibited enhanced thermal stability and reduced viscosity degradation during processing. Standau et al.[22] confirmed that 1 wt% Joncryl represents the upper limit of efficient content in polyesters. It is also known that concentrations below 0.5 wt% can contribute somewhat to branching efficiency. To avoid excessive branching at higher concentrations or potential inefficiencies at lower concentrations, this study adopts a middle-limit approach by focusing on 0.5 wt% Joncryl. In this context, the study aims to evaluate the re-processability of neat and 0.5 wt% Joncryl-modified PBAT through multiple injection molding cycles. By assessing the tensile, flexural, thermal, and rheological properties of the materials after multiple injection cycles, we seek to provide comprehensive data on their performance under re-processing conditions. The focus is to determine whether Joncryl modification can mitigate the property loss typically observed in biodegradable polymers during repeated processing, thereby offering a more sustainable route for managing PBAT waste.

To simulate recycling conditions, both neat and modified PBAT specimens were subjected to multiple rounds of injection molding. Initially, the injection-molded specimens were granulated into small flakes using a granulating machine. These flakes were then fed into the next round of injection molding. This cycle was repeated several times to mimic the practical recycling process. After each round, the specimens were tested for their tensile, flexural, and rheological properties to monitor the changes in mechanical performance and processability. These tests provide insights into how the material properties evolve with each re-processing cycle, thereby indicating the feasibility of multiple recycling processes.

The focus on mechanical properties is crucial as these parameters determine the mechanical robustness and usability of the recycled material in various applications. Rheological properties, on the other hand, offer information about the flow behavior and processability of the polymer melts, which are critical for efficient manufacturing.

This research is significant in the broader context of sustainable materials management. By understanding the recyclability of PBAT and the potential benefits of Joncryl modification, this study aims to provide a more sustainable approach to managing PBAT waste. Enhanced recyclability means that PBAT can be processed multiple times with minimal degradation, reducing the need for new raw materials and decreasing environmental impact. By proving the efficacy of Joncryl-modified PBAT in maintaining its properties through multiple re-processing, we propose a viable alternative to traditional end-of-life options, aligning with the global pursuit of sustainability.

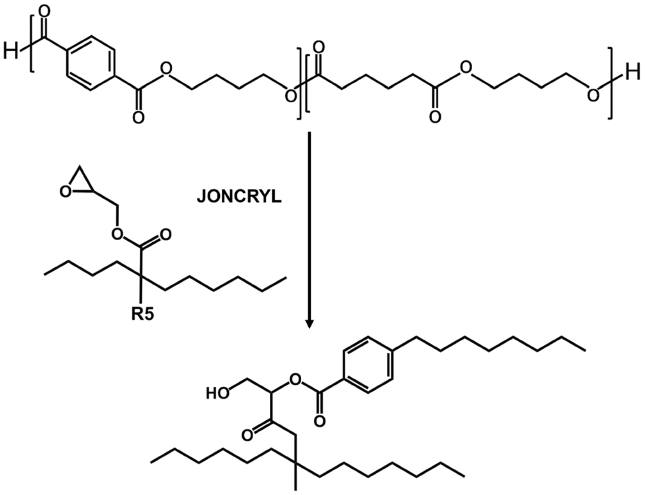
2 | MATERIALS AND METHODS

2.1 | Materials

Polybutylene adipate-co-terephthalate (PBAT) ecoflex® F Blend C1200 was kindly supplied by BASF Corporation (USA). The commercial grade is characterized by a density of 1.25–1.27 g/cm^3 and a melt flow index of 2.7–4.9 g/10 min at 190°C. Chain extender was used as a functional additive Joncryl® ADR 4468 (CAS number: 106-91-2) kindly supplied by BASF Corporation (USA). Chemical structures of PBAT, Joncryl, and their possible reaction mechanism are shown in Scheme 1.[16]

2.2 | Polymer Processing

Prior to injection molding, polymer was dried for 4 h at 60°C in an oven to remove any absorbed moisture. PBAT polymer pellets were processed with the help of injection molding using a Billion 50T injection molding machine at mold temperature of 60°C. The temperature profile was set to 145–185°C from feeder to nozzle respectively. Sample preparation for each round was divided into pure PBAT and PBAT with Joncryl. The modified PBAT, labeled as branched (B)PBAT consisted of the Joncryl additive (0.5 wt% proportion). In every round, nearly 10 tensile and flexural tests samples were



SCHEME 1 Chemical structure of PBAT, Joncryl, and their proposed reaction mechanism according to Al-Itry et al.[16]

produced. After every test, the remaining product was granulated using a granulator machine where further injection molded into test specimens. Unmodified PBAT, labeled as linear (L)PBAT was injection molded up to seven times, however, modified (B)PBAT could only be injection molded up to five times since the sizes of fifth-time granulated (B)PBAT flakes were not capable of going through further injection cycles using the same conditions. It was only possible to re-process a small amount to do the rheological and thermal tests of (B)PBAT for the sixth round.

2.3 | Mechanical testing

The fabricated samples were placed in Desiccators to remain dry for nearly 24 h prior to every test round. For tensile tests, Zwick 50 kN tensile tester with computer control was used for the dumbbell specimens according to ASTM D638. The crosshead speed was set to 300 mm/min with an elongation limit up to 600%. The results were generated using the average of 10 test specimens.

The bend test was carried out on Lloyd tensile tester with the bend test rig and the speed was set to 1 mm/s for each test round with a span of 25 mm. The test was conducted following ASTM D790 standard. The machine was equipped with a load cell of 2 kN and the crosshead speed was set at 1 mm/s. The experimental procedure is similar to the tensile strength testing. The only difference is the load application, maximum flexural strength, flexural stress, elongation, and flexural strain. At the beam center, vertical bending load was applied, and the test specimen is 10 mm width, and 4 mm thick. The results were generated using the average of 10 test specimens.

In order to analyze the effect of re-processing cycles on the thermal properties of modified and unmodified PBAT, the differential scanning calorimetry (DSC) tests were carried out using a DSC Q200 (TA Instrument) under a nitrogen atmosphere. Specimens weighing between 5 and10 mg were prepared and subjected to a heating process from 0 to 160°C at a heating rate of 10°C/min. Subsequently, the samples were cooled to 0°C at a cooling rate of 10°C/min. The DSC analysis allowed the determination of several thermal properties, melt crystallization temperature (T_c), melting temperature (T_m), and the heats of melting (ΔH_m) and crystallization (ΔH_c). Additionally, the degree of crystallinity of PBAT, denoted as $\%X_c$ was calculated using the following equation:

$$X_c\,(\%\text{crystallinity}) = \frac{\Delta H_m}{\Delta H_m^0\,\text{Ø}_{\text{PBAT}}} \times 100,$$

where ΔH_m^0 is the heat of fusion of 100% crystalline PBAT which is reported as $114\,\mathrm{J\,g^{-1}}$ and Ø_{PBAT} is the weight fraction of PBAT in Joncryl-modified PBAT samples.[15,16]

Rheological measurements were carried out using an ARES-G2 rheometer (TA Instrument) with a 25 mm parallel plate geometry at 180°C under a nitrogen atmosphere. Linear viscoelastic (LVE) properties were studied using frequency sweep tests from frequency (ω) 0.1 to 100 rad/s and at a strain amplitude of 1%. LVE regions were detected from strain amplitude tests at a frequency of 1 rad/s from 0.1% to 1000%.

Samples labeled as (L) or (B) PBAT_*Rn* where *R* stands for Round and *n* indicates the number of re-processing. For instance, (L)PBAT_R4 represents unmodified PBAT which is re-processed 4 times.

3 | RESULTS AND DISCUSSION

3.1 | Mechanical properties

The tensile properties of (L)PBAT and (B)PBAT were assessed at room temperature. The determined parameters were Young's modulus (MPa), and tensile strength (MPa). Figure 1 shows the effect of injection cycles on the tensile properties of PBAT.

During the tensile tests the samples elongated to the maximum set limit (600%) and did not undergo failure. The most common modulus of elasticity ranged from 53 to 57 MPa, showing consistency. In order to examine the applicability of the re-processed/recycled PBAT, the mechanical properties were evaluated during each injection cycle. The results from Figure 1, shows that tensile moduli and strength of the recycled (L)PBAT remained somewhat consistent with only a gradual insignificant decrease of ~6% and ~ 7% in modulus and strength after seven injection cycles.

This is in contrast to the results of Badia et al.[11] where a ~ 28% decrease in modulus of PLA was observed after five5 injection cycles. The authors claimed that the reduction in mechanical properties was primarily due to chain scission mechanism imposed on the molecular structure of PLA during re-processing cycle. However, Pillin et al.[23] reported similar trend with the current study with PBAT in modulus of the PLA where the moduli of the PLA remained constant after seven injection cycles. They stated that molecular weight reduction is compensated with an enhanced crystallinity, therefore, the strength is unchanged within the elastic deformation regions. The current study's result indicates that PBAT can be considered a recyclable material with minimal changes in

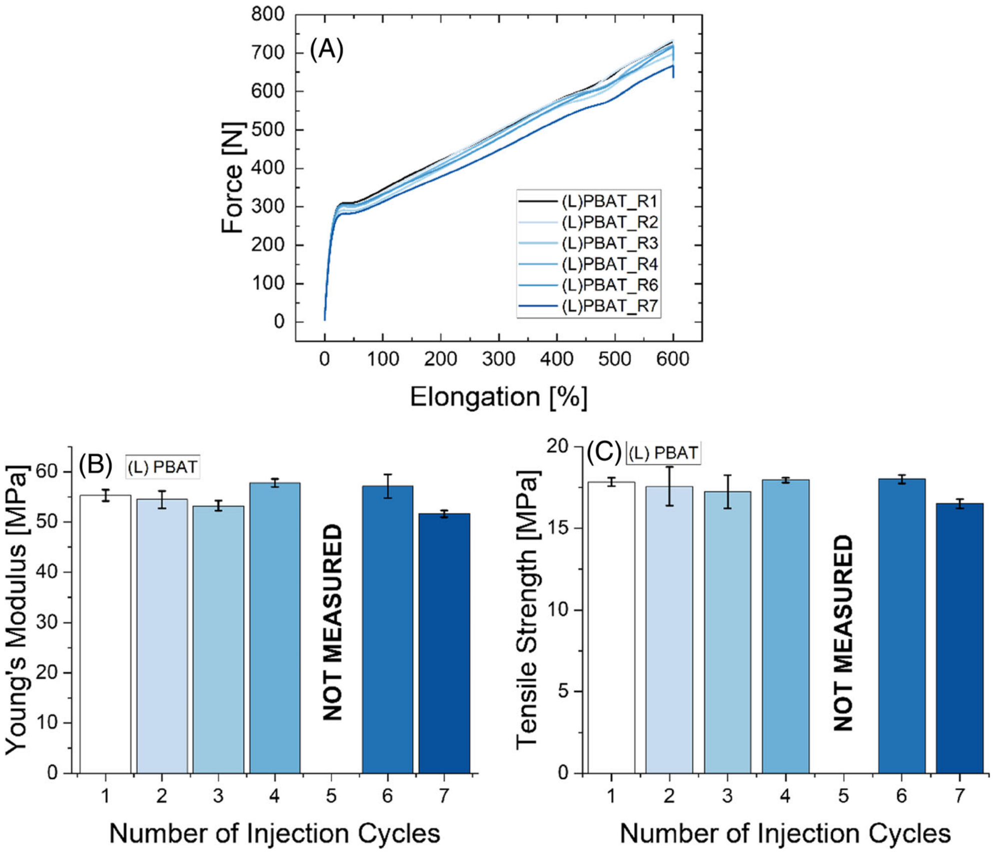


FIGURE 1 (A) Tensile curves, (B) Young's modulus, and (C) tensile strength of the unmodified (L)PBAT at different injection cycles.

tensile strength and modulus. However, it must be noted that in the current tests, specimens did not fail, therefore, we can not specify the changes that might have happened at break. This is in agreement with the results reported by Nomadolo et al.[24] where they reported that tensile strength and strain at break of PBAT remained steady up to seven reprocessing/recycling rounds.

Now that we demonstrated that PBAT can be considered an alternative material with stable properties after reprocessing, it should be noted that these experiments are carried out in controlled conditions where the chances of weathering upon exposure to UV light and degradation due to hydrolysis from humidity are ruled out. It is due to such conditions that polyesters are often modified with chain extenders to compensate the molecular weight reductions due to thermally induced degradation at higher processing temperatures.[17,18] Therefore, as far as recycling concerned, it is necessary to observe the effects of reprocessing cycles on the properties of modified (B)PBAT with chain extenders, Joncryl® ADR 4468, here. Hence, Figure 2. shows the effect of 0.5 wt% Joncryl on the tensile properties of PBAT when subjected to multiple injection molding cycles. It is interesting to note that modulus and tensile strength of the modified (B)PBAT (Figure 2B, C) are like those of unmodified (L)PBAT (Figure 1B, C) at first injection cycle, ~55 and 17.8 MPa respectively. This is in accordance with the results of Tang et al.[17] where they also observed no change in tensile strength of PBAT when Joncryl® ADR 4370 was added up to 1.5 wt%. However, the difference manifests itself in the gradual increase in the modulus of modified (B)PBAT after reprocessing where Young's modulus was increased nearly 27% after five times injection. ANOVA indicated that this increment was statistically significant ($p < 0.05$).

This could be due to the fact that Joncryl residual within the PBAT gradually reacts with PBAT molecules during each injection cycle. It should be remembered that polymers residence time in injection molding process is relatively shorter than in an extruder, hence, it is expected that unreacted Joncryl would participate in branching reactions in the next injection cycle.

Furthermore, crosslinking between polymer chains can boost polymer strength. It may be stated that branching inhibits the mobility of the chains, requiring additional stress to distort the material. It means there occurred branching between the PBAT and additive molecules which then leads to the increase in strength of the polymer blend. This indicates that (B)PBAT modified with Joncryl is stiffer and less flexible than unmodified (L)PBAT. This is the reason why, unlike the (L)PBAT, the re-processed modified (B)PBAT eventually broke before the set limit (Figure 2D).

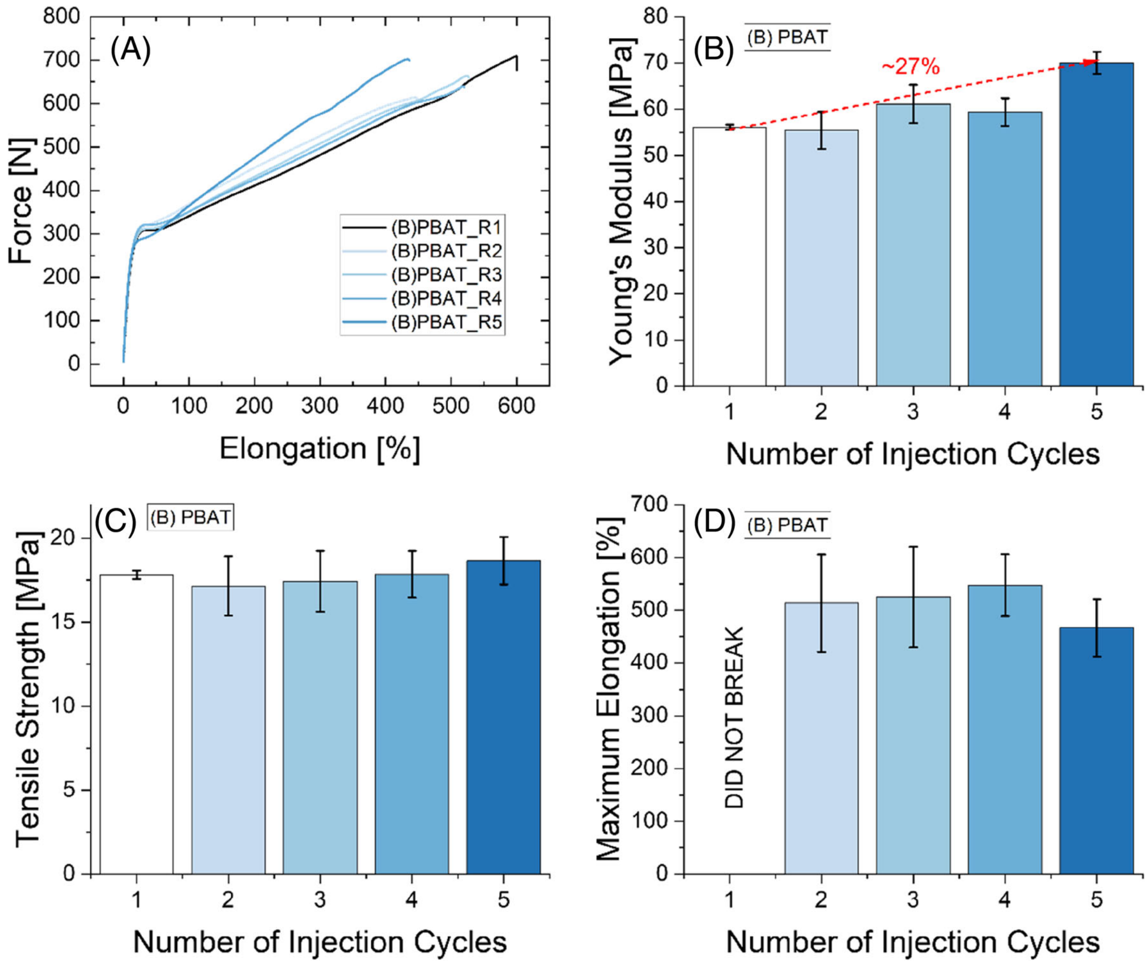


FIGURE 2 (A) Tensile curves, (B) Young's modulus, (C) tensile strength, and (D) elongation at break of the Joncryl modified (B)PBAT as a function of number of injection cycles.

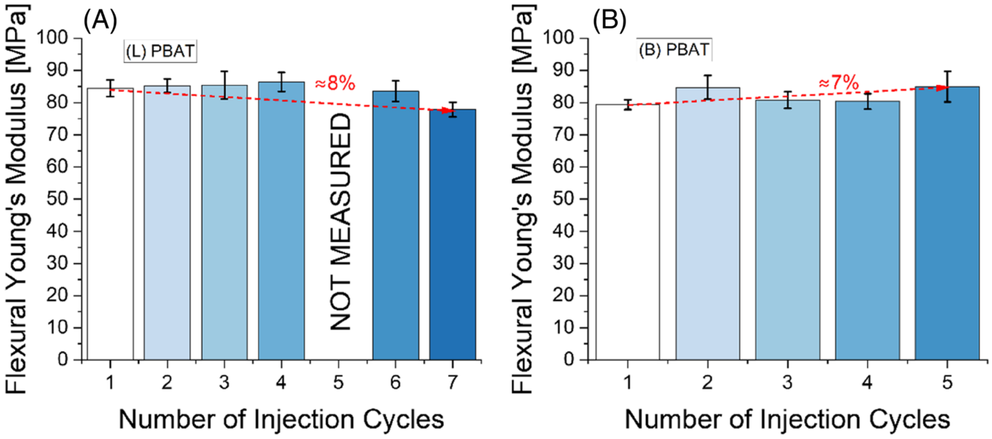


FIGURE 3 Flexural moduli of the (A) unmodified (L)PBAT and (B) Joncryl modified (B) PBAT polymers as a function of number of injection cycles.

Furthermore, the three-point bending test was carried out to determine the flexural strength on standard beam specimens. Flexural Young's modulus ranged between 77 and 89 MPa. Figure 3 shows the comparison of (L) PBAT and modified (B)PBAT based on Young's modulus of bending versus number of injection cycles.

The Young's modulus of bending of (L)PBAT decreased (84.489–77.867 MPa) after seven rounds of re-processing as seen in the graph. The result here indicates the flexural modulus of (L)PBAT is decreased after seven rounds of re-processing. Although both exhibit relatively steady behavior, the trend in neat (L)PBAT (Figure 3A) appears to be descending, as ANOVA indicated that the difference in moduli between the first and seventh cycles is statistically significant. In contrast, modified (B)PBAT (Figure 3B) shows more stable results across five injection cycles, with ANOVA indicating that the differences are not statistically significant ($p > 0.05$).

3.2 | Rheological analysis

Thus far, it has been deduced that PBAT can alternatively be recycled as the mechanical properties showed no significant changes after each cycle. On the other hand, modified (B)PBAT demonstrated improved properties even after simulated recycling conditions, promising a durable product even after re-processing where the elongation is still within reasonably high values ≥500% at the high tensile speed of 300 mm/min. Despite previous studies reporting similar steady trends in mechanical properties after re-processing steps; concurrently it is shown that a substantial increase in melt flow index MFI of PBAT (@2.16 kg and 160°C), ~92%, after the seventh re-processing cycle considering that their studies involved extruding the materials multiple times and each time injection molded into final testing specimens.[24] That is, the main changes observed were in the melt strength and viscosity, which occur primarily due to molecular-level degradation when the material is in its molten state. This means that the material's flow behavior and melt strength are impacted more by how the molecules break down and interact. Similarly, in this study, the rheological properties of neat and modified (B)PBAT and their re-processed counterparts have been considered to have better insight into molecular level degradation after each re-processing cycle. Figure 4 shows storage modulus G' (ω) and complex viscosities $\eta^*(\omega)$ of unmodified (L) PBAT (Figure 4A, C) and modified (B)PBAT (Figure 4B, D) and their corresponding re-processed counterparts.

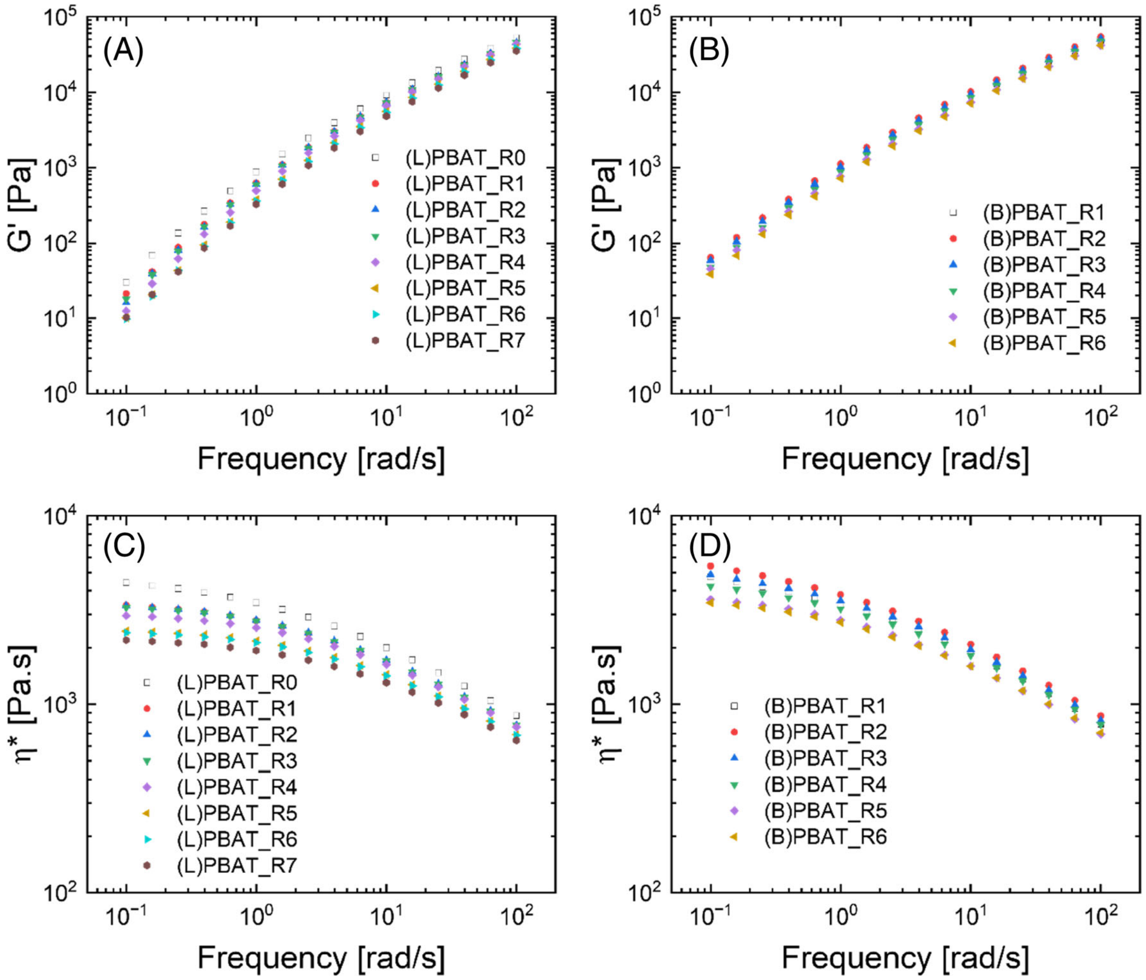


FIGURE 4 Linear rheological responses (A, B) storage modulus G' (ω) and (C, D) complex viscosity $\eta^*(\omega)$ of (A, C) unmodified (L) PBAT and (B, D) modified (B)PBAT under small amplitude oscillatory shear tests at temperature of 180°C, nitrogen ambient, and strain amplitude of 1%. (L)PBAT_R0 represents the unprocessed PBAT before injection molding.

Overall, Figure 4 clearly demonstrates that the elastic moduli and viscosities of the modified (B)PBAT underwent fewer changes and exhibited significantly less reduction compared to the unmodified (L)PBAT.

Unlike mechanical properties, both storage modulus and viscosities exhibit tangible descending behavior after each injection cycle. It can be seen that generally, the rheological properties of modified (B)PBAT are higher than those of unmodified (L)PBAT. It seems addition of 0.5 wt% did not lead to formation of plateau modulus in low-frequency regions. The lack of a plateau modulus at low frequencies suggests that a continuous, percolating network structure has not been fully formed. In other words, while chain extension has occurred, it has not reached the extent necessary to create a stable, elastic network that dominates the material's behavior at long timescales.[25] The increase in modulus values compared to the neat (unmodified) sample indicates that the chain extension has still increased the elastic modulus of the material. This means that some branching has occurred, enough to enhance the material's overall rigidity and resistance to deformation. It is previously reported that the reactivity of chain extenders with polyesters is dependent on chain extender type (number of functional groups), processing time and temperature as well as molecular structure of polyester itself.[16,26–28] In order to have a closer look at longer timescale responses, the rheological responses at frequency of 0.1 rad/s from Figure 4 are extracted and compared in Figure 5.

Figure 5 demonstrates changes in linear rheological responses at frequency of 0.1 rad/s to correlate the longer timescale properties of both modified and unmodified (L) PBAT against each injection cycle. It is known that low-frequency regions, corresponding to longer relaxation time of polymers, are more sensitive to microstructural changes of materials,[25,29] therefore, G' ($\omega = 0.1$ rad/s) and η^* ($\omega = 0.1$ rad/s) of the modified and unmodified (L)PBAT are collected against their number of injection cycles. It is seen that values of modified (B)PBAT with 0.5 wt% Joncryl stands higher at all injection cycles (Figure 5A). Moreover, the decay behavior is less pronounced in modified (B)PBAT as opposed to unmodified (L)PBAT. The G' ($\omega = 0.1$ rad/s) of (B)PBAT decreased nearly ~35% compared to that of unmodified with a~ 54% decrease from R1 to R6 of injection cycle. The rheological values remained consistent up to the third injection cycle in (B) PBAT where it starts to drop with a weaker decay manner (Figure 5C) unlike the properties of (L)PBAT which showed a gradual decrease from the first injection cycle (Figure 5B). However, it leveled off after the fifth cycle yet with a smaller value than those of (B)PBAT.

Furthermore, the same materials went through a large amplitude oscillatory shear test to observe their behavior under larger deformation.

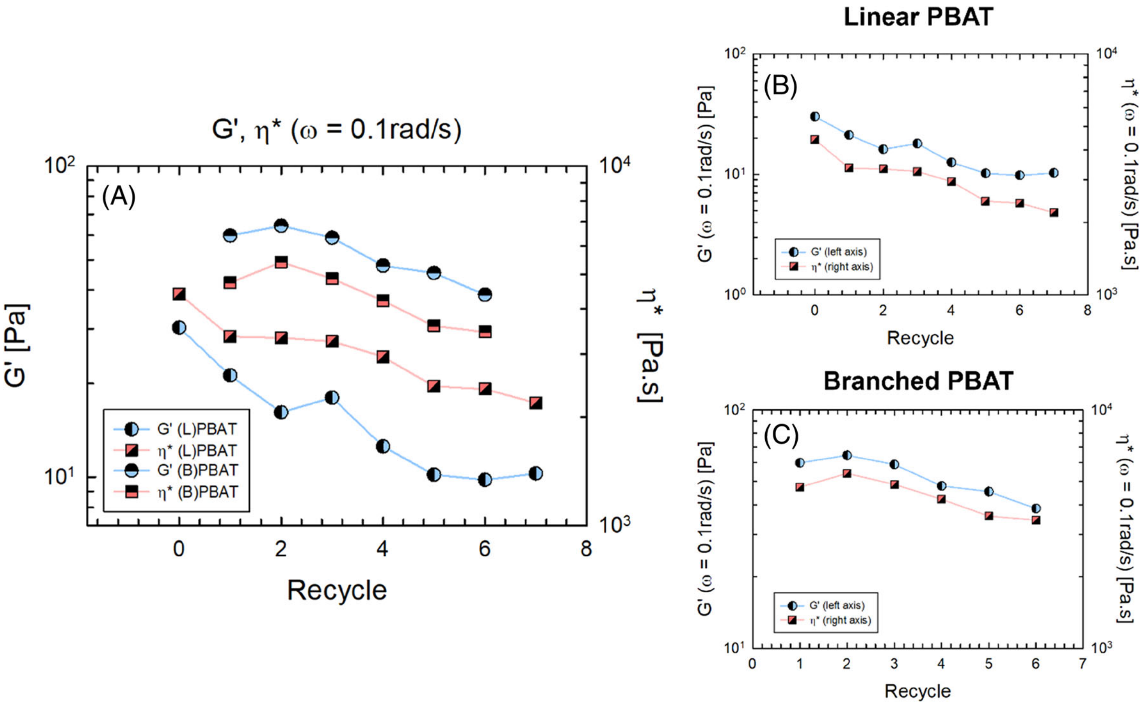


FIGURE 5 (A) Elastic modulus G' ($\omega = 0.1$ rad/s) and η^* ($\omega = 0.1$ rad/s) of the (B) unmodified (L)PBAT and (C) Joncryl modified (B) PBAT polymers obtained from frequency sweep tests as a function of injection cycles at temperature of 180°C, strain amplitude of 1%, and nitrogen environment.

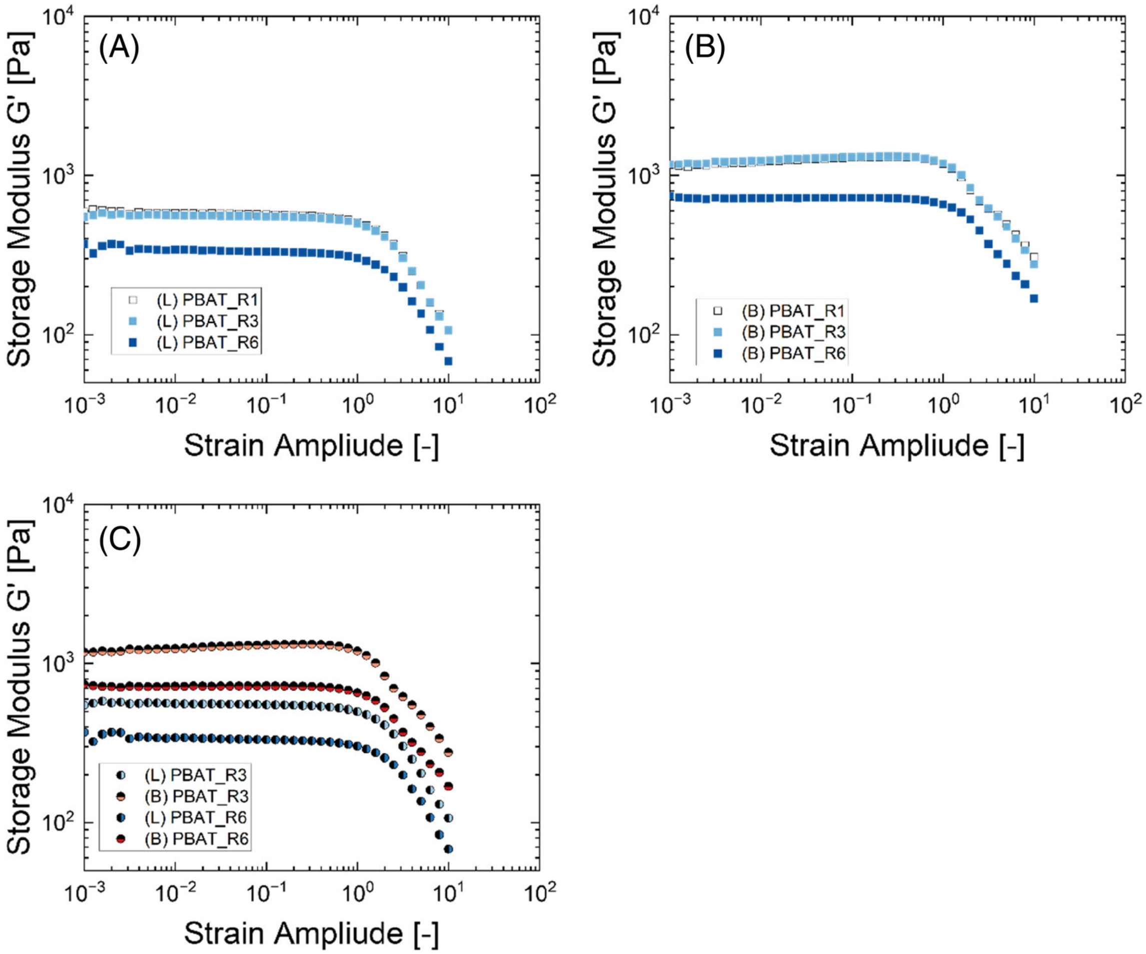


FIGURE 6 Nonlinear rheological responses of re-processed (A) unmodified (L)PBAT and (B) Joncryl® modified (B)PBAT under large amplitude oscillatory shear tests at a fixed frequency of 1 rad/s, temperature of 180°C and nitrogen ambient. The strain amplitudes were swept from 0.1% to 1000%. (C) represents the comparison between the amplitude sweep results of the third (R3) and the sixth (R6) injection cycles of both modified and unmodified (L)PBAT.

Strain amplitude sweep tests reaffirmed similar trends with frequency sweep tests. The decrease in values of LVE regions from R1 to R6 was exactly similar (~42%) (Figure 6A) to that from frequency sweep results at $\omega = 1$ rad/s (Figure 4A). However, the trend is different in the case of modified PBAT. It can be seen that the drop percentage from R1 to R6 is not consistent even within so-called "LVE" region where it is initially dropped 36% at lower deformation and reaches 45% around critical strain amplitude. The critical strain refers to the strain beyond which the G' (γ) starts to drop (strain softening). This indicates that the "LVE" region in modified PBAT-R1 and R3 is not accurately an LVE region where modulus shows a slight increase. This is due to the in situ reaction of Joncryl with PBAT during the strain amplitude test. To confirm this, the stability of (L)PBAT and (B)PBAT at 180°C was assessed by monitoring the storage modulus G' over time at a strain amplitude of 1% after the first and sixth injection cycles (Figure 7A, B). Two distinct behaviors were observed. The unmodified (L)PBAT exhibited a significant decrease in modulus over time (~17%) after six injection cycles (Figure 7A) due to chain scission reactions, while (L)PBAT after the first injection showed relatively stable behavior. In contrast, the reactivity of Joncryl with PBAT was quite remarkable, as shown in Figure 7B, with almost a 93% enhancement in G' after 1 h of annealing. This growth in modulus over time is associated with branching and crosslinking reactions during the annealing period.[25] This indicates Joncryl's reactivity with PBAT even after the first injection cycle. More interestingly, unlike (L)PBAT, the modified (B)PBAT remained thermally stable even after six injection cycles, suggesting that Joncryl-modified PBAT can be considered a viable alternative for extending the end-of-life of PBAT.

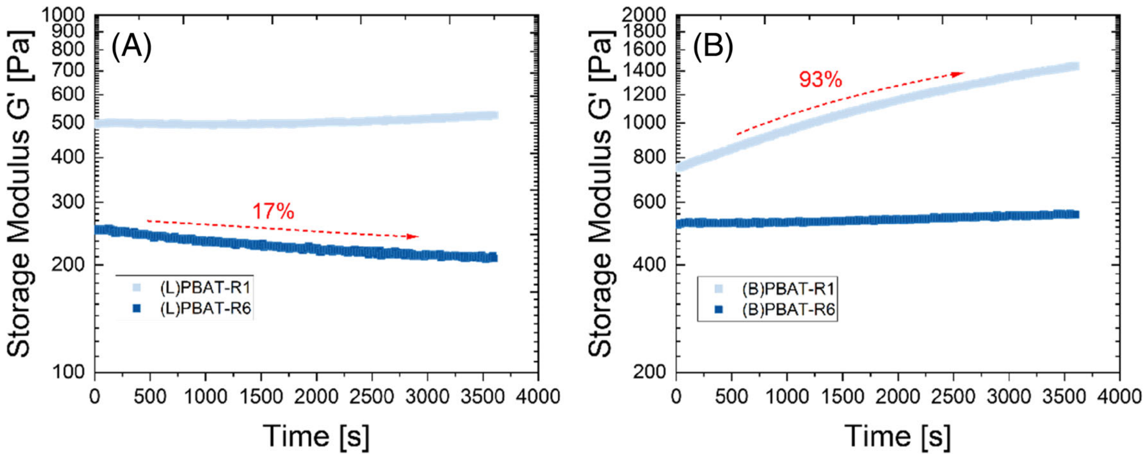


FIGURE 7 Time sweep tests of unmodified (A) (L)PBAT and (B) Joncryl modified (B)PBAT at 180°C, frequency of 1 rad/s and strain amplitude of 1%, under nitrogen atmosphere after first (R1) and sixth (R6) injection cycle.

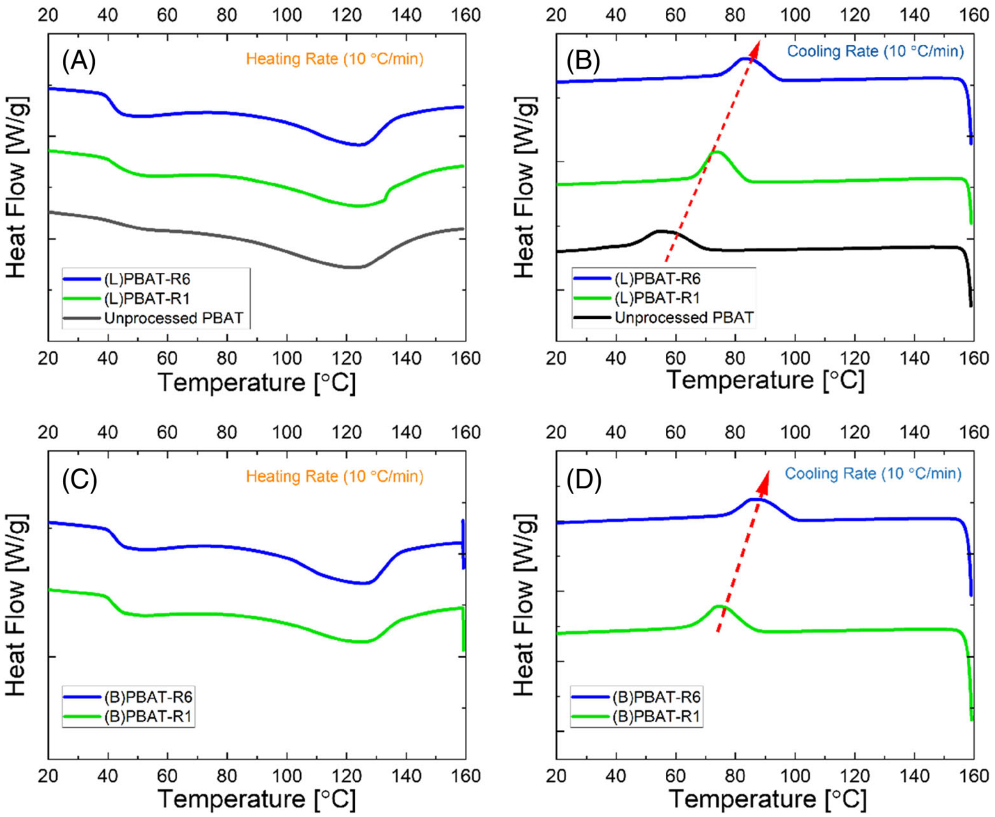


FIGURE 8 DSC thermograms of the (A, B) unmodified and (C, D) Joncryl-modified PBAT after the first and sixth injection cycles. First heating scans are showing the melting behavior of the polymers (A, C) and (B, D) the cooling scans at the rate of 10°C/min and under nitrogen environment.

3.3 | Thermal properties

In order to further investigate the thermal properties and crystallinity of the polymers, DSC analysis was employed. Figure 8 shows the thermal properties of the modified and (L)PBAT after sixth injection cycle. For the sake of comparison, the results of unprocessed PBAT are also included. The heating scans (Figure 8A, C) confirm that both injected modified (B)PBAT and unmodified (L)PBAT demonstrate two endothermic transitions around ~40°C (weaker) which is attributed to the melting of the butylene adipate (BA) crystalline phase and a stronger one associated with crystalline phase of poly butylene terephthalate around ~122–126°C.[30,31] Thermal properties of the polymers are shown in Table 1. It is interesting to note that melting and crystallization temperature of PBAT is significantly increased from ~122 and ~ 54°C, respectively, to ~126 and ~ 73C° upon the first injection cycle. There is nearly 20° increase in crystallization temperature. Further increasing the injection cycles to sixth time is

TABLE 1 Thermal properties of multiple injected molded modified (B)PBAT and unmodified (L)PBAT determined from DSC measurements at the rate of 10°C/min and nitrogen atmosphere.

Polymer	T_m (°C)	ΔH_m (J g^{-1})	T_c (°C)	ΔH_c (J g^{-1})	% X_c
Unprocessed PBAT	122.67	17.44	54.25	19.92	15.29
(L)PBAT-R1	126.39	14.36	73.20	17.12	12.59
(L)PBAT-R6	124.91	11.43	83.81	13.41	10.02
(B)PBAT-R1	126.10	11.63	74.17	16.56	10.25
(B)PBAT-R6	126.33	13.38	86.05	15.81	11.67

shown to have increased the crystallization temperature by 10 more degrees to nearly ~84°C. This is despite the reduction in degree of crystallinity from ~15% in unprocessed PBAT to ~10% in six-time injected (L)PBAT. It can be said that during repeated injection molding cycles, the polymer chains can undergo chain scission due to thermal and mechanical stresses. This results in a reduction in the molecular weight of the polymer.[12] This in return, allows the shortened molecules to re-arrange and crystallize more easily, thus leading to an accelerated crystallization process. However, simultaneously thermal degradation during repeated processing can lead to fewer and less perfect crystalline regions, hence the reduction in ΔH_c and $\%X_c$. That is, the melting temperature of six-time injection molded (L)PBAT-R6 is also reduced nearly 2°. It is for the same reasons that the rheological properties of (L)PBAT dropped (Figure 5B). Alternatively, when Joncryl is incorporated into the PBAT, similar trend with crystallization temperature can be seen due to the enhanced chain mobility and nucleation effect of the Joncryl particles itself. It is due to the existence of such branches and irregularities that the degree of crystallinity of modified (B) PBAT is slightly lower 10% than that of the unmodified (L)PBAT 12% after the first injection. It is interesting to note that the melting temperature of modified (B)PBAT remains unchanged (126°C) after the sixth injection cycle unlike that of the unmodified (L)PBAT. This again reiterates less degradations in modified (B)PBAT, supporting the rheological responses shown in Figures 5 and 6.

4 | CONCLUSION

This study demonstrates that both neat PBAT and Joncryl® ADR 4468-modified PBAT exhibit good mechanical and thermal properties after multiple reprocessing cycles, exhibiting the viability of mechanical recycling as a sustainable end-of-life option for biodegradable polymers. The addition of Joncryl significantly enhances the recyclability of PBAT by mitigating degradation during processing, thus maintaining mechanical integrity over repeated cycles. The findings suggest that Joncryl-modified (B)PBAT can be processed multiple times with minimal property loss, reducing the need for new raw materials and decreasing the environmental impact. Unmodified (L) PBAT exhibited slight changes in tensile properties where only insignificant ~6% and 7% drop in tensile modulus and strength was observed after the seventh cycle. On the other hand, Joncryl-modified (B)PBAT showed a ~ 27% increase in tensile modulus after the fifth injection cycle. The flexural modulus trend was almost unaffected with only slight decrease in unmodified PBAT after seven-time injections. Rheological properties however were more sensitive to molecular degradations where unmodified (L) PBAT showed more significant drop after each injection cycle. On the other hand, Joncryl modified (PBAT) was less affected to the re-processing cycles compared to the unmodified PBAT. This was in agreement with thermal properties from DSC. It was interesting to see that re-processed polymers were crystallized faster than the first injection cycle. This was again an indication of molecular degradation where shortened chains due to chain scission can crystallize faster than the long chains. Despite these changes, the material still exhibited good mechanical properties, as shown by the tensile and flexural results. This is due to the improved stress transmission between different phases of the material, meaning the material could handle stress better and distribute it more evenly, leading to enhanced performance in mechanical tests. Moreover, rheological and DSC results could demonstrate more sensitivity to molecular degradation than mechanical properties. The research supports the notion that recycling biodegradable plastics is not only feasible but also beneficial from both economic and environmental perspectives. By enhancing the durability and recyclability of PBAT, this study provides valuable insights into sustainable materials management and aligns with the global pursuit of sustainability.

AUTHOR CONTRIBUTIONS

RS contributed to conceptualization, funding acquisition, manuscript writing, and supervision. MK and SJ carried out the rheological testing. LC carried out the injection molding. TX helped with draft preparation and conceptualization, MN, contributed to conceptualization and drafting the manuscript, and KH supervised and validated the rheological tests and edited the manuscript. All authors reviewed and agreed to the published version of the manuscript.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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