Korea-Australia Rheology Journal (2023) 35:203–212
https://doi.org/10.1007/s13367-023-00059-w

ORIGINAL ARTICLE

Mechanical degradation of poly(ethylene terephthalate) and its structural modification by chain extender

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Received: 10 February 2023 / Revised: 13 May 2023 / Accepted: 16 May 2023 / Published online: 30 May 2023

Abstract
Characterized by high strength to unit weight, poly(ethylene terephthalate) (PET) remains one of the most widely used engineering plastics, hence the attention to its associated waste and recycling technology development has been paid from academic and industrial perspectives. Herein, we investigate the mechanical degradation of PET through degradative compounding process cycles and the effect of chain extender (Joncryl® ADR 4468) to prevent molecular degradation of PET during melt processing. They are characterized based on rheological and mechanical measurements. Characterization of the bottle-grade PET samples reveals low viscosity and crystallinity owing to isophthalic acid units within the PET copolymer structure over PET homopolymer. Mechanical shear and thermal impact by virtue of the increase in rotor speed and temperature are employed to study the degradation of the PET samples. Both samples respond to degradation in successive processing cycles with as much as 70% decrease in their complex viscosity and moduli. The molecular weight of PET copolymer accordingly decreases from 23,400 to 8010 g/mol. Chain scission arising from thermo-mechanical degradation results in high crystallinity by more than five folds in the processed PETs. Attributed to recoupling of the degraded short chains, the chain extender compensates with the increase in viscosity and moduli up to 20% whilst serving to increase crystallinity but almost ineffective in appreciating mechanical performance with barely any significant variation in tensile strength and elongation at break. This study shows that mechanical shear is verified to impact a pronounced degradation on PET more than thermal action on the samples.

Keywords Polyethylene terephthalate · Degradation · Melt-processing · Rheology · Recycling

1 Introduction

Devastating concerns of waste plastic deposits and its repercussion influence on nature have exponentially increased and they inclined research into finding effective recycling routes to counter such menace [1–3]. PET is a linear polyester of carboxylic functional group (COOH) and hydroxyl groups (OH), synthetized with terephthalic acid and a dicarboxylic aromatic acid with a large aromatic ring on six sides which provides the polymer with good mechanical properties that spans to high impact strength and good abrasive resistance over other polymers [4, 5]. However, these properties are compromised owing to manufacturing conditions, usage, and different recycling procedures. Degradation of PET has been studied to develop PET-recycling technology. Several studies echo the most vulnerable unit in the PET structure at the ester linkages which serves as an avenue for attack, initiating degradation in PET. Characterized by the minimum critical activation bond energy at the ester linkage, degradation reactions in most forms of hydrolysis, oxidation, and thermal reaction break up the ester bonds through chain scission. This increases the number of carboxylic end groups. Many studies employed this ideology to measure the concentration of carboxylic end groups to quantify the degree of degradation in the PET Chain [6–8]. Zimmerman and Kim [6] measured the amount of carboxyl end groups to characterize the chain scission as a function of degradation time in PET where they declared an autocatalytic mechanism at the initial carboxyl group content. Härth et al. explored thermo-oxidation degradation routes developing kinetic models to explain the viscosity variance in both air and

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nitrogen atmosphere rooting from the ester linkage [9]. Additionally, a radical formation which initiates chain scission was studied as a secondary complement to degradation by hydrolysis and thermo-oxidation as described by Zhang et al.[10]. To prevent degradation of PET, diverse functional additives such as plasticizer, stabilizer, and chain extender were employed to augment advanced properties to base polymer performance with respect to ductility, mechanical strength, resistivity, and bond stabilization among others. Chain extender has been extensively explored to reinstate and improve rheological and mechanical performance of polyesters [11, 12]. The addition of chain extender to polymer forms new covalent bonds through a reaction between chain extender and polymer with the carboxylic and hydroxyl end groups [13–15]. Pandey et al. [16] studied three types of chain extenders (pyromellitic dianhydride (PMDA), polymeric epoxy (Joncryl ADR), ethylene carbonate (EC)) and their effect on performance of the recycled PET in melt extrusion. Owing to higher number of epoxide functional groups, it was confirmed the increased activity in viscosity and modulus by PMDA and Joncryl ADR over EC [16]. It is well known for its net effective action increasing molecular weight and viscoelastic property of PET [17, 18].

This paper aims to investigate the mechanical degradation of PET and effect of chain extender on the degraded PET. For the purpose, we organized series of experiments with two different PETs for bottle usage using an internal batch mixer employed with twin screw with varying rotor speed and temperature. The processed PETs were blended with chain extender, Joncryl® ADR 4468 (ADR) and quantified based on its rheological, thermal, and mechanical measurements. ADR is a multifunctional oligomer chain extender composed of up to 9 epoxy groups which is designed to react effectively with carboxyl and hydroxyl ends of polyester. We explore the minimum activity of chain extension with the addition of only 0.4 phr of ADR in blend with PET to characterize the rheological and mechanical behaviors in respect to viscosity, modulus, tensile mechanical properties. Thermal characterization through thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis are employed to differentiate the relative crystallinity and study crystallization behavior of pure, degraded, and modified PETs. This preliminary study on PET regarding degradation and chain extension confirms that the impact of mechanical shear in a higher degree of degradation over its thermal counterparts, is deemed to be a major contribution to the polymer processing of recycled PET.

2 Materials and method

2.1 Materials: samples and reagents

Poly(ethylene terephthalate) (copolymer, melting temperature $(T_m) = 245 \pm 3°\mathrm{C}$, intrinsic viscosity $([\eta]) = 0.77 \pm 0.03\mathrm{dl/g}$) and Poly(ethylene terephthalate) (homopolymer, $T_m = 253 \pm 2°\mathrm{C}$, $[\eta] = 0.8 \pm 0.02\mathrm{dl/gr}$) were generously acquired from Lotte Chemical and SM TK Chemical Ltd respectively. Due to almost the same intrinsic viscosity, both PETs were assumed to have almost the same level of molecular weight. Joncryl® ADR 4468 (epoxy functional group: 9 per molecule, granule particle mean size: 2.5–4 mm) (ADR) was purchased from BASF, Asia–Pacific region and used as received.

2.2 Sample preparation

All sample resin was dried under vacuum conditions for 18 h at 110 °C before use. Through two processing degradation cycles, Thermo Scientific™ HAAKE PolyLab OS batch mixer was used to simulate degradation of the samples (Fig. 1). Composed of two rotors in clockwise and counterclockwise motion fitted in a 350 ml space volume, samples were fed through the barrel and corked in the chamber as indicated in Fig. 1b. Each sample was compounded in the Polylab OS batch mixer for 40 min at 260 °C. Two nominal rotor speeds were employed as a measure for mechanical impact at 40 RPM and 80 RPM. The 0.4 phr of ADR was incorporated with PET after the first cycle and the PET sample was allowed to cool down under atmospheric conditions as illustrated in the experimental procedure in Fig. 1a. Thermal impact on the samples was investigated at 260 °C and 270 °C. After sample preparation, the samples were molded for rheological, thermal and mechanical measurements under hot press compression and denoted as virgin PET copolymer (vPET-C), virgin PET homopolymer (vPET-H), the first and second extruded PET-C (ePET-C1, ePET-C2) and in the same manner for homopolymer.

2.3 Sample characterizations

2.3.1 Thermal characterization (DSC and TGA)

Crystallinity and thermal decomposition behavior of pure, extruded and modified PET were verified through differential scanning calorimetry (Discovery DSC, TA Instrument) (DSC) and thermogravimetric analysis (TA instrument, Newcastle, DE, USA) (TGA) respectively. At a heating and cooling ramp rate of 10 °C/min with DSC, the samples were subjected to two heating profiles spanning from 30 to 300 °C. Crystallinity $\left(\chi_c\right)$ of pure and modified PET was calculated as follows,

$$\text{Pure PET}: \chi_c(\%) = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H^0_{PET\,\chi_c 100\%}} \times 100,$$

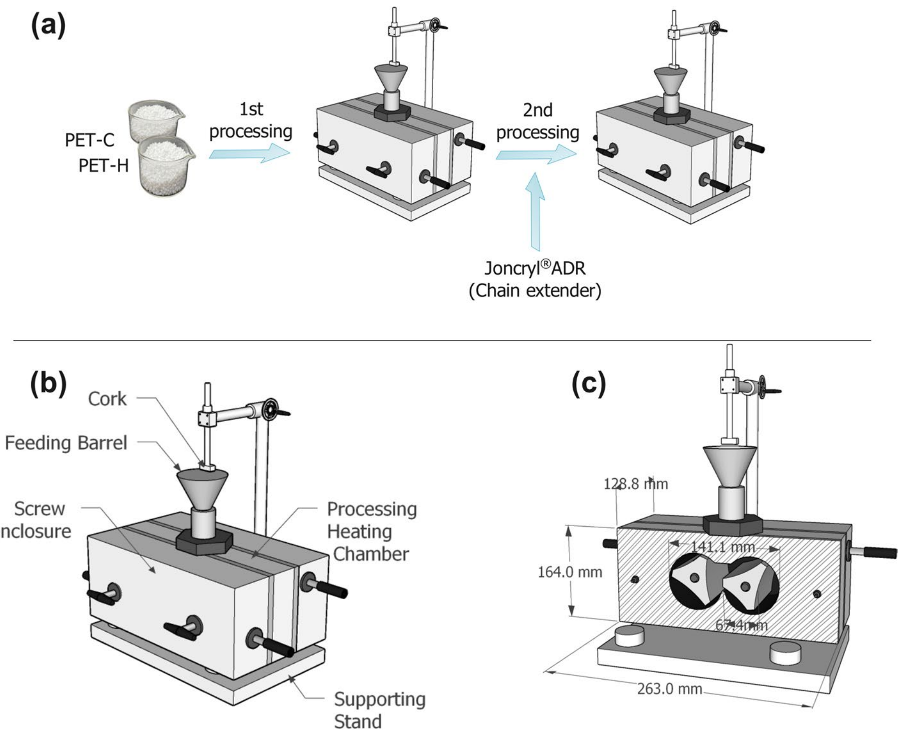


Fig. 1 **. a** Experimental procedure for degradative processing of PET samples. **b** Schematic design of internal batch mixer (Haake Polylab OS) for degradative processing and **c** its sectional view

$$\text{Modified PET}: \chi_c(\%) = \frac{\Delta H_m - \Delta H_{cc}}{W \times \Delta H^0_{PET\,\chi_c 100\%}} \times 100, \tag{1}$$

where ΔH_m is the enthalpy of polymer melting, ΔH_{cc} is the enthalpy arising from cold crystallization, $\Delta H^0_{PET\,\chi_c 100\%}$ is the enthalpy at 100% crystalline PET which is verified at 140 J/g and W is the weight fraction of the added ADR. TGA was proceeded under nitrogen (N2) gas atmosphere over heating from 30 to 800 °C.

2.3.2 Rheological characterization

Rheological properties were examined using a stress-controlled rheometer (MCR-102, Anton Paar). The samples were dried and molded into 25 mm disc for rheological analysis at 260 °C and 270 °C. Small amplitude oscillatory stress sweep tests were conducted over 1–1000 Pa at a frequency of 1 rad/s to determine the linear viscoelastic region. Dynamic frequency sweep was then proceeded over a frequency range of 1–100 rad/s at stress values within the linear viscoelastic region. Viscosity as well as linear viscoelastic moduli (storage (G') and loss modulus (G'')) were studied for all the samples.

2.3.3 Mechanical characterization

Mechanical tensile properties were evaluated using UTM (LF plus, Lloyd instruments Ltd.) and standardized to ASTM D638 type V. The samples were molded into dog-bone shape through compression molding for analysis. Under strain rate of 10 mm/min, samples were subjected to at least 5 uniaxial tensile test and results were averaged to obtain tensile strength and elongation at break values.

3 Results and discussion

Owing to the susceptibility of PET to moisture and shear, hydrolysis causes a remarkable loss in molecular weight of PET and residual rheological properties during reprocessing [19]. This study intends to investigate the degradation of PET by repetitive processing based on thermal, rheological, and mechanical measurements. As shown in Fig. 1a, PET undergoes mechanical shear at melt state repetitively and the processed PETs (ePET) are characterized based on rheological, thermal, and mechanical analyses.

3.1 *Rheological analyses of PETs*

3.1.1 Rheological behavior of PETs

Processing in a laboratory scale was compounded in a batch mixer (Fig. 1b, c) to mimic the degradation of the samples. First of all, two different types of PETs (PET-H, PET-C) are characterized before they go through processing. Incorporation of isophthalic units during polymerization within the PET copolymer (PET-C) alters molecular interaction for advanced properties in PET. This modification fruits low viscosity, better processability, enhanced ductility, and better clarity. Inferably, lower melting temperature also favors the cost of production of PET-C. Strain amplitude oscillatory sweep tests were conducted to determine the linear viscoelastic region of strain for the samples (Fig. 2a). Because of the high fluidity of the PETs, the tests were ruled by stress over the traditional strain sweep test. At a frequency of 1 rad/s, the PET homopolymer (PET-H) exhibits a wide region of linear viscoelasticity averaging a storage modulus of 10 Pa fairly over decades of observation stress region where the polymer's modulus became dependent on the oscillatory shear applied. PET-C portrayed a similar behavior but at a lower storage modulus averaged at 2.5 Pa. For further linear viscoelastic measurements, dynamic oscillatory sweep tests were conducted under the linear deformation region of stress of 10 Pa (equivalent strain < 10%) at 260 °C. Figure 2b, c show outcome of dynamic oscillatory frequency sweep tests of virgin PETs. Viscosity curves prove both PETs exhibit fairly Newtonian behavior with constant viscosity over several decades of frequencies. It also characterizes PET-C with a much lower complex viscosity than PET-H. This is attributed to the presence of the isophthalic acid units within its structure that impedes entanglement of polymer chain under the assumption of almost identical molecular weight hence reduces the resistance to flow thus the overall viscosity is reduced [20]. Linear viscoelastic moduli (storage and loss modulus) as a measure of molecular structure and chain entanglement are greatly influenced by the incorporation copolymerized unit realizing lower moduli in PET-C than PET-H.

3.1.2 Rheological behavior of Processed PETs

These two PETs, PET-H and PET-C were processed repetitively through an internal mixer as shown in Fig. 1. In each processing, the samples were compounded at 40 RPM for 40 min until complete melting was realized at 260 $°C$ to obtain the processed PET samples (ePET-1, ePET-2). Figure 3a, b show small amplitude oscillatory stress sweep test outcomes of ePETs depending on repetition of processing. The value of critical stress indicating linear-nonlinear viscoelastic transition is effectively decreased for ePET-C compared to ePET-H. It is reduced from 80 to less 5 Pa for ePET-C. Its storage modulus shows decrease not only in the value but also its linear region is effectively decreased. It clearly shows that PET goes through chain scission during processing, resulting in a change in molecular weight. Correspondingly, the degradation of PET decreases complex viscosity of both PETs. For PET-C, the viscosity is decreased in order 56.6 Pas, 16.7 Pas to 4.5 Pas for vPET-C, ePET-C1 and ePET-C2 respectively (Fig. 3c). For PET-H followed suit with a decrease in the viscosity in order 158.7 Pas, 49.9 Pas, and 9.3 Pas (Fig. 3d). PET-H shows further degradation as the repetition of processing increases compared to PET-C (Fig. 3c–e). The samples were mainly exposed to two degradation parameters: mechanical and thermal impact. In practice, because PET is processed under mechanical shear at high temperature, shear and temperature collectively impose thermo-mechanical effects that led to cleavages and eventually chain scission of the polymer, reducing molecular weight below a critical molecular weight. This was correspondingly verified with a gel permeation chromatography (GPC) test which characterized the weight-average molecular weight at 23,400 g/mol and 8010 g/mol for vPET-C and ePET-C1 respectively. It was known that when PET is subjected to thermal degradation, volatile and non-volatile residue including cyclic oligomers, vinyl ester and acid ends are produced [21]. This process is facilitated under two mechanisms through intramolecular back biting and B-C-H hydrogen transfer. Mechanical shear accelerates the action of radicals in initiating β-scission decreasing chain length and hence overall rheological properties [22, 23]. Moreover, the aliphatic end groups of PET are more susceptible to the cleavages than aromatic units [24]. Thus, in PET copolymer with incorporated isophthalic units composed of more aromatic carboxylic –COOH groups, further degradation is probably minimal as compared to PET-H counterparts with more aliphatic ends which experienced more degradation. As such, viscosity of PET-H is further decreased as shown in Fig. 3d.

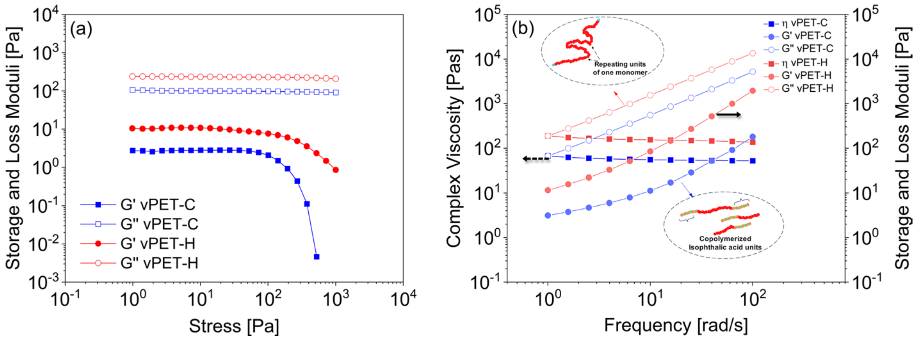
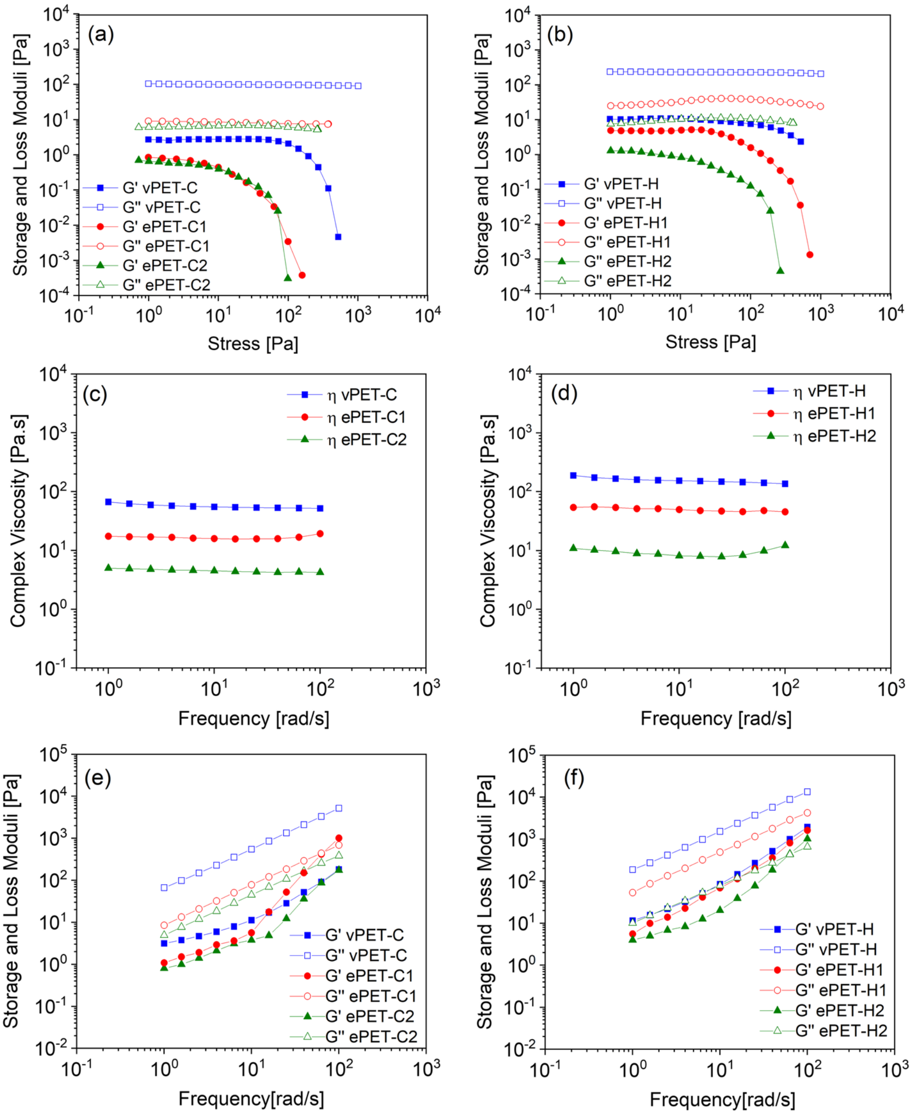


Fig. 2 Comparison of storage (G′), loss modulus (G″), and complex viscosity of virgin PETs from a small amplitude oscillatory stress sweep test and **b** dynamic frequency sweep tests

Fig. 3 Small amplitude oscillatory stress sweep test: **a** PET copolymer (PET-C) and **b** PET homopolymer (PET-H) and **c**–**f** dynamic frequency sweep tests of PET-C and PET-H depending on repetition of processing



3.1.3 Rheological behavior of processed PETs with chain extender

To compensate molecular degradation of the processed PETs, a chain extender additive was introduced. A small amount of chain extender (Joncryl® ADR 4468) (ADR) was added to the processed PETs as shown in Fig. 1a. Due to multiple epoxide functionals, ADR expects to show a faster reaction with PET [25]. The previous study [26] reported that ADR with epoxide functional coupled with polymer chains increased molecular weight, viscosity, and modulus with apparently as little as 0.2–0.4 phr under 30 s reaction time. Chain extenders play a multifunctional role to recouple with distorted carboxyl and hydroxyl group at the chain ends of the degraded polymer, thereby extending the chain length [14]. Recoupling of long chains increases the molecular weight of chains and favors entanglement during melt flow, hence appreciating viscosity of the sample [27]. In this study, because of a short reaction time of the chain extender, pre-melting of the solid PET samples was performed before the concurrent addition of the chain extender ADR and the rotor speed was increased from 40 to 80 RPM to enhance the reaction. Rheological analysis presented in Fig. 4 through small amplitude stress and frequency sweep test proves that, chain extension is effective in increasing viscosity and moduli of degraded chains, as the previous showed [28]. With ADR, the critical linear viscoelastic region of ePET is expanded from less 5–20 Pa (Fig. 4a). The viscosity curve depicts a clearer chain extension merit as viscosity of the modified ePET returns to virgin level at 54.2 Pas in average. From Fig. 4c, storage modulus at frequency of 1 rad/s is increased by chain extension effect from 1.08 to 8.35 Pa.

In addition, the in-depth effect of both thermal and mechanical impacts on the degradation of PETs are verified by virtue of increasing the rotor speed and processing temperature. Then, the effect of thermal and mechanical

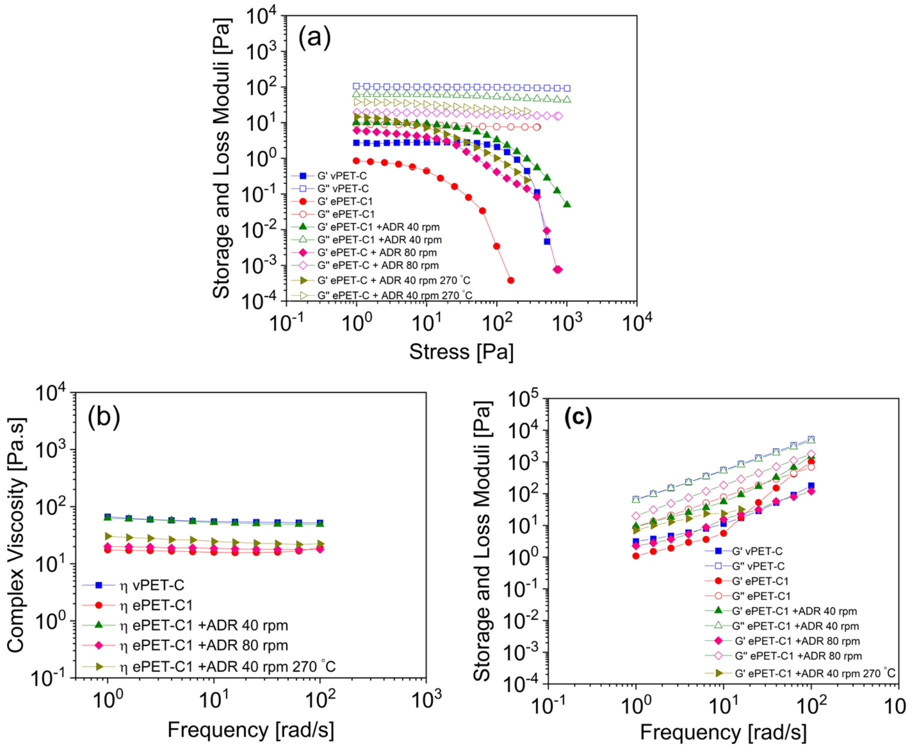


Fig. 4 Effect of thermo-mechanical degradation on the processed ePETs: **a** small amplitude oscillatory stress sweep test and **b**, **c** dynamic frequency sweep test

degradation on modified ePETs with chain extender was investigated by adjusting the rotor speed and increasing temperature from 260 to 270 °C. It was realized that the increase in rotor speed (from 40 to 80 RPM) and temperature reduce rheological properties but not as much in depth as without the chain extender. Linear viscoelastic region had depreciated in both cases. All samples exhibited Newtonian behavior in the viscosity as shown in Fig. 4b. However, from frequency sweep test outcome presented in Fig. 4b, c, the increase in rotor speed as a measure of mechanical shear impact reduces viscosity more than the increase in temperature. Processing at 80 RPM in rotor speed at 260 °C, the value of viscosity is reduced greatly to 18.7 Pa whilst 40 RPM at 270 °C stands considerably at 25.3 Pas, recording a 12% more reduction in viscosity by mechanical shear. Storage and loss moduli follow suit with minimal reduction to increase in temperature whilst at 80 RPM, the samples suffer a greater loss. It proves that the effect of mechanical shear forces initiate degradation in higher degree than thermal impact.

3.2 Thermal analyses of PETs

The thermal decomposition behavior of the PET samples is analyzed and presented in Fig. 5. Virgin PETs remain thermally stable over several decades of temperature until above 350 °C when it started to deteriorate. All samples exhibited a two-step decomposition process characteristic of copolymer as seen with a sharp first step loss around 420 °C and the second step at about 550 °C respectively. PET-C exhibits relatively higher residual mass loss than PET-H, which is attributed to the presence of isophthalic acid units which acts as impurities within the copolymer chains hence lowers the thermal stability at loss onset above 200 °C [29]. The curves prove that the thermal decomposition of the modified or processed PET from 80 °C, which is far inferior to the stability of virgin PETs. A distinctive weight loss disparity in an increase in rotor speed at 80 RPM against temperature increase at 270 °C was observed. An effect that will be confirmed later in further test. Corresponding derivative weight curves present for all the samples in Fig. 5b. The tolerable thermal processing zone of 0 to 300 °C is referenced from the results of the TGA curves.

Figure 6 compares DSC thermal analysis of PETs. The samples were subjected to first and second heating–cooling cycles at a ramp rate of 10 °C/min. The former intended to erase any thermal history so that the latter can reflect the true thermal behavior of the samples. The outcomes are listed in Table 1. Melting peaks are verified at 252.5 °C and 248 °C for PET homopolymer (vPET-H) and PET copolymer (vPET-C) respectively. From the cooling curve, PET shows crystallization temperature at 166 °C and 163 °C for PET-H and PET-C, respectively, where maximum crystallization as high as 33.9% is observed in homopolymer as shown in Fig. 6a. Both PETs show the glass transition temperature (T_g) near at 80 °C. PET copolymer exhibits cold crystallization peak at 172 °C. This phenomenon arises from the exothermic crystallization wherein during the cooling ramp

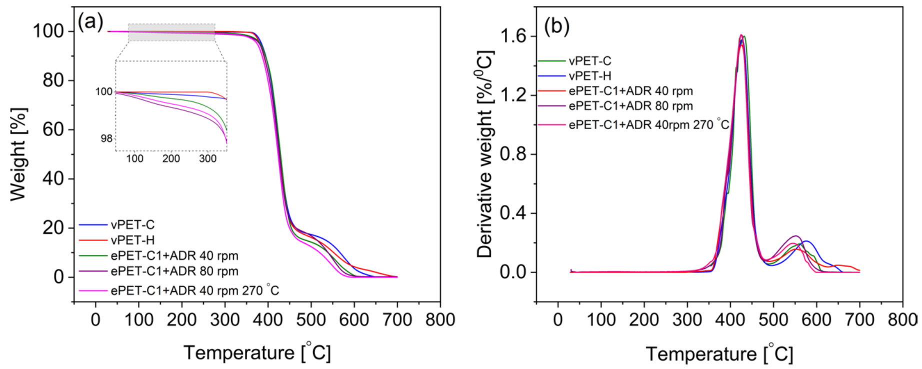


Fig. 5. **a** TGA and **b** its weight derivative curves of PETs depending on ADR and processing condition

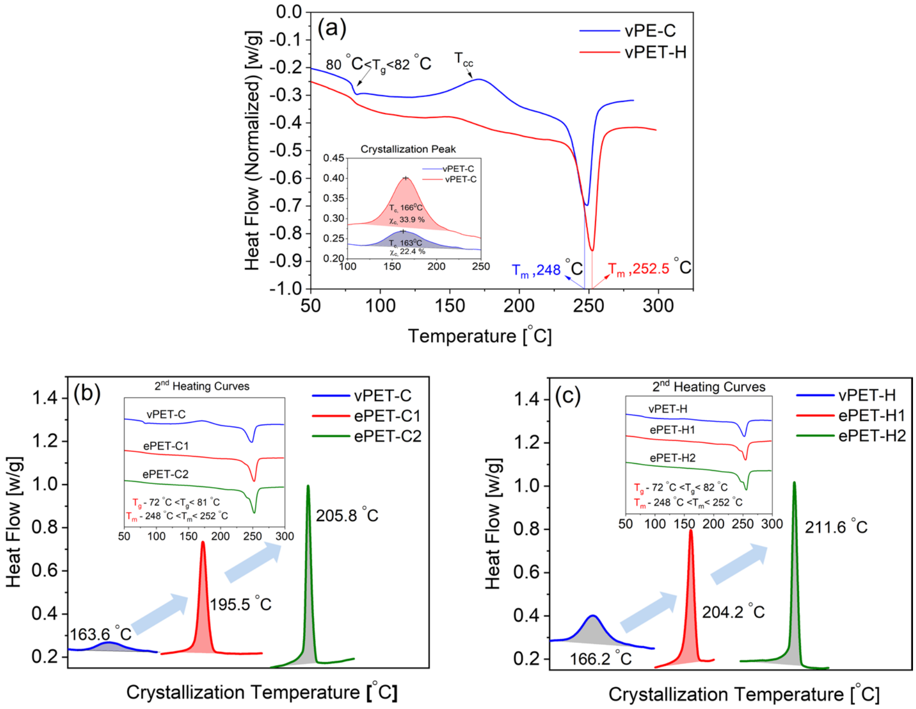


Fig. 6 DSC thermal curves of PETs: **a** virgin PETs **b**, **c** PETs processed at 260 °C and 40 RPM

Table 1 DSC analysis of pure and processed PETs

Sample	Glass Transition Temperature °C	Melt Peak Temperature °C	Enthalpy of fusion J/g	Crystallization Temperature °C	Enthalpy of cold crystallization J/g	Crystallinity %
vPET-C	80.2	248.6	44.5	163.6	13.2	22.4
ePET-C1	81.6	252.2	52.0	195.5	0.0	37.1
ePET-C2	78.3	252.5	59.7	205.8	0.0	42.6
vPET-H	81.9	252.5	47.4	166.2	1.3	32.9
ePET-H1	77.4	254.6	62.8	204.2	0.0	44.8
ePET-H2	72.5	255.8	60.7	211.6	0.0	43.4

molecules did not have much time to fully crystallize [30]. Below the glass transition temperature, mobility is seized, as such during the second heating, above the glass transition temperature molecular mobility is once again established and the molecules reconstruct to form crystallites. Interestingly, PETs show a significant change in crystallization as the processing number increases. Figure 6b presents the DSC curves of PETs depending on the repetition of processing.

The crystallinity of both samples increases after the first processing from 22.4 to 37.1% for PET-C and from 32.9 to 44.8% for PET-H. This change in crystallinity is attributed to favored crystallite formation by short chains arising from the chain scission caused by the thermo-mechanical degradation during the processing. A characteristic shift in crystallization temperature towards higher temperature is observed, which means that the degraded PET chains induce crystallization in the processed PET samples. Correspondingly, there is a gradual shift of glass transition temperature towards lower temperature as the repetition of processing increases. This is expected to influence the mechanical performance of the processed PET.

With the addition of a chain extender, ePETs are ensured the compensation of molecular degradation based on rheological analysis. It also reflects in DSC thermal analysis. DSC curves in Fig. 7 (and Table 2) confirm the decrease in crystallinity of modified ePET-H with chain extender but not ePET-C probably owing to the presence of the isophthalic units which may have coupled with chain extender creating nucleation sites that increased the crystallinity of ePET-C1 ADR beyond virgin level and ePET-C1 [30]. The results clearly infer that ePETs do not simply extend molecular weight of PET with the addition of a chain extender. By increasing rotor speed and temperature as a measure of mechanical and thermal degradation, the effect of ADR is slightly varied. When RPM is increased, crystallinity is slightly decreased as shown in Fig. 7 and Table 2. To understand why the addition of ADR increases or decreases crystallinity of PETs depending on the types of PET, further study is necessary. In the next section, the tensile mechanical performances of PETs are investigated.

3.3 *Mechanical tensile analyses of PETs*

The presence of the aromatic ring in PET chain gives an increasing effect on the mechanical strength of PET compared to its molecular weight [5]. It is one of the characteristic functions that portray PET as a loving polymer in the industry. However, these properties are compromised under reprocessing conditions during recycling. Tensile test outcomes of the processed PET (processed for 10 min) are compared in Fig. 8. Both virgin PETs exhibit high tensile strength and elongation at breaks as expected. Again, PET copolymer flaunts higher mechanical properties than PET homopolymer. Evidently, the incorporation effect of isophthalic acid units within the copolymer structure comes to bear. This introduces ductility within the polymer, as such PET copolymer stretched to 51.2% over PET homopolymer at 24.7%. However, after one cycle of processing, the mechanical tensile ductility of PET-C decreases drastically in magnitude down by five (5) folds. Elongation at break reduces from 51.2 to 11.4% in PET-C. Compared to this, PET-H shows less reduction from 24.7 to 11.0%. The higher crystallinity after processing makes them enormously brittle to extension. Unexpectedly, the action of chain extension

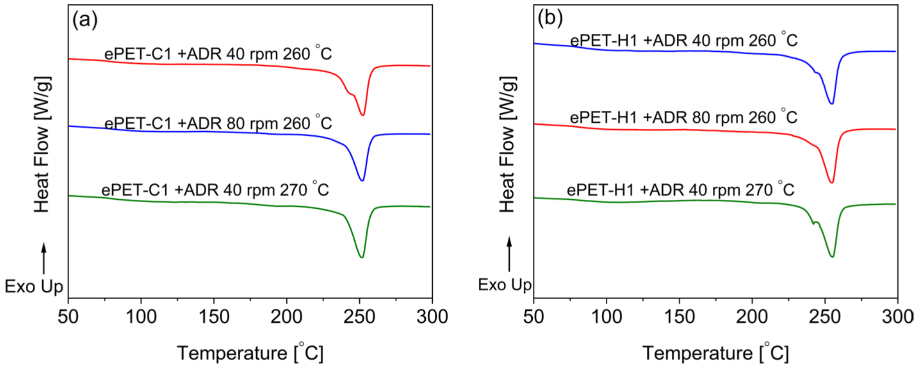


Fig. 7 DSC curves of modified ePETs: **a** PET copolymer **b** PET homopolymer

Table 2 DSC analysis of modified PETs

Sample	Glass transition temperature °C	Melt peak temperature °C	Enthalpy of fusion J/g	Crystallization temperature °C	Crystallinity %
ePET-C1 + ADR 40 RPM 260	83.2	252.47	55.8	208.8	39.9
ePET-C1 + ADR 80 RPM 260	83.5	252.00	47.2	192.8	33.8
ePET-C1 + ADR 40 RPM 270	81.2	251.76	52.7	190.1	37.7
ePET-H1 + ADR 40 RPM 260	85.2	254.76	51.2	197.6	36.7
ePET-H1 + ADR 80 RPM 260	82.3	254.92	49.9	196.5	35.7
ePET-H1 + ADR 40 RPM 270	85.1	255.27	47.9	196.0	34.3

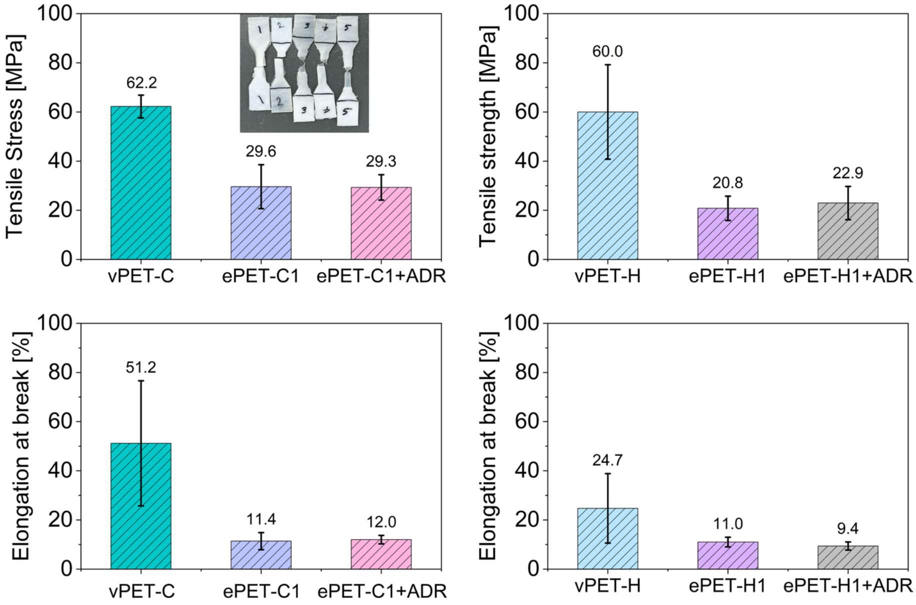


Fig. 8 Mechanical characterization of samples depending on ADR and processing

does not compensate for poor mechanical properties of the processed PETs. Tensile strength and elongation at breaks are fairly the same. For reflective mechanical property behavior, an increase in the content of chain extender can probably appreciate the tensile and strain values.

4 Conclusions

In this study, the mechanical degradation of PETs (PET-C, PET-H) through degradative processing cycles was investigated based on rheological, thermal, and mechanical characterizations. Also, the processed PETs were blended with a chain extender (Joncryl® ADR 4468) to investigate the chain extension effect of the processed PET. Both PET samples responded to degradation in successive processing cycles in a magnitude of 70% decrease in their complex viscosity and moduli. Chain scission arising from thermo-mechanical degradation favored the increase in short chains for broadened crystallite distribution which results in high crystallinity by more than 5 folds in processed PETs. Attributed to recoupling of the degraded short chains, the chain extender compensated with the increase in molecular weight, viscosity, and moduli up to 20% whilst serving to increase crystallinity but ineffectively affecting mechanical performance with barely any significant variation in tensile strength and elongation at break. This study showed that mechanical shear is verified to impact a pronounced degradation effect on PET more than thermal action on the samples. Also, it showed that the processed PET samples became more brittle per the processing number of cycles which posed difficulty especially in application of recycled PET. Reduction in molecular weight below a critical molecular weight turned the PET polymer from ductile to brittle rendering them undesirable for applications. It will provide a fundamental understanding on degradation of PET and development of recycling PET technology.

Acknowledgements This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIP) (No. 2020M3H7A1098305).

Data availability All datasets generated and analyzed during this study are available upon request from the corresponding author.

Declarations

Conflict of interest The authors declare no competing conflict of interest.

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