Mechanical Recycling of PET Waste from Non-Woven Fabrics by Reactive Extrusion with Chain Extenders

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Abstract: Mechanical recycling of poly (ethylene terephthalate) (PET) is an important industrial activity with direct effect for environmental saving. However, recycled PET (R-PET) undergoes progressive degradation during each recycling process, leading to considerable loss of properties such as mechanical, thermal and melting strength. Chain extenders have been successfully used to increase molecular weight of R-PET, improving process ability and mechanical performance of the material. The aims of this work was to evaluate the performance of the compounds polymeric methylene diphenyldiisocyanate (PMDI) and bis-(2,4-di-t-butylphenol) pentaerythritoldiphosphite (Irgafos®126) for potential use as chain extenders when compared to the traditional chain extender pyromelliticdianhydride (PMDA). Tensile testing, differential exploratory calorimetry, viscometry and dynamic rheometry were used to evaluate changes in mechanical properties, crystallinity, molecular weight and rheological properties of R-PET. PMDI showed effective action on increase in molecular weight and improvements in mechanical and rheological properties of R-PET, while Irgafos 126 causes depreciation of properties of the R-PET after initially to increase the molecular weight of the polymer. Thus, the use of PDMI as chain extension can represent an important alternative for mechanical recycling of highly degraded PET.

Keywords: PET, recycling, diisocyanate, phosphite, PMDA, chain extender.

INTRODUCTION

In the last years, the management of polymeric waste has gained importance due to the need to ensure environmental sustainability. Mechanical recycling, chemical recycling, incineration for energy recovery and landfilling are, basically, the alternatives applied to manage polymeric waste [1]. Landfilling and incineration are not environmentally recommendable, while chemical recycling can have high cost [1, 2]. Therefore, mechanical reprocessing is an interesting alternative for polymeric waste recycling [1-4]. On the other hand, mechanical recycling of polymers can also be very complex. The polymer degradation caused by reprocessing or exposition to environmental conditions and mixture of polymeric waste with several organic contaminants from different sources can generate materials with mediocre performance [3-8].

The mechanical recycling of postconsumer poly(ethylene terephthalate) (PET) for production of carpets, rugs, strings, bristle broom, brushes, nonwoven fabrics, for example, has been consolidated as a viable industrial activity with important consequence for environmental saving. However, recycled poly(ethylene terephthalate) (R-PET) undergoes progressive degradation during each recycling process, leading to considerable loss of properties such as mechanical, thermal and melting strength. The decrease in molecular weight due to scission of chemical bonds in main polymeric chains has been proposed as the most important cause of the depreciation of these properties [9].

Nonwoven fabrics (NWF) production is based in extrusion of R-PET, leading to the formation, besides desired product, of other wastes as oddments of molded parts and reject post extrusion. These materials present high level of degradation and cannot be directly reinserted in the process. Some studies have been carried out with the use of chain extenders to recover properties of R-PET with low molecular weight [10-14]. Chemical compounds such as anhydride, organophosphorus and isocyanine are some agents used as chain extender for PET [11-14].

Chain extenders should have at least two molecular reactive sites to form stable chemical bounds with terminal groups of polymeric chain. Pyromellitic-dianhydride (PMDA) is a well-known chain extender anhydride kind and their performance can serve as a basis for further studies. Anhydride functionalities of the PMDA react with PET hydroxyl end groups, forming two carboxyl groups per incorporated moiety (couping) and increasing molecular weight of the polymer. However, the incorporation of high amount of PMDA leads to formation of branching structure in the polymer during thermo-mechanical processing [15].

The aim of this study was to evaluate the effects of the reactive incorporation of polymeric methylene diphenyldiisocyanate (PMDI), bis-(2,4-di-t-butylphenol)

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pentaerythritoldiphosphite (Irgafos® 126) and 1,2,3,5-benzenetetracarboxylic anhydride (pyromelliticdianhydride – PMDA) on crystallinity, molecular weight and rheological and mechanical properties of the PET waste.

EXPERIMENTAL

Materials

R-PET generated from extrusion molding of recycled PET flakes from drink packing for production of NWF was supplied by Fiberweb Bidim Ltd. The additive bis-(2,4-di-t-butylphenol) pentaerythritoldiphosphite (Irgafos 126®) was donated by Ciba Specialty Chemicals, polymeric methylene diphenyldiisocyanate (PMDI) was supplied by Dow Chemical (Hortolândia, Brazil), while the 1,2,3,5-benzenetetracarboxylic anhydride (pyromelliticdianhydride – PMDA) was acquired from Acros Organics BVBA.

Samples Preparation

R-PET in the form of plates with varying sizes was grounded initially in a knives mill to produce size particles with dimension lower than 1 mm. Then, the polymer was dried at 120 ºC for 4 h in a Quimis 0314N242 oven with air forced system. Immediately after drying, the additives were incorporated to the material by mechanical pre-mixture in a closed container of polyethylene and mixed up by tumbling for subsequent reactive extrusion molding in a single screw extruder (Imacon) with screw diameter of 25 Ø at 40 rpm of rotation, using a temperature profile of 200, 290, 310 and 260 °C in the zones of feeding, compression, mixture and matrix, respectively.

For mechanical testing, a portion of extruded samples was dried again at 90 ºC for 13 h and molded for injection in an BATTENFELD HM60/350 equipment using a temperature profile of 220, 255, 255 and 270 ºC in the injection system and 70 ºC in the mold and a pressure of 650 bar was used for injection. Specimens for tensile testing were produced according to standard practice ASTM D-638.

The samples were identified according to the concentration and kind of chain extender (Table **1**).

Table 1: Samples Identification

Sample	Additive	Concentration (wt %)
R-PET	------	--------
IRG05	Irgafos 126®	0.05
IRG15	Irgafos 126®	0.15
IRG30	Irgafos 126®	0.30
PMDI05	PMDI	0.05
PMDI15	PMDI	0.15
PMDI30	PMDI	0.30
PMDA05	PMDA	0.05
PMDA15	PMDA	0.15
PMDA30	PMDA	0.30

Differential Exploratory Calorimetry (DSC)

DSC analyses were carried out by using an equipment TA Instruments, model Q10, under nitrogen atmosphere, employing 10 mg for all samples. First, each sample was heated from room temperature (25 ºC) to 350 ºC at a rate of 10 ºC min^{-1}, followed by isotherm of 5 minutes to remove thermal history. Then, the material was cooled to room temperature at 10 ºC min^{-1} and a second heating was performed in same conditions of the first heating to determinate the crystallinity degree (*Xc*) [16]. Thus, crystallinity degree was calculated by the equation 1 [16-18]:

$$Xc = (\Delta H_m/\Delta H^o_m) \times 100 \qquad \text{Eq. 1}$$

Where, ΔH_m and ΔH^o_m are fusion enthalpy of polymer and hypothetic fusion enthalpy of the PET 100% crystalline, respectively. ΔH_m is calculated from area of the endothermic signal, while ΔH^o_m is 140 J/g [16, 17].

Viscometry

Solution viscosity measurement of the R-PET samples was carried out in order to determine the intrinsic viscosity, and an Ubbelohde-1B viscometer was used. A solvent mixture composed of phenol/1,1,2,2-tetrachloroethane (w/w = 60/40) was used to prepare the PET solutions. R-PET samples (0.1 g), previously grounded, were dissolved in the solvent mixture (20 mL) at 110°C for 5 h. After complete solubilization, the solutions were filtered and tested at 30°C in a water bath [19]. From the flow time of the pure solvent mixture (t_0) and of R-PET solutions (t), it was possible to obtain the relative (ηr), specific (η_{esp}), reduced (η_{red}) and inherent (η_{iner}) viscosities by means of the following equations [20, 21]:

$$\eta_r = \frac{\eta}{\eta_0} \cong \frac{t}{t_0} \qquad \text{Eq. 2}$$

$$\eta_{esp} = \eta_r - 1 = \frac{(t - t_0)}{t_0} \qquad \text{Eq. 3}$$

$$\eta_{red} = \frac{\eta_{esp}}{C} \qquad \text{Eq. 4}$$

$$\eta_{iner} = \frac{\ln \eta_r}{C} \qquad \text{Eq. 5}$$

Where: t is the flow time of polymer solutions, t_0 is the flow time of pure solvent mixture and C is the polymer solution concentration (g/100 mL).

The extrapolation of η_{red} or η_{iner} to zero polymer concentration gives intrinsic viscosity ([η]) [20, 21]:

$$[\eta] = (\eta_{esp} / C)_{c=0} = [(\ln \eta_r) / C]_{c=0} \qquad \text{Eq. 6}$$

Therefore, for determination of [η] initially were inserted 9 mL of polymeric solution at 0.5 % w/v in viscometer and measured the flow time. Then, were inserted successive amounts of 2 mL of solvent in viscometer to determination of the flow time of diluted solutions. Five measures of flow time of polymeric solutions with different concentration were obtained to produce a linear regression curve of η_{iner} *vs.* concentration, whose limit to concentration zero was used as [η], according to equation 6.

By means of the Mark–Houwink equation (eq. 7) was possible to determine the molecular weight M_v [22]:

$$[\eta] = K\, M_v^{a} \qquad \text{Eq. 7}$$

Where the constants K and a are 2.37×10^{-4} and 0.73, respectively.

Tensile Testing

The specimens produced by injection molding were tested in equipment EMIC DL 3000 with load cell of 20 kN. According to standard practice ASTM D 638, the specimens were conditioned at 23 ºC and 50% of relative humidity for 40 hours before testing. A minimum of 10 specimens were tested for each material.

Dynamic Rheometry

Dynamic rheological measurements were performed by using an apparatus Anton Paar PHYSICA MCR301 of parallel-plate, setting a chamber temperature of 285 ºC, frequency of 1 rad/s and tension of 200 Pa. The control of temperature, pressing and inert conditions was carried out under nitrogen flow, which was previously heated and inserted in the system. Before testing, pelletized samples were dried in vacuum oven at 120 ºC for 8 h using a Vacucel VUK/VU55.

RESULTS AND DISCUSSIONS

Crystallinity and Molecular Weight

Effects of the chain extenders on R-PET can be verified since molding extrusion processing. Initially, the temperature profile in the extruder for R-PET processing without additives was adjusted to 200, 230, 250 and 250 ºC from feeding to matrix zones, respectively. However, with incorporation of chain extenders have been need to adjust this temperature profile to 200, 270, 290 and 260 ºC, respectively. Molecular weight of polymers increases when chain extenders are incorporated by reactive extrusion,

Table 2: Results of DSC and Viscometry

Samples	Crystallinity (%)	Intrinsic Viscosity -[η] (dL/g)	Molecular Weight (g/mol)
R-PET	36.02	0.4963 ± 0.0015	35423± 149
IRG05	39.10	0.5469 ± 0.0015	40466± 150
IRG15	37.45	0.5672 ± 0.0015	42533± 157
IRG30	34.36	0.5692 ± 0.0015	42741± 154
PMDI05	38.63	0.5224 ± 0.0015	38003± 148
PMDI 15	37.34	0.5807 ± 0.0015	43937± 147
PMDI 30	30.34	0.6090 ± 0.0015	46889± 156
PMDA05	40.92	0.4953 ± 0.0015	35324± 150
PMDA15	35.56	0.5165 ± 0.0015	37419± 145
PMDA30	36.62	0.5267 ± 0.0015	38427± 154

leading to a higher melting strength. Thus, the increase in the temperature of processing decreases the melt viscosity and it equilibrates the extruder's torque.

The action of the chain extenders on molecular weight of R-PET was evaluated by solution viscosimetry (Table **2**). It is noted that R-PET without chain extenders presents molecular weight of 35423 g/mol, while R-PET containing PMDI at 0.30 wt% reaches values above 46000 g/mol.

Although each chain extender presents a characteristic behavior, the increase in molecular weight of R-PET is proportional to concentration of chain extenders (Figure **1**). For Irgafos 126, the concentration of 0.05 wt% causes significant increase in molecular weight of R-PET, reaching 40466 g/mol. However, only few differences are noted in values of molecular weight on concentration of 0.15 and 0.30 wt%. On the other hand, a nearly linear correlation between concentration and molecular weight gain is verified for chain extender PMDI. For chain extender PMDA, the concentration at 0.05 wt% is insufficient to produce significant changes in values of molecular weight, while at 0.15 and 0.30 wt% a small and progressive increase in molecular weight can be noted.

Table **2** and Figure **1** also present the percent crystallinity and behavior of the crystallinity for the R-PET as a function of chain extenders concentration. It is noted that R-PET with 0.05 wt% of chain extenders shows an increase of crystallinity, mainly to the R-PET containing PMDA. Likely, the presence of chain extender at low concentration may conduce to formation of heterogenic nucleus such as illustrated in Figures **2**, **3** and **4**, which are quantitatively sufficient to induce a heterogenic crystallization in the material.

However, as the concentration of chain extenders increases, the degree of branched and crosslinked structures in the material also increase, leaving difficult the packing of polymeric chains and consequently decreasing crystallinity. Thus, the crystallinity of the R-PET containing 0.30 wt% is inversely proportional to the increase in molecular weight.

Mechanical Properties

Mechanical properties represent the main response of materials performance that will be required for practical application. Figure **5** shows the results of tensile strength for R-PET in presence of chain extenders.

Independently of the kind of chain extender, the tensile strength of R-PET containing 0.05 wt% of additive was lower than R-PET without additive. This effect can be result of the increase in crystallinity that has been verified for concentration of chain extender at 0.05 wt%. The highest value of tensile strength was verified for R-PET containing 0.30 wt% of PMDI, whose result is coherent with the highest value of molecular weight presented by this material. For R-PET containing the PMDA at 0.15 and 0.30 wt% the results of tensile strength were few significant when compared with R-PET without additive, while for R-PET containing the Irgafos 126 the results were slightly lower than R-PET only, showing that other factors in addition to molecular weight, can affect the mechanical response of material.

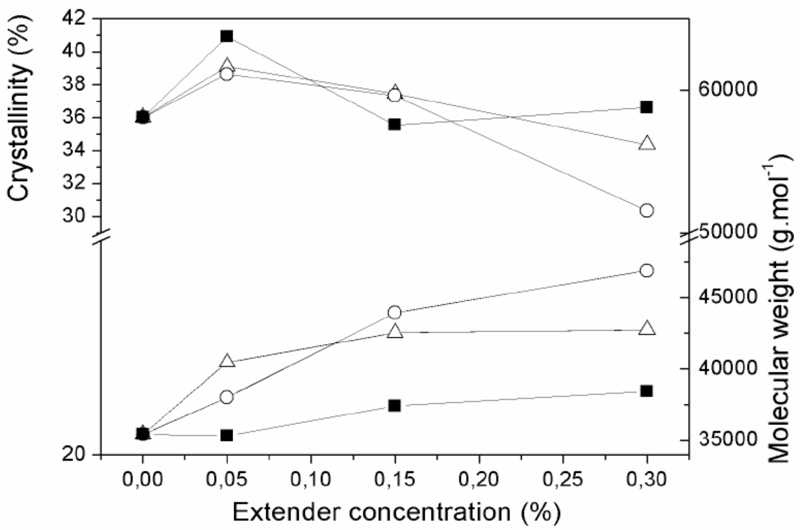

Figure 1: Crystallinity and molecular weight for R-PET on different concentration of the chain extenders: Irgafos 126 (-Δ-); PMDI (-○-) and PMDA (-■-).

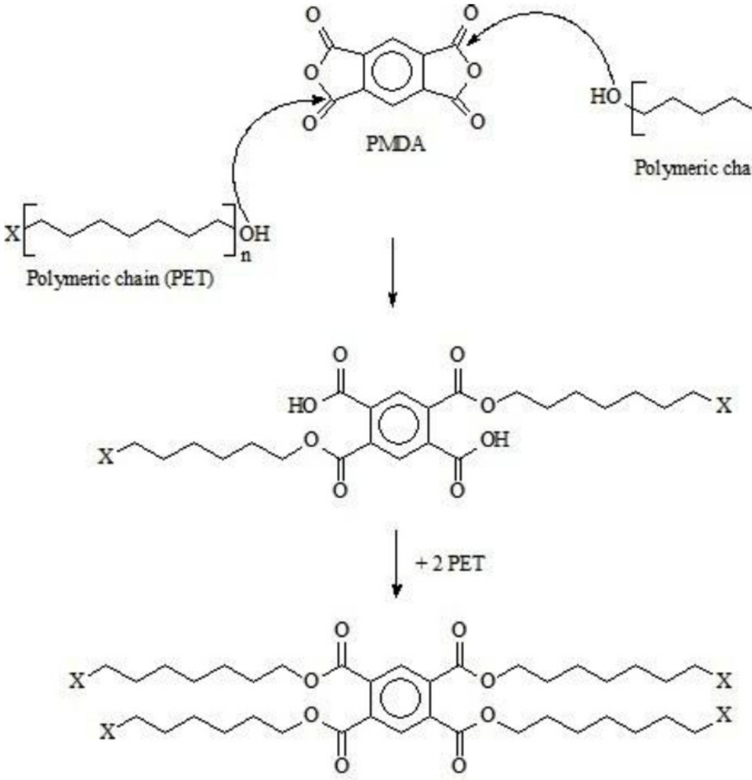

Figure 2: Chain extension mechanism for PET with PMDA [13].

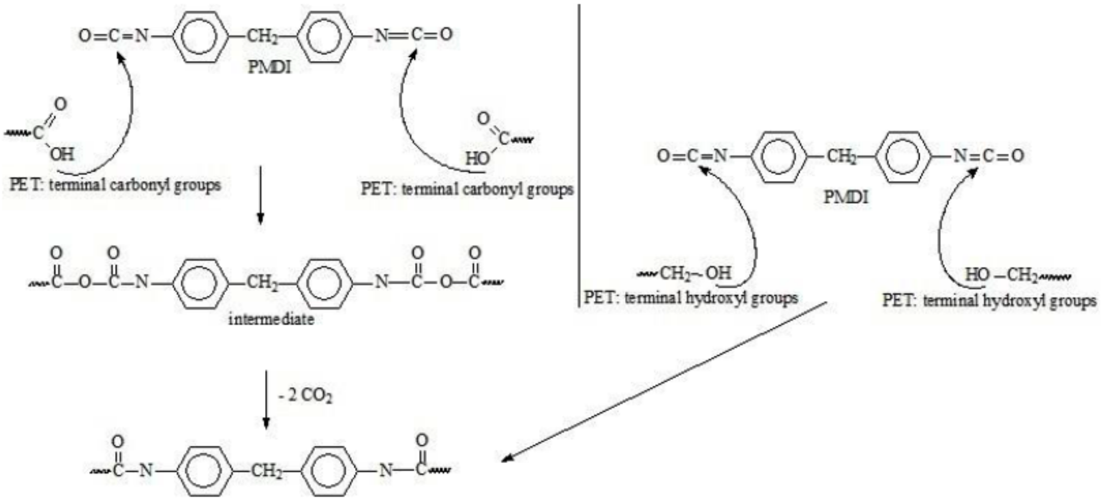

Figure 3: Chain extension mechanism for PET with PMDI [14].

The results of Young's modulus (Figure **6**) also shows that the mains modifications on R-PET have been caused by PMDI. In this situation, the values of Young's modulus present progressive decrease with increasing concentration of PMDI. The decrease in Young's modulus represents a material less rigid and better for application. It is verified than Irgafos 126 causes increase in Young's modulus, while the PMDA produce few significant changes on the Young's modulus of the R-PET.

Rheological Properties

Melting viscosity and melting strength are parameters that define thermo-mechanical process ability of the PET. Highly degraded PET presents low melting viscosity and melting strength, invalidating the extrusion processing. Figures **7**, **8** and **9** illustrate the results of apparent melting viscosity as function of shear rate for each material compared to the R-PET without chain extender. For R-PET containing Irgafos

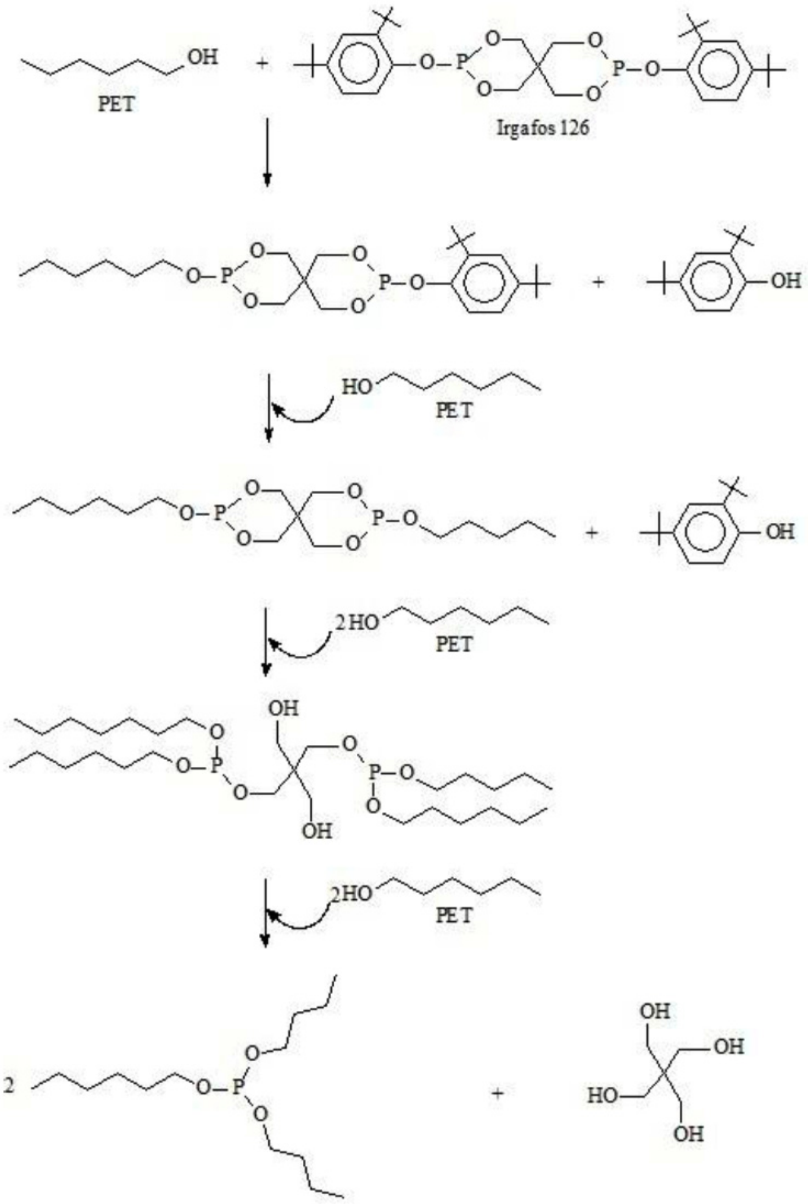

Figure 4: Chain extension mechanism for PET with Irgafos 126 [4].

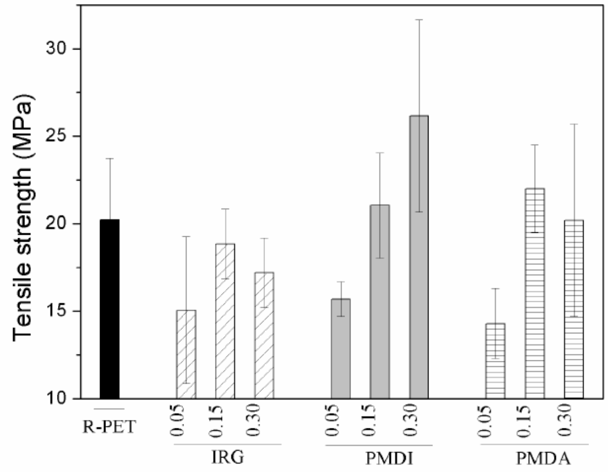

Figure 5: Results of tensile strength for R-PET containing chain extenders.

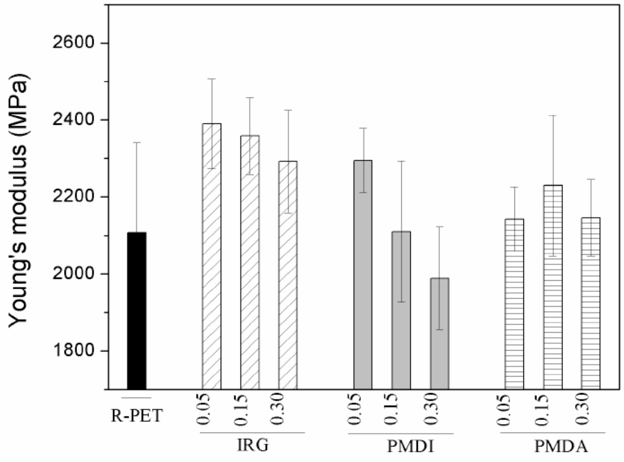

Figure 6: Results of Young’s modulus for R-PET containing chain extenders.

126 (Figure **7**), the apparent viscosity gradually decreases with increasing concentration of chain extender and remains constant to higher shear rates. Thus, despite Irgafos 126 to cause increase in molecular weight of R-PET, important properties such as mechanical and rheological are depreciated in presence of this additive, confirming the previous results of mechanical testing.

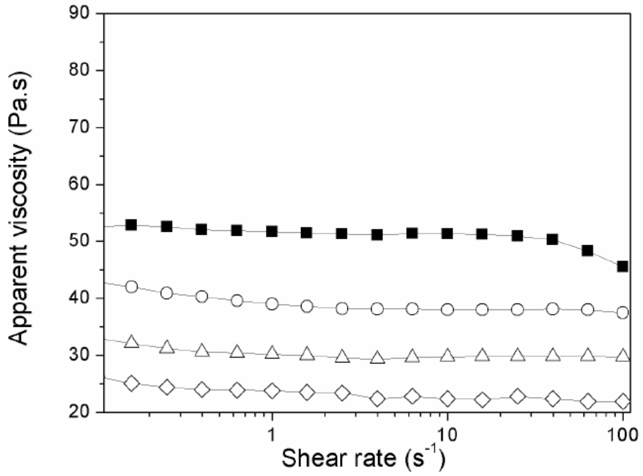

Figure 7: Results of dynamic rheometry for R-PET containing Irgafos 126:R-PET (-■-); IRG05 (-○-); IRG15 (-Δ-) and IRG30 (-◊-).

PMDA is a traditional and well known chain extender for PET. The results of apparent viscosity of the R-PET containing PMDA at 0.05 wt% shows a decrease of property independent of the shear rate imposed (Figure **8**). This behavior is coherent with the values of molecular weight and tensile strength previously observed for this material. No significant change in apparent viscosity is noted for R-PET containing 0.15 wt% of PMDA when compared to R-PET without additive. However, considerable increase in apparent viscosity can be observed for R-PET containing 0.30 wt% of PMDA. In this situation, the apparent viscosity at low shear rates is almost the double that presented for R-PET without additive, showing a slight downward trend for higher shear rates. Thus, PMDA at concentration lower than 0.15 wt% should produce negative response of proprieties of R-PET, while on concentrations higher than 0.15 wt% there is an improvement in rheological properties.

In R-PET containing PDMI at 0.30 wt% the apparent viscosity at low shear rates is higher than R-PET without additive (Figure **9**). However, apparent viscosity decrease with increasing shear rates. Similar behavior is also noted for PDMI15, although the performance of this material has been lower than R-PET only. At 0.05 wt% of PDMI, R-PET showed apparent viscosity lower than R-PET and independent of shear rate applied, according to results mentioned above for other chain extenders.

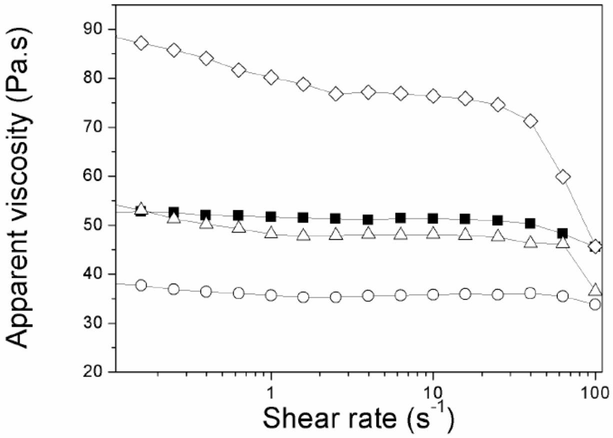

Figure 8: Results of dynamic rheometry for R-PET containing PMDA:R-PET (-■-); PMDA05 (-○-); PMDA15 (-Δ-) and PMDA30 (-◊-).

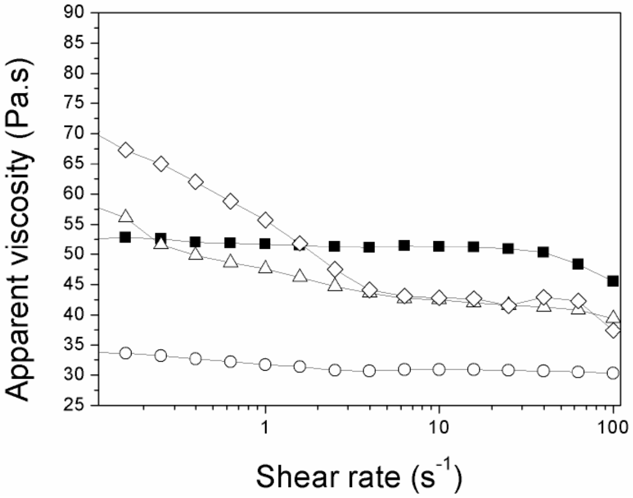

Figure 9: Results of dynamic rheometry for R-PET containing PMDI: R-PET (-■-); PMDI05 (-○-); PMDI15 (-Δ-) and PMDI30 (-◊-).

CONCLUSIONS

All chain extenders used in this work had an effect on properties of R-PET. Molecular weight increases with increasing concentration of chain extender, while crystallinity presents an opposite behavior, although an increase in crystallinity of the R-PET is verified for concentrations at higher values to0.05 wt% of chain extenders.

In spite of Irgafos 126 to cause increase in molecular weight, mechanical and rheological properties of R-PET are depreciated with incorporation of this additive. PMDA improvements mainly apparent viscosity at concentration of 0.30 wt%, while others properties of R-PET are less affected. On the other hand, PMDI causes the highest increase in molecular weight at comparable concentration and the best performance of mechanical properties. However, apparent viscosity is unstable with increasing shear rate.

PMDI as well as the well-known PMDA can be successfully used to recovery properties of degraded waste PET, allowing other reprocessing and recycling of these materials.

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