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# Thermo-rheological analysis of various chain extended recycled poly(ethylene terephthalate)

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## Abstract

Three chain extenders, pyromellitic dianhydride (PMDA), ethylene carbonate (EC), and a polymeric-epoxide, were investigated for improving recycled p(ethylene terephthalate) (r-PET) properties with melt extrusion. The amount of additives and processing temperatures were also varied to check for melt degradation. Small amplitude oscillatory shear experiments were performed to probe rheological changes with different chain extenders. Capillary rheometry with haul-off was also performed to measure extensional viscosity and melt strength. Higher loadings of the chain extenders were found to improve properties of r-PET. These chain extenders definitely increased melt viscosities when incorporated at the higher level of the ranges examined, matching that of virgin PET. EC addition resulted in high shear thinning of the polymer. Epoxy and PMDA added to r-PET produced products with the same extensional viscosity as v-PET. Haul-off experiments demonstrate superior performance by epoxy-modified r-PET compared to v-PET.

## KEYWORDS

chain extension, poly(ethylene terephthalate), processing, recycle, rheology

## 1 | INTRODUCTION

Poly(ethylene terephthalate) (PET) is one of the most commonly used thermoplastic polymers, finding applications in fibers, strapping, rigid bottle and thermoformed packaging, and films, taking advantage of its excellent combination of mechanical, thermal, and good barrier properties. One of its most important applications is in the manufacture of beverage bottles. The high consumption of PET in bottles necessitates their recycling; making PET one of the most recycled thermoplastics in the world. Further advances are needed, however, to ensure the production of recycled PET (r-PET) products, which maintain the properties required for market application.<sup>[1–6]</sup>

Reduction in molecular weight occurs when post-consumer PET is recycled in a normal extrusion scheme, due both to thermal and hydrolytic degradation, resulting

in the loss of molecular weight (commonly measured indirect as intrinsic viscosity  $[\eta]$ ) and loss of overall mechanical properties. The presence of retained moisture (hydrolysis) and contamination by poly(vinyl chloride) (hydrogen chloride) generation are two key reasons for polymer degradation during processing of r-PET.<sup>[7–10]</sup>

To limit PET degradation during recycling, intensive drying with vacuum degassing processing and solid state processing have been tested and produced molecular weights higher than those obtained with simply re-extruded r-PET. These engineering solutions are slow and expensive, whereas chemical modification such as use of chain extenders is potentially less expensive, easy to implement, and is a demonstrated method of building molecular weight during melt processing.<sup>[11]</sup>

Chain extenders are polyfunctional additives and capable of reacting with the hydroxyl or carboxyl end

groups of PET. The concentration of the modifier in the reactive extrusion process has been studied the most in recent years with the intention of increasing IV of PET.<sup>[12–16]</sup> Pyromellitic dianhydride (PMDA) has been testified as one of the efficient chain extenders.<sup>[11]</sup> Multifunctional epoxy additives have also been used as chain extenders in improving r-PET properties but are not used as extensively as PMDA.<sup>[6,8,17]</sup> From the industrial point of view, this melt processing of r-PET with chain extender is very interesting as it involves only one-step processing for getting modified r-PET with improved properties.<sup>[18–25]</sup>

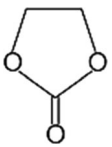
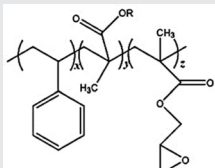
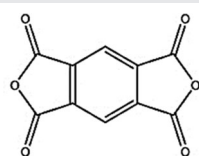
The main objective of the present work is to compare three promising chain extenders, PMDA, polymeric epoxide, and ethylene carbonate (EC), in their role as a compensator for reduction in chain length of r-PET during extrusion. The effects of additive loading upon melt processing and mechanical properties will also be explored herein.

## 2 | EXPERIMENTAL

### 2.1 | Materials

Recycled PET (r-PET) flakes were obtained from Verdecro Recycling Inc. (Los Angeles, CA); virgin PET (v-PET), Laser+ DAK Americas (0.84 IV, ~2% isophthalate copolymer), bottle resin grade was obtained from the producer. PMDA, Joncryl polymeric epoxy (epoxy) and EC were obtained from Acros Organics (NJ), BASF (Ludwigshafen, Germany) and Huntsman International LLC (Houston, TX), respectively. Table 1 represents the

**TABLE 1** Structures and chemical names of the chain extenders used

Abbreviation	Chemical structure	Chemical names
EC		Ethylene carbonate
Epoxy		Joncryl ADR-4368C
PMDA		Pyromellitic dianhydride

structure of the chain extenders used and their chemical names as well as abbreviation used later.

### 2.2 | Extrusion and characterization

Reactive extrusion was performed using a Eurolab 16 corotating twin-screw extruder (Thermo Scientific, Hillsboro, OR) at 275°C and 285°C using r-PET and chain extenders at 0.25 wt% and 0.5 wt%. Before performing extrusion or any other characterization, the flakes or extrudates were dried at 80°C under vacuum for 48 hours.

Rheological characterization in linear viscoelastic regime was performed using an ARES G2 rheometer (TA instruments, New Castle, DE) at 30% strain and at the same temperature as during processing. All experiments were performed on a 25 mm diameter parallel plate configuration.

Differential scanning calorimetry (DSC) experiments were used to investigate changes in melting temperature and percent crystallinity. The experiments were performed under nitrogen atmosphere on a DSC250 (TA instruments). Second heating curves were taken into account for comparison, as we are more interested in seeing structural changes and not processing effects. Temperature ramps from 25°C to 300°C at 10°C/min were imposed.

Extensional viscosity measurements were completed using a RH10 Capillary rheometer (Malvern Instruments, Westboro, MA). Bagley corrections were performed with 1 mm dies of 32 and 0.25 L/D. A temperature of 270°C was used, as the viscosity of the melts became too low for accurate measurements at a higher temperature. Haul-off experiments were necessary to evaluate extensibility of melts at higher take up forces, which is useful to see its applicability in blow molding operations. The haul-off experiments were performed at a temperature of 259°C, determined after performing various trial experiments to identify when the melt strand becomes stable for stretching. A constant piston speed of 3 mm/min was used. The haul-off force vs take-up speed data was converted to melt stress ( $\sigma$ ) vs Hencky strain ( $\epsilon_H$ ) using Equations (1) and (2).<sup>[26]</sup>

$$\epsilon_H = \ln \frac{V_f}{V_0}, \quad (1)$$

$$\sigma = \frac{FV_f}{Q}, \quad (2)$$

where  $V_f$  is take up velocity,  $V_0$  is the initial velocity at die exit,  $F$  is the haul-off force, and  $Q$  is the flow rate.

IV measurements were carried out by a third-party laboratory, PTI (Toledo, OH) following ASTM D4603, using 60/40 phenol/tetrachloroethylene solvent at 30°C.

### 3 | RESULTS AND DISCUSSION

A laboratory-scale extrusion of r-PET with and without 0.25 and 0.50 wt% of the three chain extenders of interest was carried out at 275°C and 285°C, respectively. All samples were dried before extrusion, though some moisture exposure was inevitable in the transfer from drying oven to extruder feed hopper. In a commercial operation, this difficulty could be eliminated by dedicated feeding from drier to extruder.

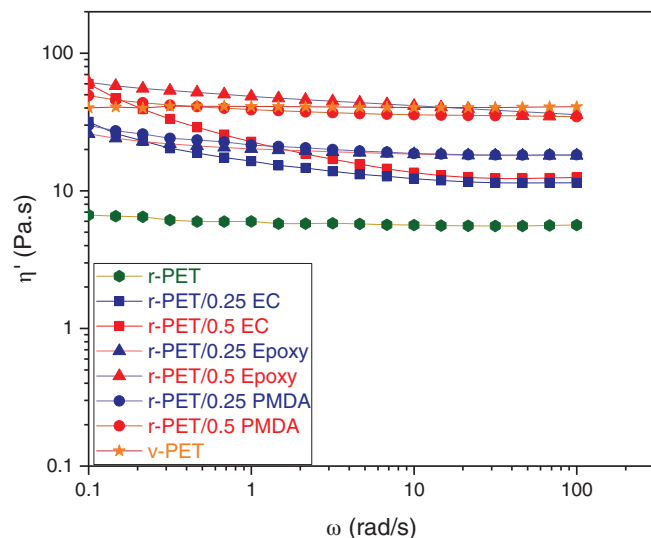
Small amplitude oscillatory shear experiments can be used to investigate the chain extension of PET. Figure 1 shows that the dynamic viscosity curve from frequency sweep at 285°C, v-PET, and r-PET as received behaves like a Newtonian fluid as expected in this frequency range. v-PET shows higher viscosity than r-PET because of its higher average molecular weight. Because this testing must be carried out in the linear viscoelastic region, 30% strain was chosen. Tested at 1 Hz, an amplitude sweep on the samples showed that  $G'$  moves downward after 50% strain and was not very stable until 10%, so the midpoint of the range, 30% strain, was selected.

When r-PET is extruded with chain extenders, PMDA and epoxy clearly provide more resistance to flow implying more successful chain extension processes than was

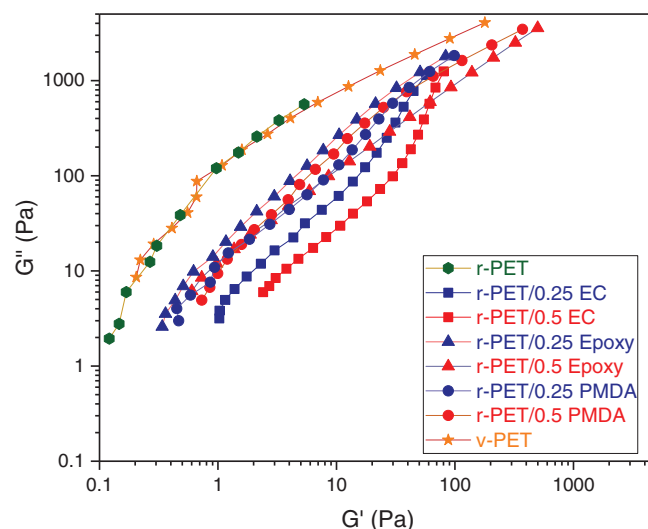
observed with EC. EC brought about greater shear thinning to the material, which is not desired, as it is important to have a higher viscosity at higher frequencies. When the amount of chain extenders was increased two-fold, the viscosities increased significantly. The 0.5 wt% of epoxy or of PMDA each increased the viscosity of r-PET back to the range of v-PET. Enhanced shear sensitivity of the dynamic viscosity or more pronounced power-law behavior may be related with a broader molecular weight distribution (MWD). Researchers have also shown that shear-thinning behavior in a lower shear rate range after the chain extension process, may be attributed to a long time relaxation mechanism, such as entanglement couplings between the high-molecular weight fraction and those associated with long-chain branches.<sup>[27,28]</sup> These might be the reasons why EC brings shear thinning to r-PET.

The Cole-Cole plot is sensitive to polydispersity and side-chain branching and independent of molecular weight.<sup>[29]</sup> The introduction of branching shifts the Cole-Cole plot to higher  $G'$  value with respect to constant  $G''$ . As evident in Figure 2, chain extension moves the curve to a higher  $G'$  value at a constant  $G''$ . EC increments the  $G'$  highest compared to PMDA and epoxy. Higher weight fraction shifts the curve toward the right. These results reveal the existence of branching and broader MWD in all the chain extended r-PET and the most in case of EC extended r-PET.

Melt processing of PET would be expected to cause thermal and hydrolytic degradation to some extent, so it



**FIGURE 1** Dynamic viscosity vs frequency for various chain extended poly(ethylene terephthalate) (PET), where r-PET is recycled PET and v-PET is virgin PET and 0.25 and 0.5 are the weight percent of chain extenders [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



**FIGURE 2** Cole-Cole plot for various chain extended poly(ethylene terephthalate) (PET), where r-PET is recycled PET and v-PET is virgin PET and 0.25 and 0.5 are the weight percent of chain extenders [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

was also important to check the rheological behavior of chain extended PET when processed at temperatures (275°C) other than 285°C. The nature of the curve remained the same as when processed at 285°C implying moving from 275°C to 285°C did not cause significant polymer degradation.

Table 2 represents the melting and recrystallization temperatures and percent crystallinity calculated from the second heating cycle. Second heating parameters were used to observe structural changes. Intrinsic viscosities of the extruded products are also included in this table. All the extruded materials showed reduced IV values compared to as-received r-PET, indicative of trace moisture reabsorption between the drying and extrusion steps. Those samples produced with PMDA addition showed slightly higher IV values than the other extruded samples (including r-PET without additives), whose IV measurements were within experimental error of one another. Awaia et al also reported higher IV values obtained incorporating PMDA in industrial scale reactive extrusions; this effect was most profound at 0.3 wt% PMDA addition.<sup>[11]</sup> Using the same epoxy grade as in the current study, added at 1.0 to 1.5 wt%, Duarte et al reported increased IV and melt torque values for virgin and postconsumer recycle PET.<sup>[30]</sup> The IV measurements for the different extruded materials were similar to one another despite the rheological difference noted above points to the fact that IV is relatively insensitive to small degrees of branching in polyesters, while rheological performance is conversely highly dependent upon this structural feature.

None of the chain extender additions brought about significant changes in the DSC transitions, implying that they do not bring about major structural changes in the polymer. Recrystallization temperatures from the melt for all of the extruded samples were very similar to one another; PMDA depressed the recrystallization

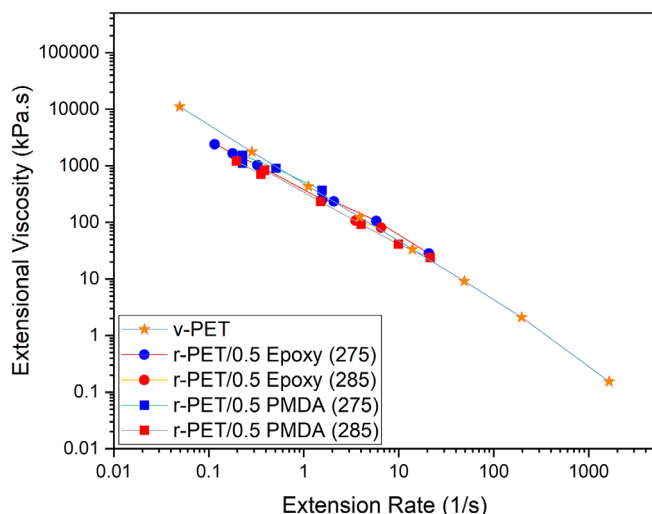
temperature by approximately 5°C and 10°C, at 0.25 and 0.5 wt% additional levels, respectively, suggestive of minor molecular branching of the polymer. All of the extruded polymers showed higher recrystallization temperatures compared to unextruded r-PET, almost certainly reflecting the loss of IV observed during the laboratory extrusions. Commercial v-PET did not show an appreciable recrystallization under the DSC conditions employed, reflecting both the considerably higher IV of the polymer and the expected retardation of crystallization rates necessary for injection blow molding applications. The  $T_m$  value for the v-PET grade chosen for this study was approximately 5°C higher than that of the r-PET polymer, which also points to higher degree of molecular substitution in the virgin product compared to r-PET, which is by definition a wide spectrum product obtained from the marketplace. These DSC results differ from those of Raffa et al, who reported that a different epoxy additive retarded PET crystallization rates in reactive extruded product.<sup>[17]</sup> This difference importantly points out that not all epoxides will react in equivalent matter; for the present study, we selected an epoxy additive specifically marketed as a PET chain extender. Liu and Xu reported that chain extension using a bis-oxazoline additive reduced the crystallinity of reactively extruded PET, while effectively preventing IV loss during extrusion.<sup>[31]</sup> It is reasonable to postulate that bis-oxazolines could bring about higher levels of branching than the other additives examined in the present work and would therefore more profoundly affect crystallinity of the product, a generally undesirable outcome.

For capillary rheometry experiments, only the epoxy and PMDA-modified r-PET were chosen for experiments as the EC-containing samples brought about undesirable high levels of shear thinning. Figure 3 shows extensional viscosity data against extension rate for epoxy and PMDA-added r-PET. At both 275°C and 285°C, the

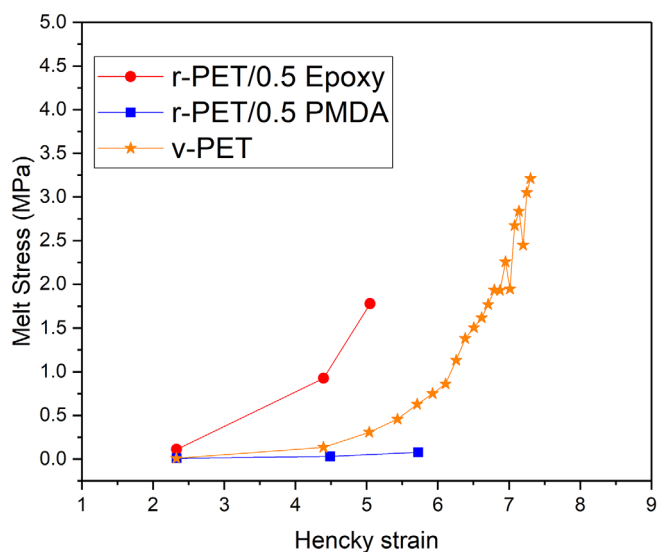
**TABLE 2** DSC and IV data for various chain extended PET, where r-PET is recycled PET and v-PET is virgin PET

Sample	Chain extender (wt%)	$T_m$ (°C)	$T_c$ (°C)	% Crystallinity ( $\Delta H_f^0 = 140$ J/g)	Intrinsic viscosity (dL/g)
r-PET	—	248	165	23.7	0.75
			197 re-extruded		0.51 re-extruded
r-PET/EC	0.25	249	194	27.7	0.52
	0.50	250	195	27.0	0.52
r-PET/PMDA	0.25	248	190	26.6	0.56
	0.50	247	185	25.5	0.60
r-PET/Epoxy	0.25	249	197	27.7	0.51
	0.50	250	198	27.4	0.54
v-PET	—	243	Not observed	23.8	0.84 as per supplier

Abbreviations: EC, ethylene carbonate; PMDA, pyromellitic dianhydride.



**FIGURE 3** Extensional viscosity vs extension rate for various chain extended poly(ethylene terephthalate) (PET), where r-PET is recycled PET and v-PET is virgin PET and 0.25 and 0.5 are the weight percent of chain extenders [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]



**FIGURE 4** Haul-off data for various chain extended poly(ethylene terephthalate) (PET), where r-PET is recycled PET and v-PET is virgin PET [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

addition of either PMDA or epoxy brought the r-PET extensional viscosity in the same range as that of v-PET, although the extension rate window for v-PET is still higher.

To approximate applicability in blow molding applications, haul-off testing was performed. The epoxy-modified r-PET performed more favorably than the polymer modified with PMDA, as its melt stress was

higher for the same Hencky strain, as depicted in Figure 4; these results were still lower than v-PET, reflecting IV differences. Even though a wider strain rate window for epoxy or PMDA modified PET could not be obtained, data were successfully collected for some Hencky strains, whereas for r-PET without chain extenders added, it was not possible to achieve equilibrium even for a single data, suggesting that a higher percentage of epoxy modifier might increase the strain window for r-PET and might bring it to a value similar to that of v-PET.

## 4 | CONCLUSIONS

The properties for r-PET were improved with one-step processing, with PMDA and an epoxy-based additive, providing a low extent of chain branching in addition to chain extension. EC as a modifier brought about increased shear thinning to r-PET, which is not a desirable property for commercial processing of the polymer into containers. Higher loadings of the modifiers increased the properties as was expected. DSC confirmed there was little discernable change in structure as melting and recrystallization temperatures and percent crystallinities does not change appreciably (though a small effect was observed with PMDA, suggestive of very light branching). Small amplitude oscillatory shear showed improved properties when PMDA and epoxy were added, matching the rheology of v-PET.

Capillary rheometry experiments provided insight into the differences between PMDA- and epoxy-modified r-PET and v-PET. Extensional viscosity data could be collected at much higher rates for the chain-extended products; haul-off experiments behaved similarly but clearly showed epoxy/r-PET performing better than PMDA/r-PET. These results suggest that at higher addition levels, extrusion performance of lower IV recycled polyester could match that v-PET. Both the epoxy and PMDA additives showed overall greater promise in bolstering the use of recycle PET polymer in extrusion applications, compared to incorporation of EC.

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