

Effect of chain extenders on mechanical and thermal properties of recycled poly (ethylene terephthalate) and polycarbonate blends

Y Srithep^{1,3}, D Pholharn², A Dassakorn¹ and J Morris¹

¹Manufacturing and Materials Research Unit, Faculty of Engineering, Mahasarakham University, Mahasarakham 44150, Thailand

²Department of Chemistry, Faculty of Science and Technology, Rajabhat Mahasarakham University, Mahasarakham 44000, Thailand

E-mail: yottha.s@msu.ac.th

Abstract. Poly(ethylene terephthalate) (PET) based thermoplastics are common, particularly in packaging. Due to both thermal and hydrolytic degradation, recycled PET (rPET) shows poor mechanical properties. The effect of adding 30% polycarbonate (PC) and chain extender (CE) on mechanical, thermal and morphological properties was investigated. rPET with PC and CE was melt blended in a single screw extruder, which was then tensile test specimens were formed by injection molding rPET and PC compatibility was improved via chain extending reactions which in turn improved the rPET and PC blend mechanical properties. With the addition of 30%PC the tensile modulus of rPET increased by 18% and it increased by 223% when 2%CE was added to rPET and 30%PC blends. Also, the CE reaction affected crystallization, monitored by differential scanning calorimetry: the melting enthalpy of blends was lowered by increased CE content.

1. Introduction

Poly (ethylene terephthalate) (PET) has become common in soft drink bottles because it is transparent, shows high chemical resistance and low diffusibility. Beverage bottles are generally thrown away and degrade the environment. Thus, to reduce environmental hazards and burden created by landfill dumping of PET, large amounts of PET is recycled and reused in various ways[1]. However, PET recycling is a complicated process because of chemical and mechanical degradation during reprocessing [2].

Polycarbonate (PC) has high thermal stability and impact resistance which lead to wide use as an engineering plastic. To improve the properties and therefore application of PET, PET/PC blends have been found to show active interphase interactions, which causes them to be described as partly compatible [3, 4]. Nevertheless, simple melt blended PET and PC mixtures in a mixer generally lead to a phase-separated PET/PC mixture; therefore there is considerable interest in improving the compatibility of PET and PC. Further, at compounding and processing of PET/PC molten blends, it is desirable to maintain the molecular weight and intrinsic viscosity which are both reduced by hydrolytic and thermal degradation that, in turn, degrade mechanical properties of recycled material [2, 5].

Many papers have proposed chemical strategies to enhance the properties of virgin, reprocessed or recycled polycondensates [6]. Commonly, bi- or multi-functional chemical compounds which can



lengthen chains and increase the molecular weight and physical properties of degraded thermoplastics by bridging functional chain end groups and thus lengthening or “chain extending” them. Chain extenders are usually low molecular weight compounds which react rapidly with the polymer end groups linking them to increase chain length [1]. Chain extension mechanisms in reactive extrusion have been surveyed [1, 7, 8].

This study investigated the effects of chain extender (CE) on mechanical and thermal properties of recycled poly (ethylene terephthalate) (rPET) and PC blends. As the multifunctional epoxide group of the CE can react with hydroxyl and carboxyl end group of rPET and PC, it also may improve the compatibility of this blending system.

2. Experiments

2.1. Materials

For rPET, we used PET bottles collected from urban waste. The measured melting temperature (T_m) was 245 °C and melt flow index (MFI) (with 2.16 kg weight) was 30 g/10 min at 260 °C and 60 g/10 min at 270 °C. Mitsubishi Lupilon S3000R (MFI 16.5 g/10min) PC was purchased from Mitsubishi Engineering Plastics Corporation. The chain extender (BASF Corporation Joncryl ADR4370) used was a styrene acrylic copolymer (oligomeric coupling agent) that has epoxy functional groups that react with condensation polymers.

2.2. Processing

rPET/PC (70/30 w/w), with the CE contents from 0 to 2wt%, were melt compounded using a single screw extruder (HAAKE PolyLab OS system) with screw diameter, $D = 20$ mm, and $L/D = 40$, where L is the screw length. Screw speed was set at 100 rpm. The barrel temperature was at 270°C. Before processing, PET and PC were dried in an oven for 12 h at 80°C to remove water to prevent hydrolysis in the molten state. After blending, the extruded strands were cooled in a water bath, palletized and dried in a vacuum at 80 °C for 10 h. Injection molding used an injection molding machine (ING-58T, Chareon Tut Co., Ltd) to obtain tensile bars (ASTM D638 Type I). The neat rPET (reprocessed PET without PC addition) and PC were processed and used as reference materials.

2.3. Material characterization

2.3.1. Differential Scanning Calorimetry (DSC). Thermal properties of the blended materials were measured with a differential scanning calorimeter (DSC 4000 PerkinElmer). Specimens of 4 to 5 mg were placed in aluminium sample pans and heated from -10 °C to 280 °C at a 10 degC/min rate and held for 3 min at 280 °C to erase any prior thermal history before cooling at 10 degC/min to -10 °C. The specimens were then reheated to 280 °C using at 10 degC/min. The *cold crystallization temperature* (T_{cc}) and its *enthalpy* (ΔH_{cc}), melting temperature (T_m), and apparent melting enthalpy (ΔH_m), crystallization temperature (T_c), were determined from DSC curves. T_m was taken from the peak temperature and ΔH_m from the area of the melting endotherm.

The absolute degree of crystallinity (χ_c) of the rPET phase was calculated from

$$\chi_c (\%) = \frac{\Delta H_m (rPET)}{\Delta H^\circ (rPET)} \times \frac{100}{w} \quad (1)$$

where $\Delta H^\circ (rPET)$ is the melting enthalpy (J per gram) of 100% crystalline material (i.e. perfect crystal) (120 J/g) and w is the weight fraction of rPET in the blend [9].

To determine the original crystallinity of the injection molded sample that was subjected to rapid cooling during the molding process. We noted that, during heating, some additional crystallites form from the amorphous material and we must subtract their heat released from the total endothermic heat flow generated from all the crystallites (i.e., initial+formed by heating) to calculate the correct % crystallinity, χ_c . The equation for the original crystallinity of the injection molded sample became [1]:

$$\chi_c(\%) = \frac{\Delta H_m(rPET) - \Delta H_{cc}(rPET)}{\Delta H^\circ(rPET)} \times \frac{100}{w} \quad (2)$$

2.3.2. Mechanical testing. Tensile tests on injection molded samples followed ASTM D638. We measured static tensile strength and strain-at-break at 25 °C and relative humidity of 50 ± 5% on an NRI-TS501 universal testing instrument. For all specimens, an initial load of 0.5 N and a constant crosshead speed of 50 mm/min were used. Averages were calculated from five specimens taken from each sample group.

2.3.3. Thermogravimetric Analysis (TGA). Thermogravimetric analysis (TGA) samples were conditioned at 50% humidity at 25 °C in the testing room and used a TGA 4000 (Perkin-Elmer) from 25 to 600 °C at 10degC/min. Each test used ~10 mg of rPET, PC and rPET/PC, with varying chain extender. Weight loss was noted and normalized versus the initial weight.

2.3.4. Scanning Electron Microscopy (SEM). SEM images of the fracture surfaces generated by tensile tests were acquired using a Hitachi SU-1500 machine at 3 kV. The samples were frozen in liquid nitrogen and then quickly impact-fractured. A thin layer of gold (~20nm) was sputter-coated onto specimens prior to imaging.

3. Results and discussions

3.1. Thermal properties

To measure thermal properties of rPET/PC blends, including crystallization and melting behaviors. The temperature plots from the first and second heating cycles appear in Figures 1 and 2. Cooling scans are shown in Figures 3. Derived thermal data is in Table 1. Values obtained from the first heating cycle were affected by the prior sample thermal history, whereas the second heating cycle allowed direct comparison of the crystallization behavior of different materials after the first heating scan thermal had been erased [1].

3.1.1. First heating cycle. DSC measurements in Figure 1 show that the glass transition temperature (T_g) around 60 to 80 °C associated with the rPET phase in all the blends was slightly higher than for neat rPET and T_g was slightly higher as the amount of CE increased. With 2%CE content, T_g was near to 74 °C, while T_g of neat rPET was ~72 °C and for neat PC was ~147 °C (see Figure 1 and Table 1). A similar effect of PC and chain extender on T_g of rPET have been reported previously [9]. The first exothermic peak for all rPET blend specimens (in the temperature range 110 to 130 °C) is labelled as the cold crystallization peak. The enthalpy of cold crystallization (ΔH_{cc}) and of melting enthalpy (ΔH_m) was lower as the amount of CE increased (ΔH_{cc} varied from 23.0 J/g to 11.9 J/g and ΔH_m varied from 17.50 to 12.32 J/g). In general, when CE was added in the blending system, the chain-extending reaction for rPET increased its molecular weight, whereas the rPET-PC reaction restrained rPET chain movements. Decreased rPET chain mobility constrained rPET crystallization compared to rPET without CE, and its cold crystallization temperature increased consistent with the decreased degree of crystallinity. Similar results have been reported for PLA/PC blends with chain extender [10].

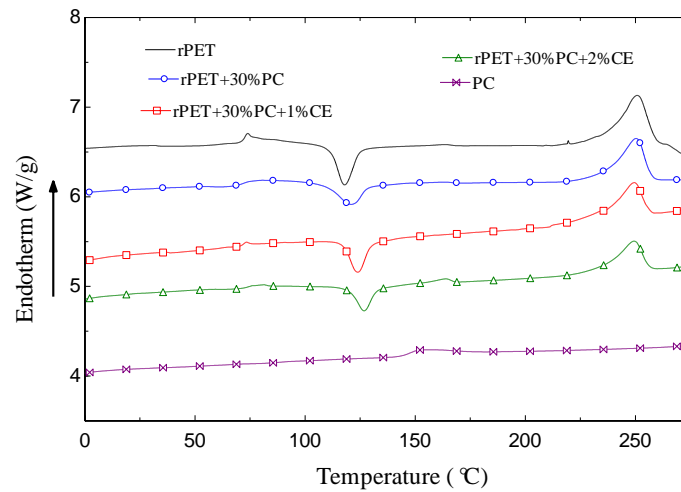


Figure 1. First heating cycle DSC curves for rPET blends.

Table 1. DSC data for rPET/PC (70/30) blends with varying CE content.

Samples	Glass Transition	Cold Crystallization		Melting		Degree of crystallinity
	T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)	χ_c (%)
First heating						
rPET	72.2	117.8	22.1	250.6	53.4	26.0
rPET+30%PC	72.8	121.0	18.0	250.1	39.5	25.5
rPET+30%PC+1%CE	73.2	123.8	15.9	249.2	32.2	19.6
rPET+30%PC+2%CE	73.9	126.6	11.9	249.1	27.7	19.3
PC	147.7	-	-	-	-	-
Second heating						
rPET	81.5	-	-	245.9	41.2	34.3
rPET+30%PC	90.5	-	-	230.6	28.3	33.6
rPET+30%PC+1%CE	88.7	-	-	222.6	17.8	21.4
rPET+30%PC+2%CE	88.9	-	-	224.1	17.4	21.3
PC	143.6	-	-	-	-	-

3.1.2. Cooling cycle. Figure 2 and Table 1 show the thermograms and data derived from the cooling cycle of rPET, PC and rPET/PC blends with 1% and 2%CE. It was found that only rPET had showed a crystallization temperature at about 215 °C, indicating that blending rPET with 30%PC decelerated the crystallization rate owing to its interactions with PC [4].

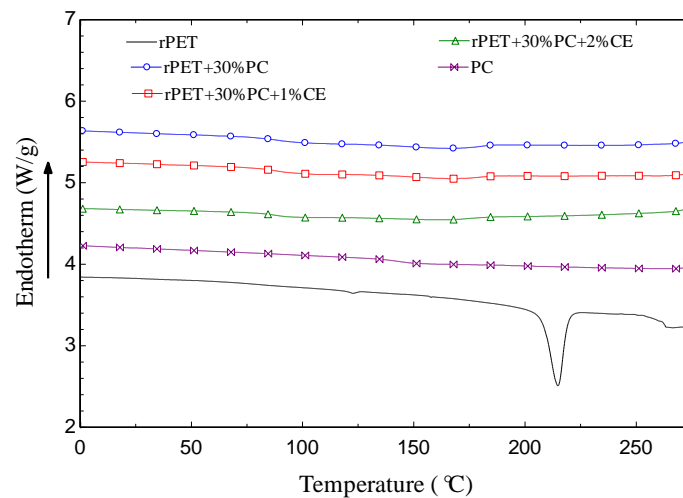


Figure 2. Cooling cycle DSC curves of the rPET blends.

3.1.3. Second heating cycle. Figure 3 shows thermograms from the second heating cycle of rPET, PC and rPET/PC blends and Table 1 also shows data derived from the second heating cycle. Unlike the first heating cycle, due to the slower cooling rate during the DSC test than injection molding process, cold crystallization disappeared and the degree of crystallinity for all samples was higher than that observed during the first cycle [1]. Moreover, melting enthalpy ΔH_m decreased significantly with added chain extender (ΔH_m was 28.3 J/g without CE to 17.4 J/g with 2%CE). The interfacial reaction between the epoxy group and the carboxyl end group of rPET at the interface [11] discourages rPET chain rearrangement (motion) and consequently cold crystallization [9].

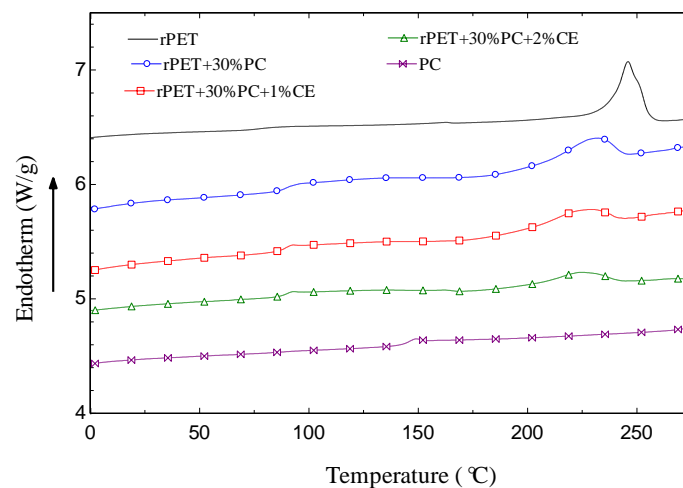


Figure 3. Second heating cycle DSC curves of the rPET blends.

3.2. Morphology

As rPET and PC are partly miscible, it is expected that simple blending would produce a phase-separated structure, leading to low mechanical properties. The CE, being a third component with active groups, can react with both end groups of rPET and PC and thus lead to better compatibility between rPET and PC. Representative SEM images of rPET blends are in Figure 4. They reveal information on the microstructure and the fracture behavior of the specimens. The rPET/PC blend clearly showed distinct phases (Figure 4(b)). With CE fed, compatibility between rPET and PC improved and the dispersed phase size reduced (Figure (c) - 1% CE and (d) -2%CE).

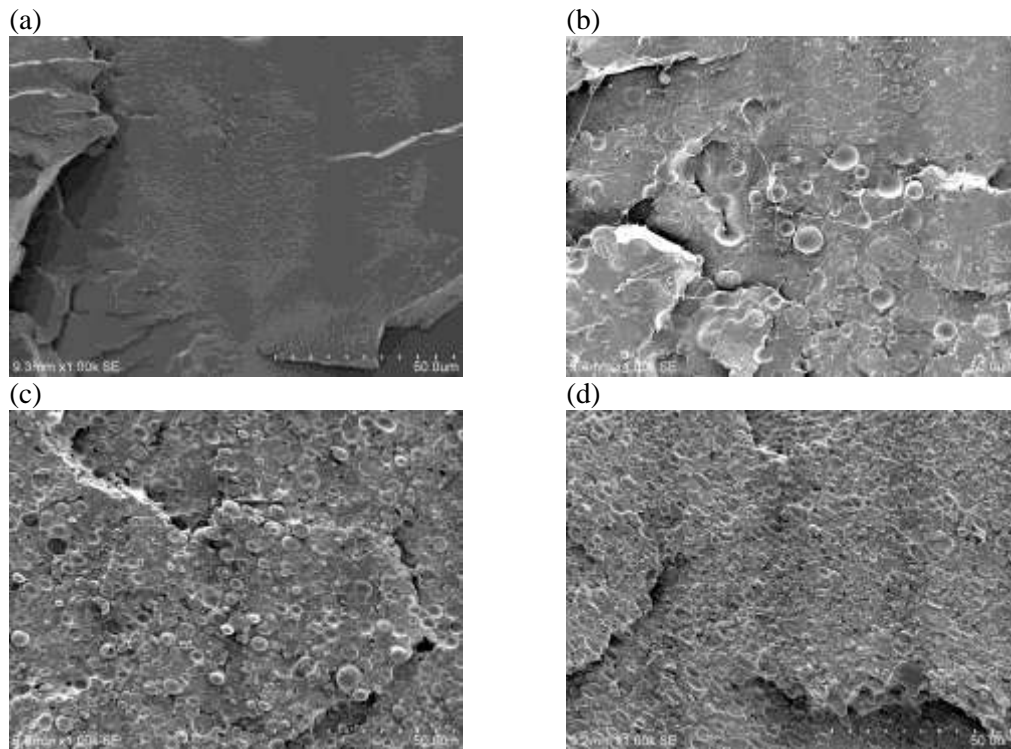


Figure 4. Scanning electron micrographs (a) rPET (b) rPET+30%PC (c) rPET+30%PC+1%CE and (d) rPET+30%PC+2%CE. All images were taken at the same magnification (scale bar: 50 μ m).

3.3. Tensile Properties

Tensile tests followed ASTM-D-638-02 on the injection molded specimens of the rPET blends. Clearly, the size of the dispersed phase of rPET/PC (70/30) blends decreased with higher CE content. This is consistent with the mechanical properties of the rPET/PC (70/30) blends, i.e. that higher mechanical strength and strain-at-break was observed with larger amounts of CE added to the blends. As shown in Figure 5, rPET had lowest tensile strength (~ 10 MPa) suggesting a reduced molecular weight as a consequence of degradation and it increased by addition of 30%PC to 17 MPa. With the addition of 1% and 2%CE, the tensile strength of rPET/PC increased to 39 and 55 MPa, respectively. As with tensile strength, a similar trend was observed for the elongation at break (Figure 6). Therefore, the blend particle size decrease suggests increased compatibility between the PC and rPET components [12].

Figure 7 shows the tensile modulus of rPET, PC and rPET/PC blends. With the addition of 30%PC the tensile modulus of rPET increased by 18%. Moreover, the addition of CE increased the tensile modulus further. The tensile modulus of rPET+30%PC was found to be 1760 MPa and with added 2%CE the tensile modulus increased to 2300 MPa.

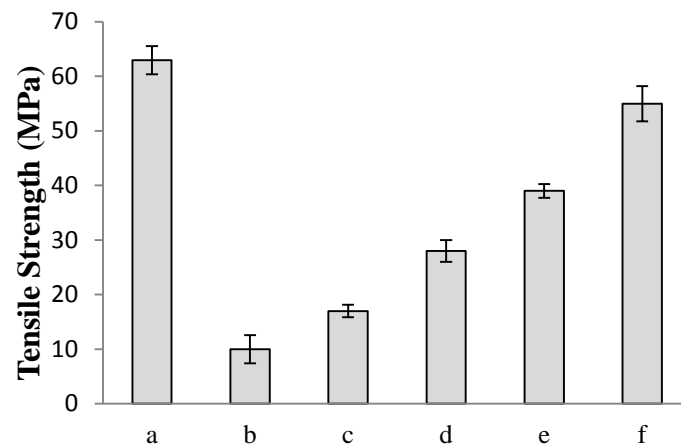


Figure 5. Tensile strength of the rPET/PC blends (a) PC (b) rPET (c) rPET+30%PC (d) rPET+30%PC+0.5%CE (e) rPET+30%PC+1%CE (f) rPET+30%PC+2%CE.

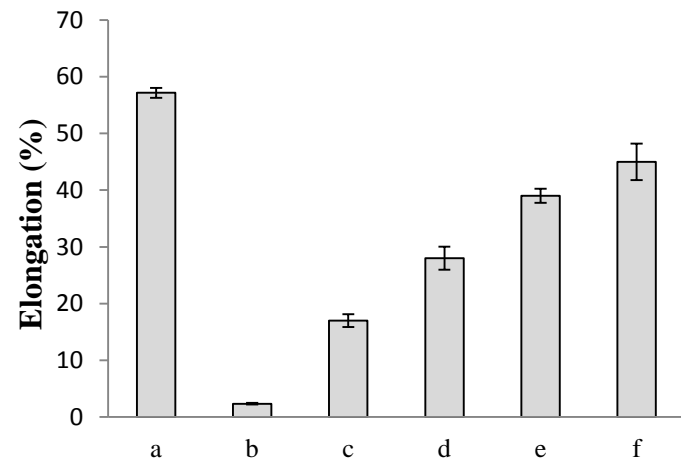


Figure 6. Elongation at break of the rPET/PC blends (a) PC (b) rPET (c) rPET+30%PC (d) rPET+30%PC+0.5%CE (e) rPET+30%PC+1%CE (f) rPET+30%PC+2%CE.

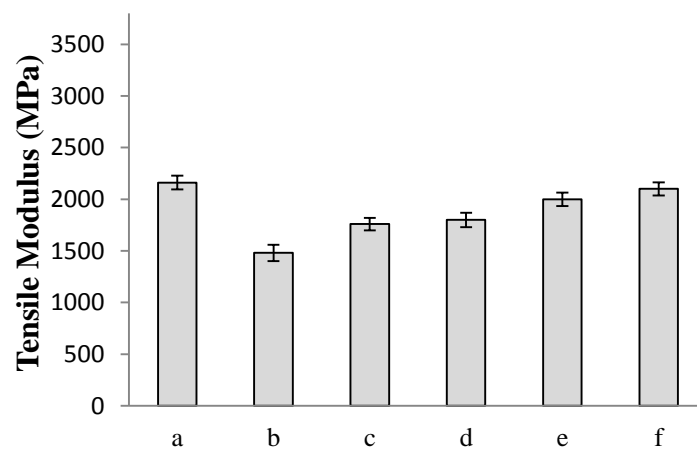


Figure 7. Tensile modulus of the rPET/PC blends (a) PC (b) rPET (c) rPET+30%PC (d) rPET+30%PC+0.5%CE (e) rPET+30%PC+1%CE (f) rPET+30%PC+2%CE.

3.4. Thermal stability

TGA was used to assess the thermal stability of rPET, PC, and rPET/PC blends at a heating rate of 10 degC/min with results shown in Figure 8. PC had much higher thermal stability than rPET. The degradation of rPET/PC blend lay between rPET and PC and any difference in the temperature loss of rPET/PC and rPET/PC with added chain extender is not obvious. However, a weight loss step at the temperature $\sim 318^\circ\text{C}$ were observed for rPET/PC blends. We attribute this to interaction between rPET and PC after blending, which leads to small amounts of short molecular weight segments, which are lost more readily [4].

Table 2 shows the temperature at 10% and 20% weight loss ($T_{10\%}$ and $T_{20\%}$) of rPET, PC, and rPET/PC blends. $T_{10\%}$ of rPET/PC blends was lower than that of neat PC and neat rPET due to the small amount of low molecular weight polymer blends produced from the interaction between PC and rPET. Moreover, $T_{20\%}$ of the rPET/PC blends lay between neat PC and rPET. Therefore, it could be concluded that thermal stability of rPET improved on addition of PC. Figure 9 shows a schematic mechanism illustrating the interfacial reaction between the epoxy group of CE, the carboxyl end group of rPET and hydroxyl end group of PC.

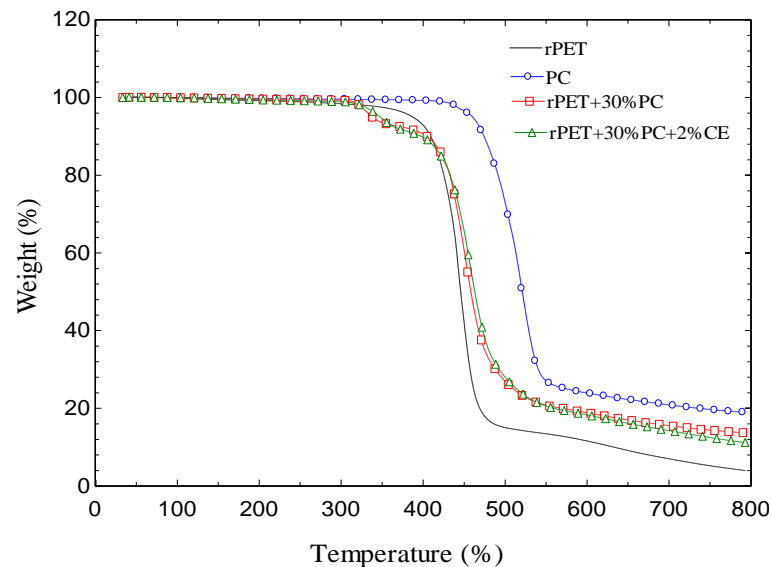


Figure 8. TGA curves for rPET blends.

Table 2. Temperature at 10% and 20% weight loss of rPET, PC, and rPET/PC blends.

Samples	$T_{10\%}$ (°C)	$T_{20\%}$ (°C)
rPET	409.1	425.2
rPET+30%PC	397.4	432.7
rPET+30%PC+2%CE	404.1	432.9
PC	474.1	491.2

4. Conclusions

Acknowledgement

References

- 9