Research Article

Rheological and Molecular Modifications of Recycled PET Induced by Chain Extenders for Enhanced 3D Printing Processability

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Received: 10 October 2025; Revised: 27 November 2025; Accepted: 21 January 2026; Published online: 23 March 2026

Abstract
This research investigated the processability of recycled poly(ethylene terephthalate) (rPET) derived from PET bottle waste to form filaments for 3D printing by modifying its molecular structure from linear to branched chains using different types and amounts of epoxide chain extenders. The rheological properties, processability, and morphology of the modified rPET were examined using a rotational rheometer, a twin-screw extruder, and a camera image technique, respectively. The highest filament performance was achieved with the addition of 12.5 parts per hundred (pph) of ethylene/n-butyl acrylate/glycidyl methacrylate copolymer, resulting in improved processability and increased shear viscosity. This material exhibited pseudoplastic flow at low shear rates. Additionally, the incorporation of 0.3 pph of styrene-methacrylate-glycidyl methacrylate copolymer further enhanced shear viscosity at low shear rates, resulting in a filament with a smoother surface. Thermal stability and the completion of interactions between rPET and chain extenders were confirmed using a rheometer in oscillatory time-sweep mode. These findings suggest that optimal modification significantly enhances the suitability of rPET for manufacturing 3D printing filaments in the industrial sector.

Keywords: Modified-rPET, Processability, Rheology, Thermal properties, Viscosity

1 Introduction

As the world's population grows and industrialization develops, demand and the global trend of plastic waste are increasing significantly [1], [2]. Statistical data show that global plastic production will reach 461 million tonnes in 2023, with estimates that the plastics industry will account for 4.5% of worldwide greenhouse gas emissions in 2023 [3], [4]. Recycling presents a viable solution for the mitigation of plastic waste. Poly (ethylene terephthalate) (PET) is the primary raw material in commercial recycling processes. In 2016, global PET production was over 56 million tonnes. Then, in 2020, it increased to approximately 70 million tonnes, reflecting a significant rise in PET consumption across various applications, particularly in drink bottles [5], [6].

Focusing on the PET bottle industry, the total production volume of PET bottles is expected to reach 56 million tonnes in 2024. This increase has become a significant waste problem worldwide, creating numerous environmental challenges. To mitigate these impacts, PET has been recycled into various products [7]–[9]. Furthermore, to reduce the amount of PET bottle waste, the European Union (EU) imposes new regulations that by 2025, all newly manufactured plastic bottles must incorporate at least 25% recycled plastic, and increase to at least 30% by the end of 2030 [10]. Recycling PET bottles for use in other industries could also help solve both environmental and economic problems [6].

PET is a semi–crystalline aromatic thermoplastic polyester with high molecular weight. Consequently, it has superb mechanical properties, high pressure resistance, high chemical and thermal resistance, high gas resistance, light weight, low production cost, and recyclability [11]–[17]. Unlike aliphatic polyesters, PET is not biodegradable. Therefore, recycling is the most effective solution to manage plastic waste in the environment. Melt reprocessing is a commonly applied method for recycling PET due to its low cost and minimal environmental impact [8]–[18]. However, PET obtained from melt reprocessing has low molecular weight and viscosity due to hydrolytic degradation. This is because PET molecules contain ester groups, capable of undergoing hydrolytic degradation.

Generally, converting PET bottles into PET flakes involves several steps. The first step is washing various types of PET bottles and grinding them into small pieces or flakes, followed by drying with a hot blower. However, even after drying, the high humidity in Thailand's climate poses a challenge and can reintroduce moisture into recycled PET (rPET) flakes. This is a significant issue because it causes oxidation, leading to thermal and hydrolytic degradation during melt reprocessing by extrusion. Additionally, the lower molecular weight resulting from the grinding process reduces the polymer's viscosity and melt strength, disrupting its processability and formability during melting. Therefore, it cannot be processed into a large extrudate or filament, such as a compounding pellet or 3D-printing filament [19]–[21].

To address this issue, the melt strength of rPET needs to be enhanced to support extrusion processability, which can be achieved by increasing its molecular weight through the addition of heat stabilisers, antioxidants, and chain extenders (CE) [16], [17]. CE becomes a key ingredient widely used to increase the molecular weight of recycled polymers during melt reprocessing [22]–[27]. CE is a type of chemical that contains a variety of functional groups and a complex molecular architecture. CEs, which are commonly used for polyesters, include pyromellitic dianhydride (PMDA) [24], bis–oxazolines [26], isocyanides [28], [29], organic phosphites [27], [30], [31], and epoxides [11], [12], [32]–[38]. Specifically, the most widely used and commercially available CE for polyester is multifunctional epoxides, namely Joncryl®ADR [39] and Elvaloy® [40]. Both could significantly enhance the melt properties of polyester [41].

Previous studies found that the molecular weight of rPET increased after adding a mixture of Joncryl®ADR 4368 and Joncryl®ADR 4370, thereby enhancing its melting properties and significantly improving its viscosity during the reactive extrusion process [6], [42]–[45]. In another study, Xiao *et al.*, found that the elasticity of extrudate PET mixed with Joncryl®4370 was higher than that of mixing with PMDA [46]. Moreover, the molecular structure of the rPET modified with Joncryl®4368 and PMDA was compared. It was observed that the high branching structure of modified–rPET was achieved when Joncryl®4368 was used, whereas the linear and tree–like structures were present in the rPET modified with PDMA [47].

Another method to enhance the melt strength and viscosity of rPET is to blend it with poly (butylene terephthalate) (PBT), high–density polyethene (HDPE), and polyamide (PA) [6], [48]. Additionally, rPET was blended with ethylene copolymers or terpolymers, which have suitable reactive sites that can interact with rPET, such as Acrylate copolymer (EAA), Surlyn®, and Elvaloy®, all of which are attractive solutions. Therefore, it also has good processability and fast crystallization [49]. Elvaloy® is a multifunctional ethylene copolymer that contains an oxirane ring in its structure and can easily interact with PET. However, it can also serve as a compatibiliser and CE during polymer blending, depending on the specific aim of the modification.

Xiangyu You *et al.*, [40] studied the compatibility, mechanical properties, rheological behaviour, and thermal characteristics of PET/PLA blends with epoxide compatibilizers at various concentrations. The compatibilizers used included Joncryl®ADR3468 and Elvaloy®PTW. It was observed that PET and PLA became compatible upon the addition of 0.7 wt% Joncryl®ADR3468, which also improved the impact strength of the blend. Furthermore, the addition of the ethylene copolymer compatibilizer, Elvaloy®, enhanced elongation and reduced the modulus of the blend. According to the thermal characteristics discussed in this research, Joncryl® and Elvaloy® can increase the amorphous and crystalline phases of PET, respectively. This research demonstrates that Joncryl® and Elvaloy® can influence the amorphous and crystalline phases of PET, respectively. This potentially affects its processability and mechanical properties. The knowledge gained from this research should be applied to produce 3D printing filament from rPET.

However, in the case of rPET modification, the proportion of Joncryl® and Elvaloy® has not yet been optimised. The rheological behaviour and the interaction between rPET and both CEs should also be clarified. Therefore, further interaction between rPET and CEs should not occur, preventing gel clogging at the nozzle during printing. However, to our knowledge, these issues have not been studied and reported.

Thus, this study aims to investigate the melt reprocessing and processability of rPET for 3D–printing filament modified by adding two types of CEs, namely Joncryl®ADR4468 and Elvaloy® PTW, under various ratios. The viscosity, thermal properties, processability, and morphology of the modified rPET were investigated using a rheometer, a twin–screw extruder, and an image analyzer. Additionally, Fourier–transform infrared spectroscopy (FT–IR) and an oscillating rheometer were utilized to gain a deeper understanding of the structure and interactions between rPET and CEs in the melt–processed samples.

2 Materials and Methods

2.1 *Materials*

rPET flakes (4–8 mm in diameter) sourced from PET bottle waste were purchased from Thai Plastic Recycle Group Company Limited. Two types of multifunctional reactive polymers, referred to as CEs, were used: an acrylic epoxy resin, styrene–methacrylate–glycidyl methacrylate copolymer (Joncryl®ADR4468, or CE–J), and ethylene/n–butyl acrylate/glycidyl methacrylate copolymer (Elvaloy®PTW, or CE–E), both supplied by Chemical Innovation Company Limited. CE–E is a terpolymer consisting of 66.75 wt% ethylene, 28 wt% butyl acrylate, and 5.25 wt% glycidyl methacrylate. CE–J is supplied in flake form, with an average molecular weight of 7250 g/mol and an epoxy equivalent weight of 310 g/mol. Based on these values, it contains approximately 45.8 wt% glycidyl methacrylate, calculated using the method described in previous research and the molecular weight of glycidyl methacrylate (142.15 g/mol). The number of epoxy groups was calculated as the molecular weight of CE–J divided by the epoxy equivalent weight. The chemical and schematic structures of both CEs are shown in Figure 1. As illustrated, both structures prominently feature oxirane rings, which are the key reactive sites. Notably, CE–J contains a significantly higher percentage of glycidyl methacrylate (approximately nine times more) compared to CE–E.

Additional additives used in this study included a phenolic antioxidant, pentaerythritol tetrakis(3,5–di–tert–butyl–4–hydroxyhydrocinnamate) (Irganox® 1010, molecular weight 1178 g/mol); a hindered amine light stabilizer, bis(2,2,6,6-tetramethyl–4–piperidyl) sebacate (Tinuvin® 770, molecular weight 481 g/mol); and a peroxide decomposer, tris(2,4–di–tert–butylphenyl) phosphite (Irgafos® 168, molecular weight 646.9 g/mol). All antioxidants and stabilizers were supplied by Merit Solution Company Limited.

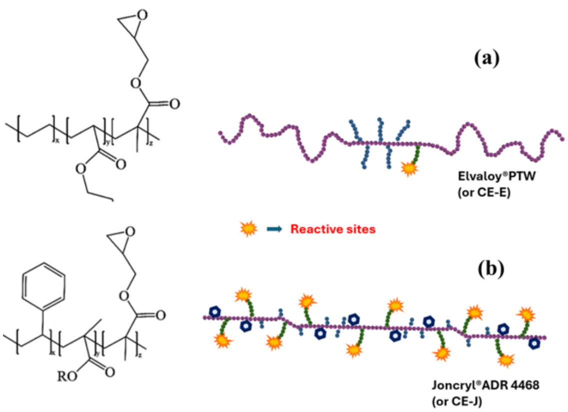


Figure 1: Chemical and schematic structures of CE–E and CE–J.

2.2 *Method*

2.2.1 Cleaning of rPET flakes

The rPET flakes were thoroughly cleaned with clean water to remove any surface impurities. After washing, the flakes were dried in an oven (Memmert, UN750plus) at 80 °C for 16 h. Proper drying is essential to prevent hydrolytic degradation of rPET during extrusion and other melt–processing steps.

2.2.2 Preparation of rPET Compounds

The cleaned and dried rPET flakes were mixed with antioxidants, stabilizers, and CEs according to the formulations listed in Table 1. The mixtures were then compounded using a co-rotating twin-screw extruder (XINDA, SHJ-200) equipped with a twin-rod die (2 mm diameter each). The temperature profile from the feed zone to the die was set at 50–115–185–200–200–185 °C, respectively. The screw rotation speed was maintained between 80 and 100 revolutions per minute (rpm). The extruded rods were cooled in a water bath and subsequently collected by a pulling unit. Finally, the extrudates were cut into pellets for further processing.

Table 1: The formulation of the rPET flake, the modified–rPET without and with Ces.

Sample Codes	rPET Flake	Content (pph)	
		CE-E	CE-J
rPET flake	100	–	–
rPET without CE	100	–	–
rPET/J0.2	100	–	0.2
rPET/J0.4	100	–	0.4
rPET/J0.6	100	–	0.6
rPET/J0.8	100	–	0.8
rPET/E5	100	5	–
rPET/E10	100	10	–
rPET/E12.5	100	12.5	–
rPET/E15	100	15	–
rPET/E20	100	20	–
rPET/E12.5–J0.0	100	12.5	0.0
rPET/E12.5–J0.3	100	12.5	0.3
rPET/E12.5–J0.5	100	12.5	0.5
rPET/E12.5–J0.7	100	12.5	0.7
rPET/E12.5–J1.0	100	12.5	1.0

*Remark: All formulations above (except rPET flake) were added Irgafos®168 (0.2 pph) as an antioxidant, and Irganox®1010 (0.5 pph) with Tinuvin®770 (0.1 pph) as stabilizers.

2.3 *Characterizations*

2.3.1 Rheological analysis method

Table 1) were dried at 60 °C in an oven for 12 hr. before measuring using a rotational rheometer (Kinexus, Lab+) to determine shear viscosity, shear rate, complex viscosity, and rheological properties, including storage modulus (G′) and loss modulus (G″). Shear viscosity of the rPET flake and the modified–rPET compounds were measured by a rotational rheometer using a 40 mm cone–diameter, with a 0.8 mm gap, and a low shear rate of 1–100 s–1 at 270 °C, under a nitrogen atmosphere.

Complex viscosity of the rPET flake and the modified–rPET compounds reported by the instrument as a function of time was used to compare the viscosity across a range of melting temperatures (250 °C) and confirm the thermal processability of the polymers during the 3D printing process (275 °C), proceeded by oscillatory mode (using time sweep mode), equipped with a parallel–plate geometry, with 25 mm plates–diameter, with a 1 mm gap, under nitrogen atmosphere, with a frequency of 1 Hz and using 0.5 % shear strain.

2.3.2 Fourier Transform Infrared Spectrophoto–metry (FT–IR)

FT–IR spectra of the modified–rPET samples with and without CEs were scanned from 500 to 4000 cm^{-1}, with 64 scans performed at a 2 cm^{-1} spectral resolution at room temperature. Using a Fourier Transform InfraRed spectrophotometer (FTIR, Thermo–scientific Nicolet iD5) in an ATR mode (iD5–ATR–Diamond). Results were analyzed using OMINC software.

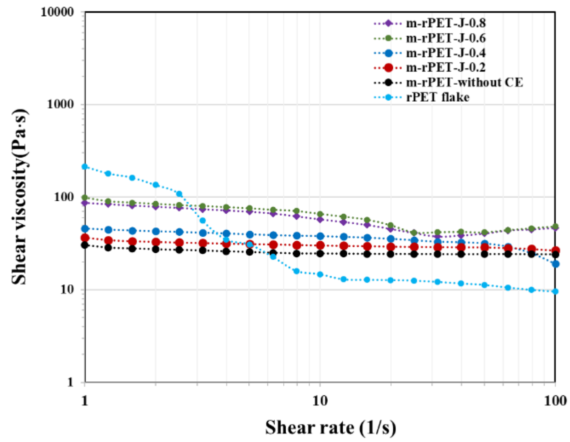
3 Results and Discussion

3.1 *Shear viscosity and rheological behavior of the modified–rPET/CEs*

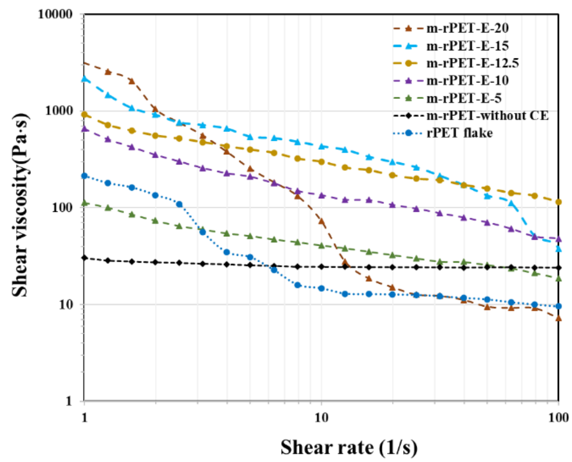
In this section, the rheological behavior and shear viscosity of neat rPET flakes and modified–rPET compounds, with and without CEs, were investigated at various concentrations. Figure 2a presents the shear viscosity of modified-rPET compounds containing CE–J at 0.0, 0.2, 0.4, 0.6, and 0.8 parts per hundred (pph), compared with neat rPET flakes. Similarly, Figure 2(b) shows the shear viscosity of modified–rPET compounds with CE–E at 0, 5, 10, 12.5, 15, and 20 pph, also compared with neat rPET flakes.

Focusing first on samples without CEs, which were only modified by the addition of antioxidants and stabilizers, it was observed that these additives significantly improved the rheological behavior. Specifically, they stabilized the flow at low shear rates, leading to more Newtonian–like behavior. This improvement is attributed to antioxidants and stabilizers reducing the free–radical content within the rPET matrix, which in turn suppressed chain scission and promoted a more uniform molecular structure compared to neat rPET flakes.

As shown in Figure 2(a), increasing the content of CE–J led to a slight increase in shear viscosity, although the effect was not particularly pronounced. Additionally, the rheological behavior remained close to Newtonian, indicating that the interaction between short–chain molecules of rPET and CE–J resulted in relatively small, isotropic (symmetrically shaped) molecules or short–chain branched structures. These structures were unable to undergo significant rearrangement or orientation under flow.



(a)



(b)

Figure 2: Shear viscosity results of rPET flakes, and modified–rPET compounds with different contents of CE–J at 0, 0.2, 0.4, 0.6, 0.8 pph (a), and CE–E at 0, 5, 10, 12.5, 15, 20 pph (b).

Furthermore, no clear shear–thinning behavior was observed, supporting the conclusion that even with higher contents of CE–J, the interactions did not produce a long–chain branching structure. This finding is consistent with the smaller diameter of the extruded filaments during reactive processing, as shown by the photograph in Figure 3(a).

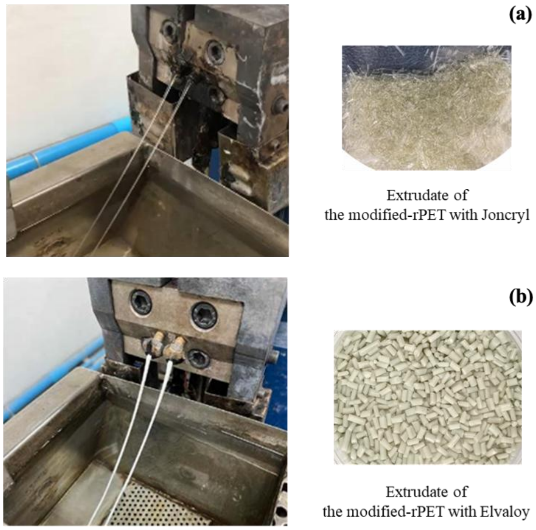


Figure 3: Extrudates of the modified rPET with CE–J (a) and CE–E (b).

In this study, efforts were made to develop a long–chain, branched modified–rPET for 3D–printing filament application, with a diameter of 1.75 ± 0.03 mm. To achieve this, CE–E was incorporated into neat rPET flakes. Figure 3(b) illustrates the rheological behavior of the modified–rPET with varying contents of CE–E. As shown, the shear viscosity increased significantly with the addition of CE–E, and all samples exhibit clear shear–thinning behavior. This enhancement is attributed to the greater molecular entanglement provided by the long ethylene chains of CE–E, as well as the formation of branched rPET structures through polycondensation reactions between the rPET and the epoxide groups of CE–E. The improved molecular architecture substantially enhances the melt strength of the polymer, as evidenced by the larger filament diameters observed during reactive extrusion (Figure 3(b)).

3.2 *Structural analysis of the modified–rPET/CEs FTIR spectra*

Figure 4 shows FTIR spectra of neat rPET flake, CE–E, and CE–J used in this research. For neat rPET flakes, the FTIR band corresponding to the -OH bending vibration (1339 cm^{-1}) can be observed. For CE-E, this spectrum can be attributed to -C-O stretching (944 cm^{-1}) and -C-H stretching (3083 cm^{-1}) of the oxirane group, and C=O stretching of the acrylate carboxyl group (1732 cm^{-1}). The band at 978 cm^{-1} shows the presence of -C-O stretching, representing the oxirane group of CE–J. These spectra, nearly identical to those above, were observed in the related literature [6]. It can be concluded that FTIR spectra in Figure 4 provide strong evidence that both types of CEs had the oxirane group in their chemical structure, which serves as a CE for rPET, as shown in Figure 5.

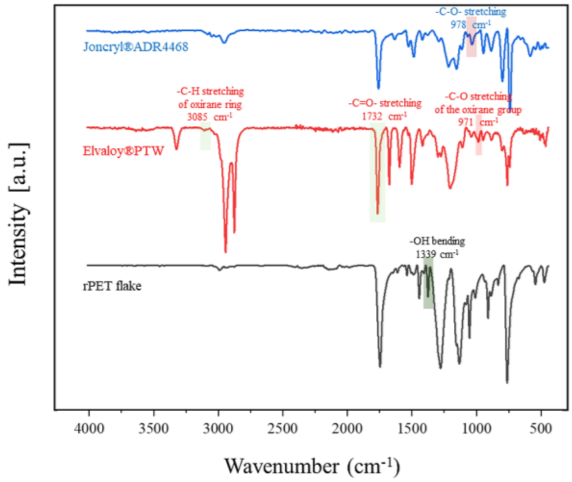


Figure 4: FT–IR spectra of rPET flake, Elvaloy® PTW(CE–E), and Joncryl®ADR4468(CE–J).

Figure 6(a) presents the ATR–FTIR spectra of rPET flake and modified–rPET containing CE–J at 0, 0.2, 0.4, 0.6, and 0.8 pph. To facilitate reliable comparison, selected spectral regions associated with the functional groups involved in the chain–extension reaction were enlarged, as shown in the inset figures. These include the -OH bending vibration of rPET at 1339 cm^{-1}, the epoxide C-O stretching of the oxirane group at 971 cm^{-1}, and the carbonyl stretching band at 1713 cm^{-1}, which was used as an internal reference for normalization.

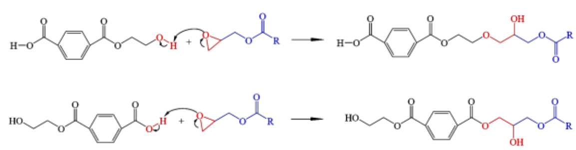
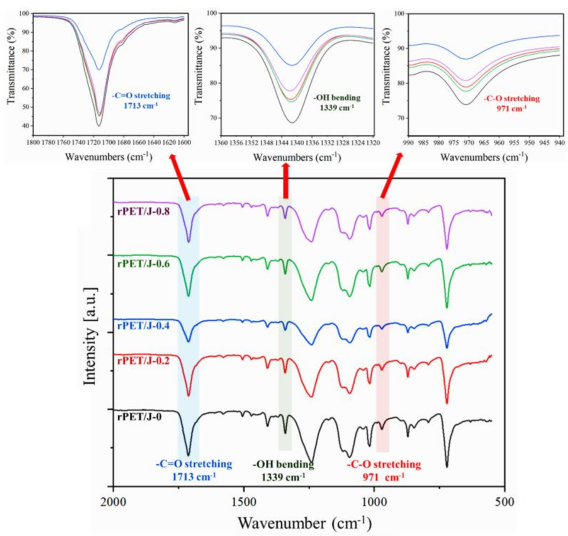


Figure 5: Polycondensation reaction between CE–E or CE–J, with rPET [42].

Upon addition of CE–J, variations in the intensities of both the -OH bending and epoxide C-O stretching bands were observed. However, even with increasing CE–J content, the decrease in these peak intensities was relatively limited, indicating that only a partial consumption of reactive functional groups occurred. This behavior can be attributed to the high density of epoxide groups within the CE–J molecular structure, which may lead to steric hindrance and competition among reactive sites, thereby restricting effective interaction with rPET chain ends.

To further clarify these trends, the intensity ratios of the -OH bending (1339 cm^{-1}) and epoxide C-O stretching (971 cm^{-1}) bands, normalized to the carbonyl reference peak at 1713 cm^{-1}, were calculated and are summarized in Figure 6(b). The relatively modest changes in intensity ratios with increasing CE–J content suggest that CE–J predominantly promotes limited chain extension or short–chain branching rather than extensive long–chain branching. This observation is consistent with the near–Newtonian rheological behavior observed for CE–J–modified rPET.



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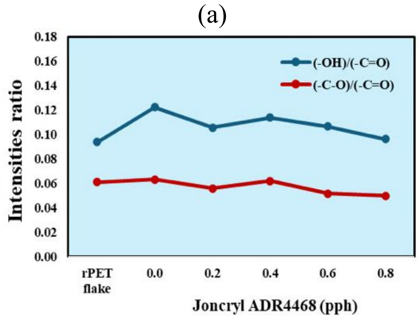
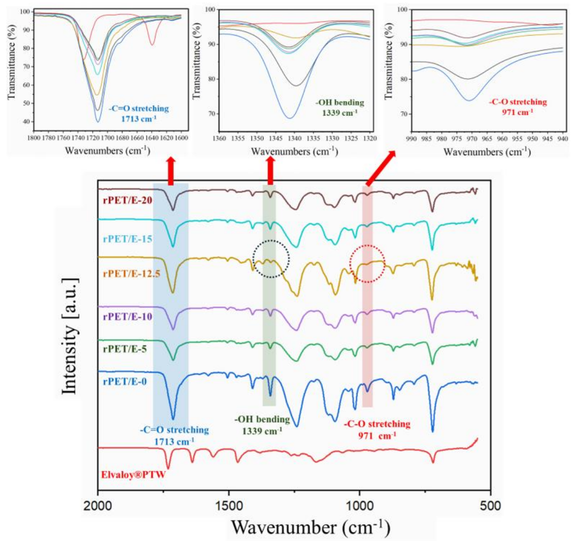


(b)

Figure 6: FTIR spectra of rPET flake and modified–rPET without and with various contents of CE–J at 0, 0.2, 0.4, 0.6, and 0.8 pph (a) and the change in intensity ratio with CE–J content (b).



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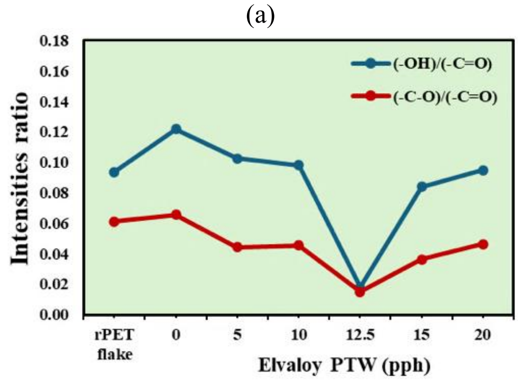

(b)

Figure 7: FTIR spectra of rPET flake and modified–rPET without and with various contents of CE–E at 0, 5, 10, 12.5, 15 and 20 pph (a) and the change in intensity ratio with CE–E content (b).

Figure 7(a) presents the ATR–FTIR spectra of rPET flake and modified–rPET containing different contents of CE–E (0, 5, 10, 12.5, 15, and 20 pph), together with enlarged spectral regions corresponding to the functional groups involved in the chain–extension reaction. Visual inspection of the enlarged spectra reveals a progressive reduction in the intensity of the -OH bending band at 1339 cm^{-1} and the epoxide C-O stretching band at 971 cm^{-1} as the CE–E content increases, with the most pronounced changes observed at 12.5 pph CE–E.

The carbonyl stretching band at 1713 cm^{-1}, used as an internal reference, remains essentially unchanged, indicating that the observed variations are associated with reactive functional group consumption rather than baseline fluctuations.

To further quantify these trends, the intensity ratios of the -OH bending (1339 cm^{-1}) and epoxide C-O stretching (971 cm^{-1}) bands, normalized to the carbonyl reference peak at 1713 cm^{-1}, are summarized in Figure 7(b). The results show a clear minimum in both intensity ratios at 12.5 pph CE–E, indicating the highest extent of epoxide–hydroxyl interaction at this composition.

Molecular structure of CE–E is a terpolymer containing long ethylene segments and a relatively lower epoxide functionality compared to CE–J. The flexible ethylene backbone increases free volume and chain mobility within the melt, facilitating more effective interaction between rPET chain ends and epoxide reactive sites. At higher CE–E contents (>12.5 pph), the intensity ratios show only marginal additional changes, suggesting that further increases in CE–E do not significantly enhance the extent of reaction.

3.3 *Effect of the ratio between CE–E and CE–J*

CE–E at 12.5 pph was selected (based on the shear viscosity results) for further investigation, with varying CE–J contents of 0, 0.3, 0.5, 0.7, and 1.0 pph. The shear viscosity behavior of the modified–rPET compound with different concentrations of CE–J is shown in Figure 8.

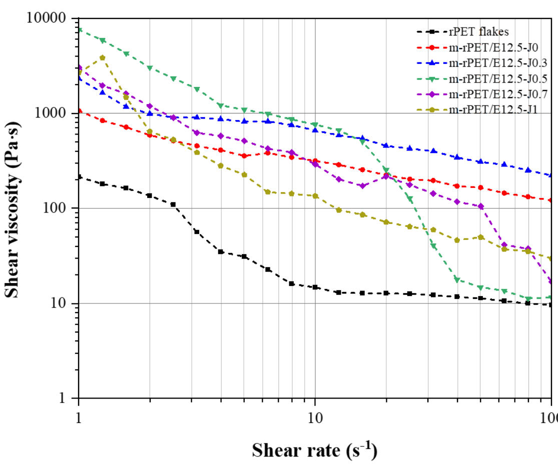

Figure 8: Shear viscosity results of rPET flake and modified–rPET compound with various contents of CE–E (12.5 pph) and CE–J (0, 0.3, 0.5, 0.7, and 1.0 pph).

All samples with 12.5 pph CE–E exhibited shear–thinning flow characteristics. The results indicate that, at 12.5 pph CE–E with 0.3 pph CE–J, the sample displayed high viscosity and shear–thinning behavior with a smooth slope. This characteristic suggests the presence of long chains with branching, which are ideal for 3D–printing filament applications, including both filament processing and 3D printing [50].

As mentioned earlier, the modified–rPET (CE–E 12.5 pph with CE–J 0.3 pph) exhibits shear–thinning behavior, providing the ideal viscosity for the 3D printing process. This behavior facilitates better extrusion through the 3D printer nozzle. Additionally, the flow behaviour of the polymer is an essential factor in controlling filament diameter during extrusion, as a consistent diameter is crucial for successful 3D printing.

Figure 9 shows the ability to control the filament diameter. As seen, the filament with CE–E at 12.5 pph and CE–J at 0.3 pph exhibits good stability and allows easy control of the diameter. However, as the CE–J content increases, filament instability occurs, making it challenging to maintain a consistent diameter during extrusion. This instability is consistent with the shear viscosity results shown in Figure 8. Additionally, gelation was observed in the filament, likely due to the high additive content, which causes agglomeration through crosslinking. Since CE–J is a multifunctional epoxide oligomer with an average functionality of 9, it is capable of reacting with rPET to form star–like (gel) structures. The high CE–J content enables rapid crosslinking [51].

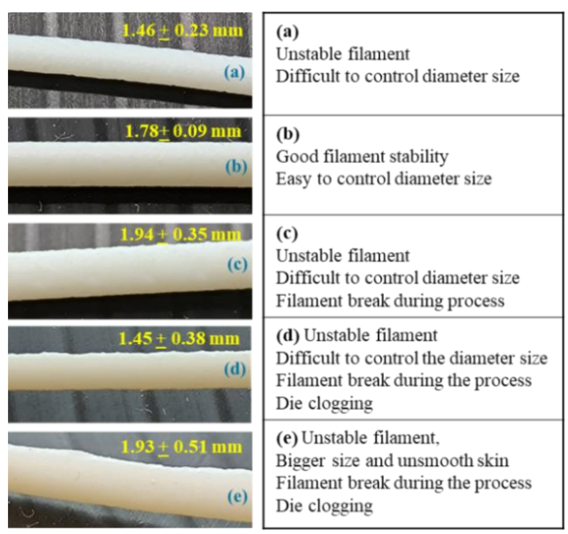

Figure 9: Camera images of the compounded filaments of modified–rPET using CE–E 12.5 pph with CE–J 0, 0.3, 0.5, 0.7 and 1.0 pph (a–e).

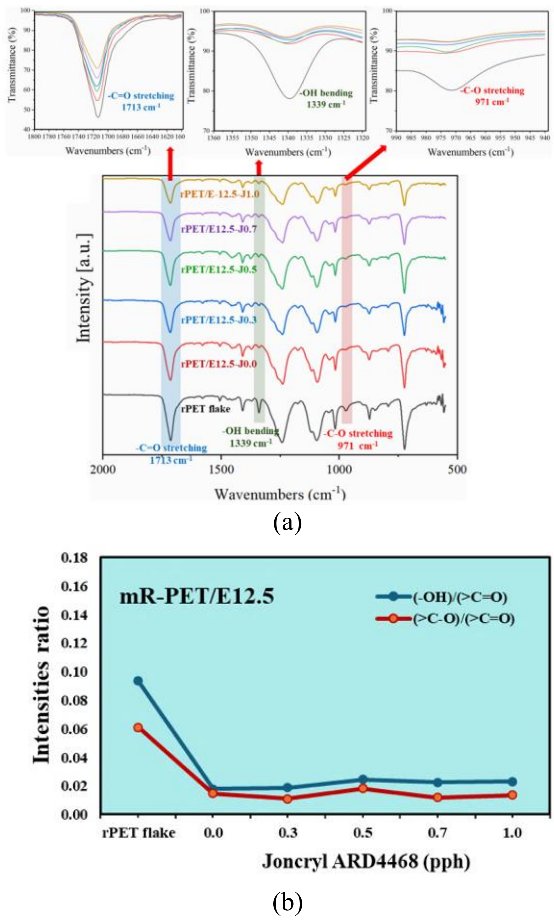

Figure 10: FT–IR spectra of rPET flake and modified–rPET compound using CE–E 12.5 pph mixed with CE–J at 0, 0.3, 0.5, 0.7, 1.0 pph (a) and the change in intensity ratio with CE–J content (b).

Figure 10(a) shows the ATR–FTIR spectra of rPET flake and modified–rPET containing a fixed CE–E content of 12.5 pph combined with different CE–J contents (0, 0.3, 0.5, 0.7, and 1.0 pph), together with enlarged spectral regions corresponding to the -OH bending vibration at 1339 cm^{-1}, the epoxide C-O stretching band at 971 cm^{-1}, and the carbonyl reference peak at 1713 cm^{-1}. Visual inspection of the enlarged spectra indicates that the intensities of both the -OH and epoxide–related bands show only minor variations with increasing CE–J content.

To further clarify this trend, the intensity ratios of the -OH bending and epoxide C-O stretching bands, normalized to the carbonyl reference peak, are presented in Figure 10(b). The results reveal that the intensity ratios remain relatively constant upon increasing CE–J content, indicating that the extent of epoxide–hydroxyl interaction does not increase significantly beyond that achieved by CE–E at 12.5 pph.

This behavior suggests that, at 12.5 pph CE–E, the majority of accessible reactive sites on the rPET chains have already participated in chain–extension reactions. Consequently, additional CE–J contributes primarily to structural modification rather than further consumption of functional groups. This observation is consistent with the rheological results, which show limited viscosity enhancement and increased instability at higher CE–J contents.

The rheological properties and thermal stability of modified–rPET were investigated at 250 °C (melting temperature) and 275 °C (processing temperature during 3D printing). Figure 11a illustrates the effect of CEs, CE–E and CE–J, on the time–sweep rheological behavior. The complex viscosity of the modified–rPET compounds increased when both CEs were incorporated. At both testing temperatures, the complex viscosity decreased over time, indicating that the CE molecules reacted completely and no longer interacted with the rPET end groups. Additionally, at the 275 °C processing temperature for 3D printing (shown in Figure 11(b)), the complex viscosity was highest in formulations containing only one CE. This behavior suggests the formation of a long–chain branching structure, in which the complex viscosity is initially high but decreases over time as the interconnected chains relax. For modified–rPET, the concentration of CEs gradually improved its thermal stability.

However, if the complex viscosity decreases significantly at the processing temperature, it may not be suitable for 3D printing, as the polymer could flow too easily [52]. In addition to the appropriate viscosity, the optimal melting time of the polymer is crucial for achieving good polymer flow while minimizing energy consumption, another important factor in 3D printing. Figure 12 shows the optimal melting time of the polymer at the processing temperature for the 3D printing process, indicated by the temperature at which G′ exceeds G″. Thus, a decrease in crossover time indicates branching. This correlation implies that the modified–rPET compound with a combination of CE–E 12.5 pph and CE–J 0.3 pph exhibited a short crossover time and a decrease in storage modulus [53].

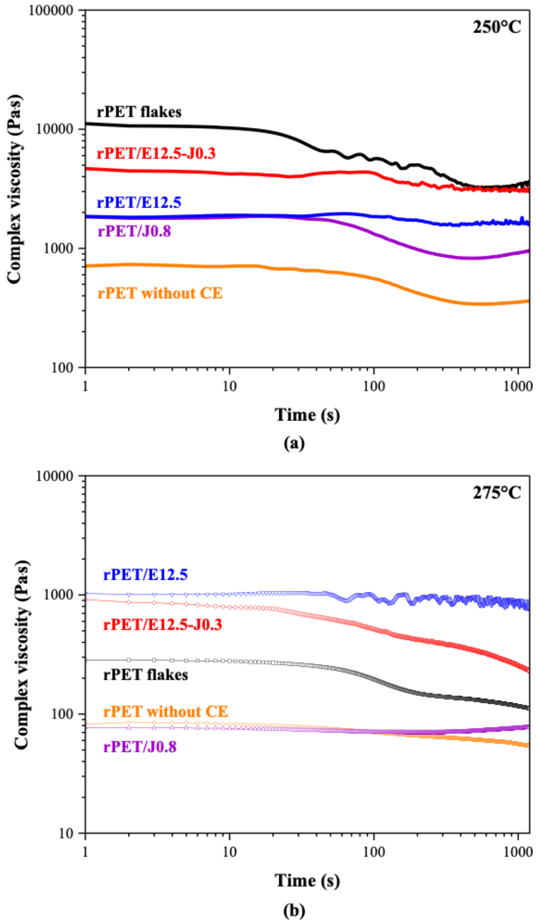

Figure 11: Complex viscosity–time sweep mode of rPET flake, and modified–rPET compounds with and without CE at 250 °C (a) and 275 °C (b).

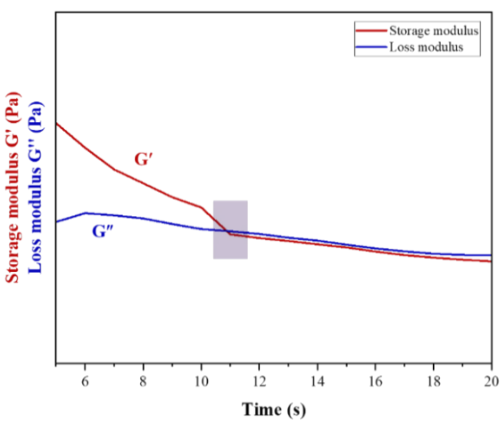

Figure 12: The crossover time and the rheological patterns G′ and G″ of the modified–rPET compound with a combination of CE–E 12.5 pph and CE–J 0.3 pph at 275 °C.

4 Conclusions

This research demonstrated that the melt processability of recycled poly(ethylene terephthalate) (rPET) derived from PET bottle waste can be enhanced by modification using a combination of CE-E and CE-J as chain extenders. The modifications were confirmed through rotational rheometry, twin-screw extrusion, and camera imaging. The use of different types of chain extenders resulted in distinct rheological behaviors of rPET. Specifically, CE-E induced shear-thinning behavior, whereas CE-J led to near-Newtonian behavior. FTIR analysis confirmed chemical structural changes in the modified rPET. Among the various formulations, 12.5 pph of CE-E was identified as the optimal content for achieving the most complete reaction. Further investigation showed that the combination of CE-E (12.5 pph) and CE-J (0.3 pph) resulted in the highest shear viscosity.

Additionally, filaments produced with this formulation exhibited the smoothest surface compared to other compositions. Over time, the complex viscosity decreased, indicating that the chain extender molecules had fully reacted and no longer interacted with the rPET end groups, resulting in a long-chain branched structure. These results confirm that CE-E and CE-J are effective additives for enhancing the processability, melt flow behavior, and rheological properties of rPET, with promising potential for 3D-printing filament applications and other specific processing needs. Although the incorporation of chain extenders increases filament cost, the resulting 3D-printing filament remains economically competitive with other heat-resistant filaments. This is particularly relevant in light of forthcoming EU regulations that may impose higher taxes or restrict plastic products that do not incorporate recycled PET. Consequently, modified-rPET filaments represent an environmentally friendly and competitive material solution.

Acknowledgments

This research was funded by College of Industrial Technology, King Mongkut's University of Technology North Bangkok (Grant no. Res-CIT0306/2022). The authors would like to thank the division of Aircraft Maintenance Engineering Technology (ACET), Department of Power Engineering Technology, College of Industrial Technology, King Mongkut's University of Technology North Bangkok. The authors would like to thank Mr.Sorawit Damdenngam, Mr.Buncha Roonthong, and Mr.Nutthanon Intarasuwan to prepare the compounds.

Author Contributions

N.P.: Conceptualisation, methodology, investigation, resources, data curation, writing - original draft, writing - review & editing; T.Y.: methodology, investigation, writing - original draft ; P.T.: methodology, investigation, writing - original draft ; K.P.: methodology, investigation, writing - original draft; N.S.: validation, investigation, review & editing, supervision; J.W.: methodology, validation, investigation, review & editing, supervision; W.C.: methodology, investigation, writing - original draft; S.I.: Conceptualisation, methodology, investigation, validation, formal analysis, writing - original draft, writing - review & editing, supervision, resources, visualization, supervision, project administration, funding acquisition.

Conflicts of Interest

The authors declare no conflict of interest.

Declaration of generative AI and AI-assisted technologies in the writing process

The authors utilized the ChatGPT tool to enhance the language and readability of the manuscript.

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