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Rheological and Mechanical Properties of Recycled PET Modified by Reactive Extrusion

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Abstract

The effect of chain extender on the improvement of molecular structure and elongational properties under molten and solidified states of recycled Poly(ethylene terephthalate) (RPET) was studied. The results suggested that addition of chain extender increased the molecular weight and broader molecular weight distribution of RPET. A gel fraction of cross-linked material was formed and the concentration of gel content being dependent of the amount of chain extender used. Increasing chain extender resulted in increases in elongational viscosity of RPET. The increases in viscosities were explained in association with the extension of RPET chains, causing a reduction in chain mobility. The tensile properties in molten and solidified state were found to increase with increasing chain extender up to 0.6 wt% before it decreased at the chain extender loading of 0.9 wt%.

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1. Introduction

Poly(ethylene terephthalate) (PET) is one of the most widely used thermoplastic polyesters. PET is extensively used in industrial productions, such as beverage bottles, packaging films and textile fibers, because of its superior chemical, physical, mechanical, and (oxygen and carbon dioxide) barrier properties. Owing to the increasing concern

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about environmental issues, recycling of PET attracts great interest. However, during the recycling processes PET undergoes hydrolytic and thermal degradations, which lead to a reduction in the molecular weight of the polymer and, consequently, its viscosity, melt strength and mechanical properties [1-4]. The property deterioration of recycled Poly(ethylene terephthalate) (RPET) may be compensated by the addition of reinforcing fillers and toughening modifiers. For example, RPET has been blended or compounded with several polymers, fillers, and nanoparticles to modify its physical properties [5]. However, the incorporation of suitable compatibilizer agents is essential to improve interaction between RPET and the other component [6-9]. On the other hand, the reactive extrusion using chain extender is an effective way to increase the properties of recycled PET. The reaction of chain extender can be accompanied by branching or even cross-linking, thus leading to a polymer with higher molecular weight (and thus melt viscosity) and significantly different properties. According to recent literatures [3, 9, 10] many attempts have been made to enhance the properties of RPET through chain extender modification. However, most studies concentrate on investigation of the flow properties under shear deformation. In many polymer processing operations such as extrusion blow molding, blow film and melt spinning, the polymer is subjected to a combination of shear and elongational flows. Very rare have been studies on the effect of chain extender on the elongational flow properties of RPET. This work is focused on the study of elongational flow properties of RPET by means of reactive extrusion using chain extender. Furthermore, attempts have been made to understand the effect of chain extender on mechanical properties under tensile deformation of RPET in both molten and solidified states.

2. Experiment

2.1. Raw materials

Poly(ethylene terephthalate) (RAMAPET N1) having a intrinsic viscosity of 0.8 dl/g, was purchased from Indorama Ventures Public Co.,Ltd. The PET was dried in an oven at 150°C for at least 15 h before use. The chain extender used was acrylic epoxy resin (Joncryl[®] ADR-4380) supplied by BASF Co., Ltd.

2.2. Preparation of RPET and chain-extended RPET

In this work, RPET was produced by passing virgin PET through a single screw extruder (Enmach Co.,Ltd) with length/diameter ratio of the screw was 23 and the temperature profiles were 270, 275, 275 and 280°C from hopper to die zones. The screw rotating speed was 30 rpm. The extrudate strands were passed through a water bath via pull-off unit before pelletizing in order to produce RPET. The RPET was dried in an oven for 15 h at 150°C. Afterward the RPET was melt-blended with chain extender in a single screw extruder with the same condition as in RPET preparation. The chain extender concentration was varied from 0.3, 0.6 and 0.9 wt%.

2.3. Molecular characterization

2.3.1 Gel content analysis

The gel analysis was determined by a solvent extraction technique. The samples were immersed and extracted via a refluxing Trifluoroacetic acid (TFA) solvent. After extraction, the samples were dried in an oven until a constant weight reached. The gel content in crosslinked RPET was then calculated as the ratio of the weights of the dried and extracted sample to the initial sample weight.

2.3.2 Gel permeation chromatography (GPC)

The molar mass distribution of modified RPET were carried out using gel permeation chromatography (Wyatt Technologies, USA) coupled with a multi-angle light scattering apparatus (MALLS) and Refractive Index (RI) detector operated at 30°C. The samples were dissolved in 1,1,1,3,3,3-hexafluoro-2-isopropanol at 30°C for 2 h prior injected into GPC column.

2.4. Elongational flow measurement

2.4.1 Melt strength measurement

The melt strengths of modified RPET were measured in term of drawdown force using a CEAST Rheologic 5000 capillary. The polymer melt was extruded through a capillary rheometer equipped with a circular die of 2 mm in diameter and 10 mm in length using a piston velocity of 1×10^{-3} m/s. The extrudate polymer was pulled down by the rollers at take-up device unit. The drawdown force was measured as a function of draw ratio until failure. All tests were carried out under an extrusion melt temperature of 280°C and distance between the die exit and the rollers of 100 mm.

2.4.2 Apparent elongational viscosity

In this work, the apparent elongational viscosity of RPET treated with various chain extender concentrations was calculated from drawdown force data. The apparent elongational viscosity ($\eta_{el,app}$) could be expressed by Equation 1

$$\eta_{el,app} = \frac{F \cdot L}{Q \cdot \varepsilon_E} \quad (1)$$

where F is the drawdown force, L is the length between die exit and rollers, Q is the volumetric flow rate, ε_E is elongational strain which is defined as draw ratio, $\ln(v_s/v_0)$, where v_s is the velocity at the rollers, and v_0 is the velocity at die exit.

2.5. Mechanical properties

Tensile test was performed on the injection molded samples of modified RPET following the ASTM D638-08. All the tests were run on Instron 5566 Universal Testing Machine (Instron (Thailand) Co., Ltd.). The tensile strength and elongation at break were measured at room temperature (25°C) using a crosshead speed of 10 mm/min.

2.6. Differential scanning calorimeter (DSC)

Differential scanning calorimeter was used to study the thermal properties of materials. DSC thermograms were recorded on a DSC-200 F3 Maia[®], NETZSCH, Germany. Specimens of 6 ± 0.5 mg were placed in aluminum pans and heated from 30 to 350°C with 10°C/min of heating rate in nitrogen atmosphere.

3. Result and Discussion

3.1. Molecular characterization

Table 1 shows the average molar mass (M_w and M_n), molar mass dispersity and gel content of modified RPET treated with different chain extender concentrations. The average molar mass of RPET was lower than those in virgin PET (VPET). This could be caused by thermo-mechanical degradation through chain scission mechanism [1-4]. It can be clearly seen that the weight average molar mass of RPET increased with increasing chain extender concentration. Moreover, some gel formation indicated cross-linking, was revealed in the modified samples, and gel content gradually increased with increasing chain extender concentration. Therefore, a chain extension did not only increase the molar mass in the soluble fraction, but also gave a non-soluble cross-linked gel. Furthermore, a broadening of the molar mass distribution was obtained by increasing chain extender concentration. This result was attributed to the chain extension during the reactive processing. In fact, chain extender, Joncryl[®] ADR-4380 has four reactive sites and can add up to four polymeric molecules. As a consequence, beside chain extension some branching can occur and the MWD of the polymer becomes broader.

Table 1. M_w , M_n , MWD and Gel content of VPET and RPET treated with different chain extender concentrations

Sample	M_w (kg/mol)	M_n (kg/mol)	MWD	Gel Content (%)
VPET	65.9	38.6	1.7	0
RPET	35.3	18.3	1.9	0
RPET+0.3 wt% CE	41.4	19.7	2.1	10.2
RPET+0.6 wt% CE	49.2	22.4	2.2	27.8
RPET+0.9 wt% CE	51.2	23.1	2.2	32.5

3.2. Elongational flow measurement

The modification of molecular structure using chain extender is reflected in the rheological characteristics of RPET. The significant increase in molecular weight usually results in the increase of viscosity. However, a large number of literatures [5, 9, 10] have been concentrated only in shear flow properties. Fig. 1 shows the elongational flow properties in term of drawdown force as a function of draw ratio for modified RPET with various chain extender concentrations. It should be noted that the drawdown force of RPET could not be detected in this measurement. This was because RPET undergoes hydrolytic and thermal degradations which lead to a reduction in the molecular weight and melt strength of RPET. However, the drawdown force of modified RPET with chain extender could be detected and drawdown force increased with increasing chain extender concentrations. This could be explained by the higher molar mass of recombination molecules, which produced entanglement networks. The drawdown force of modified RPET increased with increasing chain extender concentration up to 0.6 wt%, beyond this content, the drawdown force decreased slightly. The decrease in drawdown force at 0.9 wt% of chain extender concentration was associated with brittle rupture at the vicinity of the gel [11].

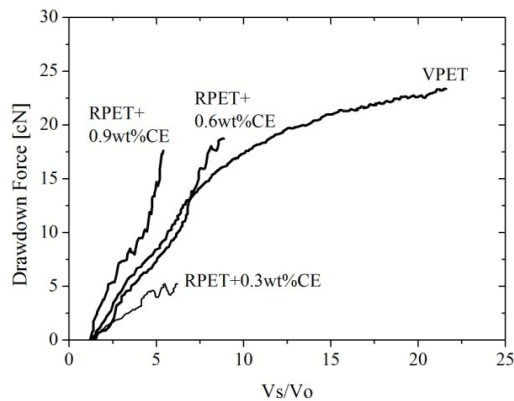


Fig. 1. Drawdown force as a function of draw ratio for virgin and modified recycled-PET.

The apparent elongational viscosities of modified RPET with various chain extender concentrations are plotted in Fig. 2. The result clearly shows that the apparent elongational viscosity of modified RPET increased progressively with amount of chain extender concentrations. This is due to the chain extension and cross-linked molecules, contributed to the hindrance of chain mobility.

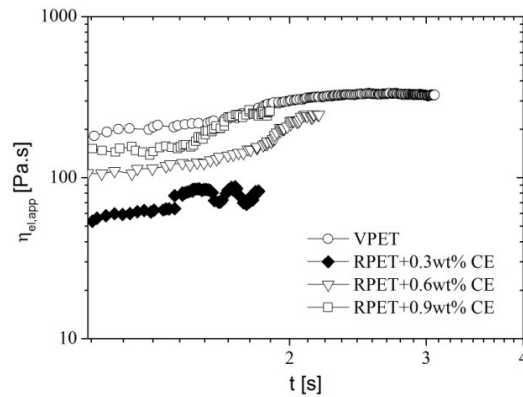


Fig. 2. Apparent elongation viscosity as a function of time for virgin and modified recycled-PET at various chain extender concentrations.

3.3. Mechanical properties

Fig. 3 and 4 show the tensile strength and elongation of solidified samples with various chain extender concentrations. The tensile strength and elongation became higher as the amount of chain extender increased up to 0.6 wt% and then tensile strength and elongation decreased slightly at 0.9wt%. The increase in tensile strength and elongation was due to the recombination of the RPET broken chains, leading to an increase in the molar mass and chain entanglement. However, the increases of mechanical properties in solidified state were not more pronounced than those in molten state. The decreases in tensile properties at 0.9wt% of chain extender were probably explained by a change in the crystallinity level of the solidified RPET. The latter reason could be supported by DSC results as given in Table 2.

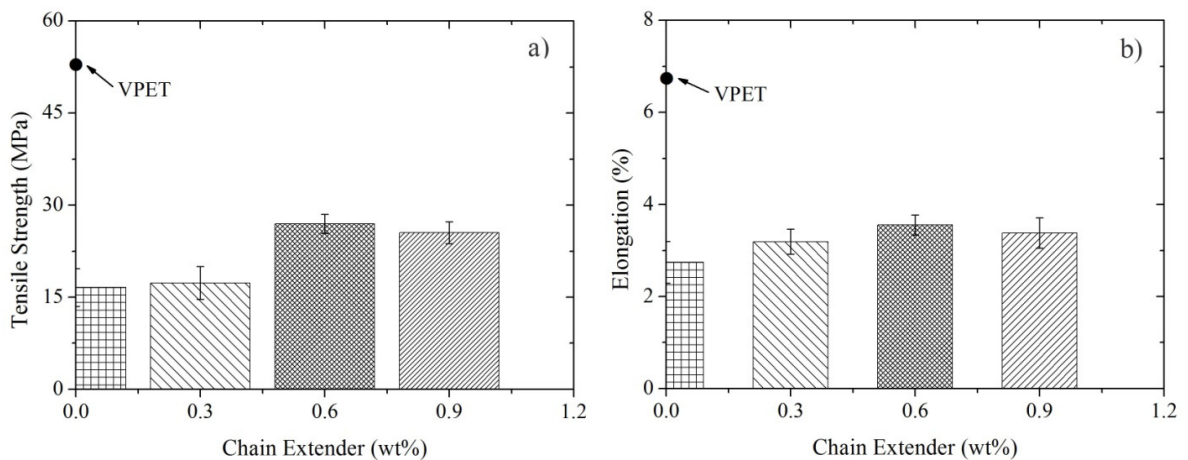


Fig. 3. Tensile properties of virgin and modified RPET with different chain extender concentrations: (a) tensile strength; (b) elongation.

The RPET sample was found to increase the degree of crystallinity (χ_c) and melting temperature (T_m) as compared with that of VPET sample. This indicated that the crystallization process in RPET occurred greater and faster than VPET. This was due to the degradation by chain scission, which facilitates the packing of the crystalline. Considering the effect of chain extender, the crystallinity (χ_c) and melting temperature (T_m) of RPET decreased with increasing chain extender concentration. This was expected because chain recombination, branching and cross-linking, lead to an increase in the degree of entanglement, thus reducing the crystallization process. The tensile strength of modified RPET was found to increase, although the crystallinity was minimized as the chain extender

concentration increased. This was because the increase in molar mass had more pronounced effect compared to the reduction in crystallinity. The chain extender concentration greater than 0.6 wt% seemed to have a small effect on the change of tensile strength of RPET. The leveling off of the tensile strength at 0.9 wt% of chain extender concentration would probably be caused by the reduction of RPET crystallinity.

The overall results suggested that the mechanical properties of RPET in both molten and solidified stages were influenced in the same way. The tensile properties increased with increasing chain extender up to 0.6 wt%. At higher chain extender concentration, the tensile strength slightly decreased. At chain extender concentration of 0.9 wt%, the decrease in tensile strength for molten stage was probably associated with the rupture of the vicinity of the gel, whereas the decrease in tensile strength for solidified stage was explained by the reduction of crystallinity.

Table 2. Mw, Mn, MWD and Gel content of VPET and RPET treated with different chain extender concentrations

Sample	T _m (°C)	χ _c (%)
VPET	246	32
RPET	243	38
RPET+0.3 wt% CE	243	36
RPET+0.6 wt% CE	242	33
RPET+0.9 wt% CE	241	31

4. Conclusion

The chain extender modified RPET was characterized by GPC, elongational properties under molten and solidified states. The gel content, molecular weight and molecular weight distribution of modified RPET were found to increase with increasing chain extender concentration. The elongation flow in term of drawdown force and elongation viscosity was gradually increased with increasing chain extender concentration. The tensile properties increased with increasing chain extender concentration up to 0.6 wt%, beyond this content, the tensile decreased slightly. Moreover, the tensile properties in molten state were corresponded to that in the solidified state.

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