

Chain Extension of Poly (Ethylene Terephthalate) by Reactive Extrusion with Secondary Stabilizer

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Poly(ethylene terephthalate) (PET) is a polymer highly susceptible to the hydrolytic reactions that occur during applications and mainly in thermomechanical processing. These reactions lead to the decrease of molecular weight of the polymer, limiting the recycling number of the material. The reactive extrusion of the PET in presence of chain extenders is an alternative to recover mechanical and rheological properties that were depreciated by the polymer degradation. In this study, PET wastes from nonwoven fabrics production were extruded in presence of the secondary stabilizer Irgafos 126 (IRG) on variable concentrations. The results showed that Irgafos 126 increased molecular weight, decreased crystallinity and changed processing behavior of the PET, similarly to the effects produced by the well-known chain extender pyromellitic dianhydride (PMDA), showing that the secondary stabilizer Irgafos 126 can also act as a chain extender for the PET.

Keywords: *PET, chain extender, recycling, reactive extrusion*

1. Introduction

During thermomechanical processing the thermoplastic polymers are subject to high temperature and shear stress conditions able to produce severe degradation to the polymer¹. Some additives, such as Irgafos 126 (IRG), are largely used as secondary stabilizer to minimize the degradation effects in polymers, causing significant effect in the preservation of the material properties². Polyolefin such as polyethylene and polypropylene can be submitted to several processing steps in presence of stabilizers without that their properties would be drastically affected³. On the other hand, condensation polymers such as PET present intense polymeric chain break during thermomechanical processing by thermo-hydrolysis reaction, leading to the decrease of their molecular weight^{3,4}.

The decrease of molecular weight in PET cause depreciation in several properties such as melt viscosity, mechanical resistance and processing features. Degradation of the PET hampers their thermo-molding and limit the number of recycle of the material. Thus, the PET can be manufactured in many products in the first time that it is recycled. However, other cycles of reutilization are not frequently viable due to the low quality of material, generating high production of post-consumer and post-industrial wastes with low recyclability potential⁴.

Nonwoven fabrics represent an import product made of PET waste, mainly generated from drink packing. During extrusion of PET waste to manufacture of nonwoven fabrics, a fraction of polymer is lost due to equipment clogging or

others factors, leading to formation of considerable amount of waste with low quality, which cannot be reinserted in extrusion system. These rejects are almost always deposited in land wastes, causing pollution or several others environmental problems^{3,5,6}. Many studies have been carried out with the use of chain extenders to recover properties of low molecular weight PET⁷⁻¹⁴. Chemical compounds such as anhydride and organophosphorus are some agents used as chain extender for PET. Chain extenders have two or more reactive sites in molecule, which can react with terminal groups of polymeric chains, bonding each other and increasing molecular weight of the polymer¹¹⁻¹⁶. In this work was studied the effects of the reactive incorporation of the stabilizer Irgafos 126 (IRG) on the PET wastes, which have showed an action as a chain extender for PET.

2. Experimental

2.1. Materials

The PET wastes used in this work was supplied by Fiberweb Bidim Ltda, which are generated during extrusion molding of recycled PET flakes from drink packing for production of nonwoven fabrics. The additive bis-(2,4-di-t-butylphenol) pentaerythritol diphosphite (Irgafos[®] 126) was also donated by Ciba Specialty Chemicals, while the 1,2,3,5-benzenetetracarboxylic anhydride (pyromellitic dianhydride – PMDA) was acquired from Acros Organics BVBA.

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2.2. Methods

2.2.1. PET processing

The first step for mechanical processing of the PET wastes was the milling, using a snake mill to produce size particles with dimension lower than 1 mm. Then, the polymer was dried at 120 °C for 4 hours in equipment Quimis 0314N242 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 Ø 25 mm 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. The samples were identified according to the concentration and kind of chain extender (Table 1).

2.2.2. Differential exploratory calorimetry (DSC)

DSC analyses were carried out in an equipment TA Instruments, model Q10, under nitrogen atmosphere, using 10 mg for all samples. First, each sample was heated from room temperature (25 °C) to 350 °C at a rate of 10 °C/min, followed by isotherm of 5 minutes to remove thermal history. Then, the material was cooled to room temperature at 10 °C/min and a second heating was performed in same conditions of the first heating to determinate the crystallinity degree (X_c)¹⁷. Thus, crystallinity degree was calculated by the Equation 1¹⁸⁻²⁰:

$$X_c = (\Delta H_m / \Delta H_m^\circ) \times 100 \quad (1)$$

Where, ΔH_m and ΔH_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_m° is 140 J.g⁻¹[18,19].

2.2.3. Viscometry

Solution viscosity measurement of the PET samples was done 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 needed to prepare the PET solutions. After ground previously, PET samples (0,1 g) were dissolved in the solvent mixture (20 mL) at 110 °C for 5 hours After the complete solubilization, the solutions were filtered and tested at 30 °C in water bath, according to standard test method ASTM D 4603²¹. From the flow time of the pure solvent mixture (t_0) and of PET solutions (t), it was possible

to obtain the relative (η_r), specific (η_{sp}), reduced (η_{red}) and inherent (η_{iner}) viscosities by means of the following equations^{22,23}:

$$\eta_r = \frac{\eta}{\eta_0} \cong \frac{t}{t_0} \quad (2)$$

$$\eta_{sp} = \eta_r - 1 = \frac{(t - t_0)}{t_0} \quad (3)$$

$$\eta_{red} = \frac{\eta_{sp}}{C} \quad (4)$$

$$\eta_{iner} = \frac{\ln \eta_r}{C} \quad (5)$$

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⁻¹).

The extrapolation of η_{red} or η_{iner} to concentration limit tending to zero gives intrinsic viscosity ($[\eta]$)^{22,23}:

$$[\eta] = \left(\eta_{sp} / C \right)_{C=0} = \left[(\ln \eta_r) / C \right]_{C=0} \quad (6)$$

Therefore, for determination of $[\eta]$ 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} versus concentration, whose extrapolation for concentration limit tending to zero corresponds to $[\eta]$, according to Equation 6.

By means of the Mark-Houwink Equation 7 was possible to determine the viscosity molecular weight M_v^{24} :

$$[\eta] = K M_v^a \quad (7)$$

Where the constants "K" and "a" at 30 °C are 2.37×10^{-4} and 0.73, respectively

2.2.4. Fourier-transform infrared (FTIR)

The solutions of PET used to viscometry analyses were filtrated in paper to retain impurities. Then, ethanol was added to the solution, generating the precipitation of the polymer. This precipitated was newly washed with ethanol and dried at 50 °C by 24 hours After purification the samples were diluted in KBr for preparation of tablets, which were used for acquisition of FTIR spectra in a spectrometer Shimadzu, model IR-Prestige 21 in transmittance mode at 32 scan and resolution of 4 cm⁻¹.

3. Results

3.1. Extrusion

The indication that the stabilizer Irgafos 126 had acted such as a chain extender occurred during the

Table 1. Samples identification.

Sample	Additive	Concentration % (w/w)
W-PET	---	---
IRG05	IRGAFOS 126	0.05
IRG15	IRGAFOS 126	0.15
IRG30	IRGAFOS 126	0.30
PMDA05	PMDA	0.05
PMDA15	PMDA	0.15
PMDA30	PMDA	0.30

extrusion molding processing. The extrusion conditions were initially adjusted to process PET waste and PET waste containing secondary stabilizer (Irgafos 126) at 200, 230, 250 and 250 °C from feeding zone to matrix, respectively. However, this temperature profile needed to be changed for higher values at 200, 270, 290 and 290 °C respectively, when irgafos 126 was incorporated at 0.15% w/w. The presence of Irgafos 126 caused increase in the torque of extruder, needing to increase the temperatures profile of the equipment to decrease the melt viscosity of the polymer. Similar effect in rheological properties of PET was also verified when equivalent amount of the chain extender pyromellitic anhydride (PMDA) was incorporated to the PET waste, indicating that the increase in melt viscosity of the polymer was caused by chain extension reaction of the Irgafos 126 on the PET such as occurs in presence of PMDA.

3.2. Differential exploratory calorimetry (DSC)

Differential exploratory calorimetry (DSC) analyses were carried out to verified possible changes in fusion enthalpy and consequently changes in crystallinity degree. Figure 1 present DSC curves of PET waste containing different amount of PMDA and Irgafos 126.

It is noted that the endothermic signals relative to the fusion enthalpy of materials around 245 °C have different intensity. Fusion enthalpy is directly proportional to the crystallinity degree of polymer that can be calculated by Equation 1.

Table 2 shows a comparison between fusion enthalpy and crystallinity degree for PET waste and PET waste containing Irgafos 126 and PMDA.

Crystallinity degree presents significant variation with the presence of PMDA and Irgafos 126 (Figure 2). The PET waste without additives has 36% of crystalline phase. However, the incorporation of 0.05% w/w of irgafos 126 increases the crystallinity degree to 39%. Similarly, the presence of PMDA in the same concentration increases of crystallinity degree to around 41%. On the other hand, the crystallinity degree become to lower levels when the concentration of Irgafos 126 or PMDA increase. The increase of molecular weight with the incorporation of chain extender at low concentration (0.05%) may be insufficient to change the crystallinity of polymer. However, the

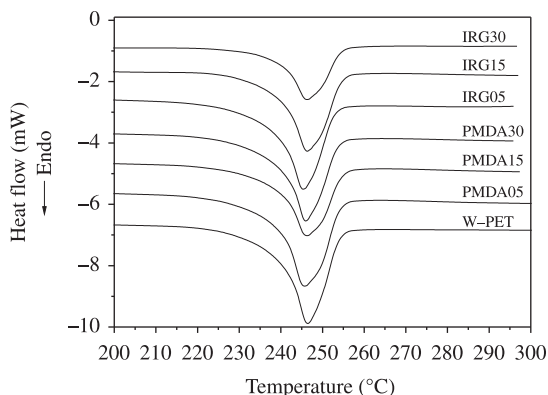


Figure 1. DSC curves of the W-PET containing Irgafos 126 and PMDA.

particles of additives and the nucleus of reaction additive-polymer represent impurities that can be the start points to the formation of heterogeneous crystallization⁷. Higher concentrations of chain extender lead to an increase in molecular weight and formation of branches, which difficult the chain organization and consequent crystallization⁷. Thus, the crystallinity degree of PET may be related to two antagonist processes: heterogeneous nucleation and molecular structure changes.

3.3. Intrinsic viscosity

Intrinsic viscosity and molecular weight are important parameters to evaluate the effective action of chain extenders on the PET. Table 3 presents values of intrinsic viscosity $[\eta]$ and viscosimetric molecular weight (M_v) of PET waste after reactive processing in presence of Irgafos 126 and PMDA. The molecular weight behavior of PET waste as a function of kind and concentration of chain extender is showed in Figure 3.

According to the effects verified in extrusion molding processing and DSC analyses, the viscosimetric molecular weight shows a tendency of increase as a function of the additives concentration. The increase of M_v in PET produced by irgafos reaches 42,741 g.mol⁻¹ at concentration of 0.30% w/w, being higher than PMDA, which is a traditional chain extender for PET. Therefore, Irgafos 126 should be reacting with PET waste such as a chain extender.

3.4. Fourier-transform infrared (FTIR)

FTIR is an important analytical method that allows evaluating possible chemical changes occurred in PET after

Table 2. Fusion enthalpy and crystallinity degree of the materials.

Sample	Enthalpy (J.g ⁻¹)	Crystallinity (%)
W-PET	50.4	36.0
IRG05	54.7	39.1
IRG15	52.4	37.4
IRG30	48.1	34.4
PMDA05	57.3	40.9
PMDA15	49.8	35.6
PMDA30	51.3	36.6

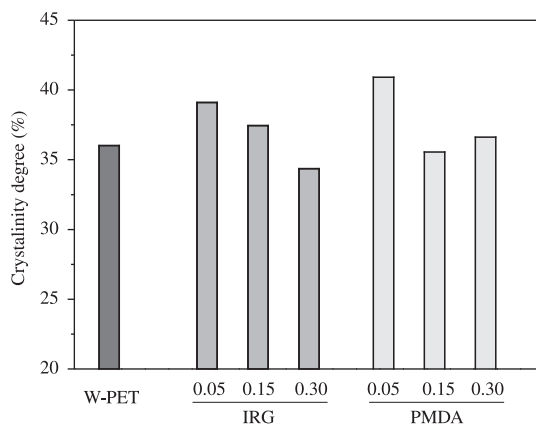


Figure 2. Crystallinity degree of the materials.

reaction with Irgafos 126 and PMDA. Figure 4 presents the FTIR spectra of the materials in wavenumber between 2500 cm^{-1} to 3800 cm^{-1} .

All FTIR spectra were normalized by the absorption band at 1958 cm^{-1} , which is related to aromatic overtone band of the PET that should not present changes of intensity after reaction of PET waste with Irgafos 126 and PMDA. The large band in wavenumber above 3100 cm^{-1} is attributed to absorption of hydroxyl groups, while the bands around 2900 cm^{-1} are attributed to C-H stretching bonding. Both Irgafos 126 and PMDA caused decrease in hydroxyl bands when compared to the PET waste without additives. However, this effect is more evident in PET waste containing PMDA. Some alterations are also verified in the bands profiles related to the C-H stretching bonding, mainly in the spectra of PET waste containing Irgafos 126. The decrease of intensity in hydroxyl band can be related to the reaction mechanism of the chain extender, which the hydroxyl group react with active sites of chain extender. Thus, the hydroxyl groups are converted to others groups such as ethers or esters that bond the polymeric chain with the chain extender molecule. The changes in absorption bands of C-H stretching bonding indicate that for Irgafos 126 others reactions or chemical interactions can also

occur with different groups of polymeric chain. Figure 5 illustrates possible reactions between hydroxyl groups of PET with Irgafos 126.

The two phosphorus atoms in molecule of Irgafos 126 represent reactive sites that can react with hydroxyl groups of PET to form a polymer-extender chain bonding, releasing a sterically hindered phenol. This reaction can also occur in the other extremity of Irgafos 126 molecule, generating the polymer extension. Subsequent reactions between hydroxyl groups of PET with phosphorus atoms lead to the formation of a chemical structure which three polymeric chains are bonded to one phosphorus atom, releasing one molecule of a tetrahydroxylated glycol.

The presence of Irgafos 126 during reactive processing of PET waste cause also changes in the FTIR band related to carbonyl groups. The FTIR spectra of materials in wavenumber between 1500 cm^{-1} and 2500 cm^{-1} presented in Figure 6 illustrate this behavior.

Carbonyl groups, intrinsic to the PET or generated in polymeric chain by oxidation process, present absorption band around 1700 cm^{-1} . The absorption bands of carbonyl groups as well as previously mentioned to hydroxyl bands present changes in the profile and intensity with reactive incorporation of Irgafos 126 and PMDA. Figure 7 shows the behavior of carbonyl index, which is calculated by ratio between area of the bands carbonyl (1723 cm^{-1}) and reference (1958 cm^{-1}). Carbonyl index presents progressive decrease for W-PET containing Irgafos 126 as a function of increase of the concentrations to 0.05 and 0.15%, remaining stable for 0.30%, while for PDMA is verified a

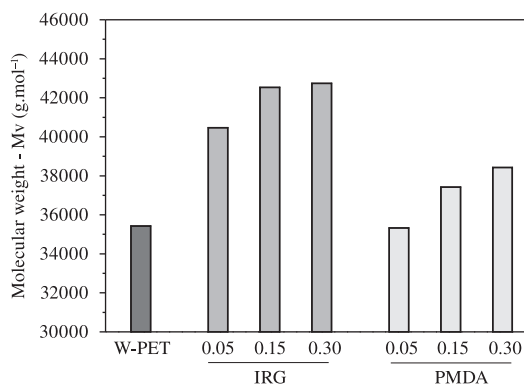
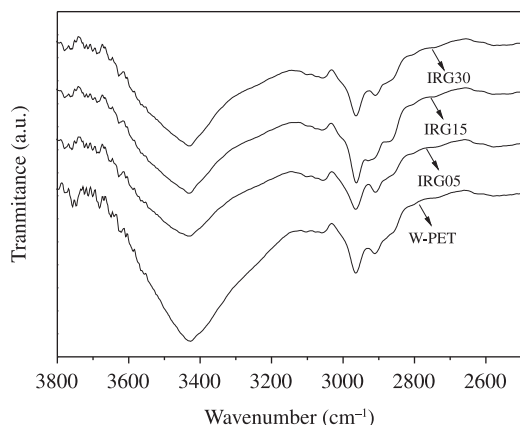


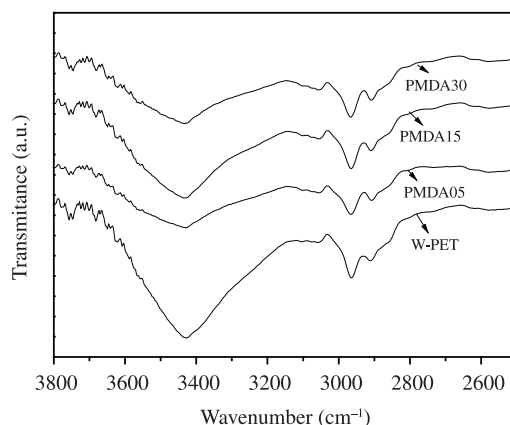
Figure 3. Molecular weight - M_v of the W-PET containing Irgafos 126 and PMDA.

Table 3. Viscometry analyses results.

Sample	$[\eta]$ (dL.g ⁻¹)	M_v (g.mol ⁻¹)
W-PET	0.49	35.423
IRG05	0.54	40.466
IRG15	0.56	42.533
IRG30	0.56	42.741
PMDA05	0.49	35.324
PMDA15	0.51	37.419
PMDA30	0.52	38.427



(a)



(b)

Figure 4. FTIR spectra of the hydroxyl region: a) W-PET containing Irgafos 126; b) W-PET containing PMDA.

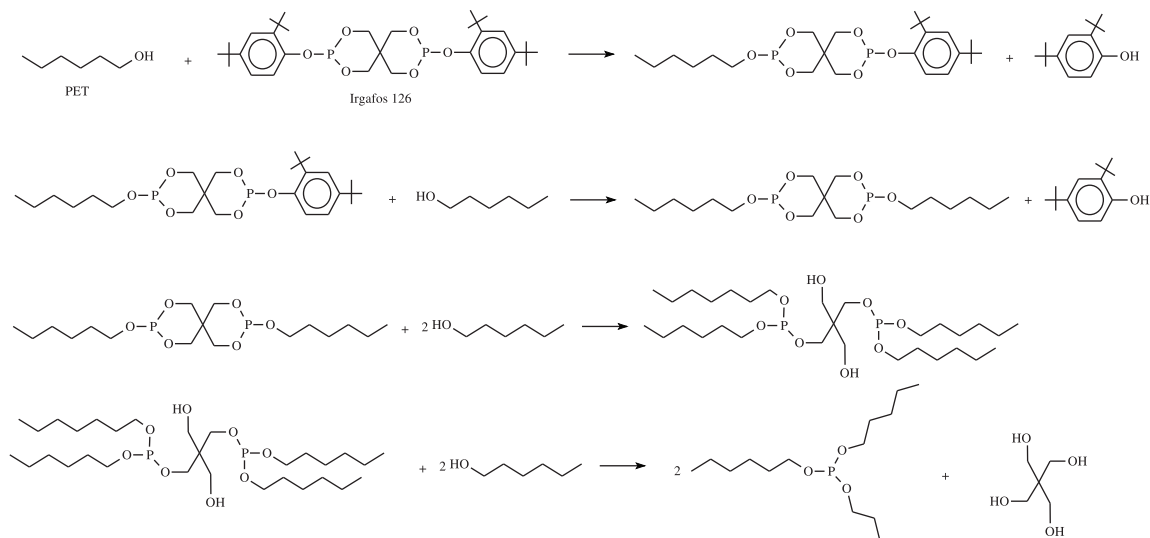


Figure 5. Mechanism of reaction between Irgafos 126 and PET.

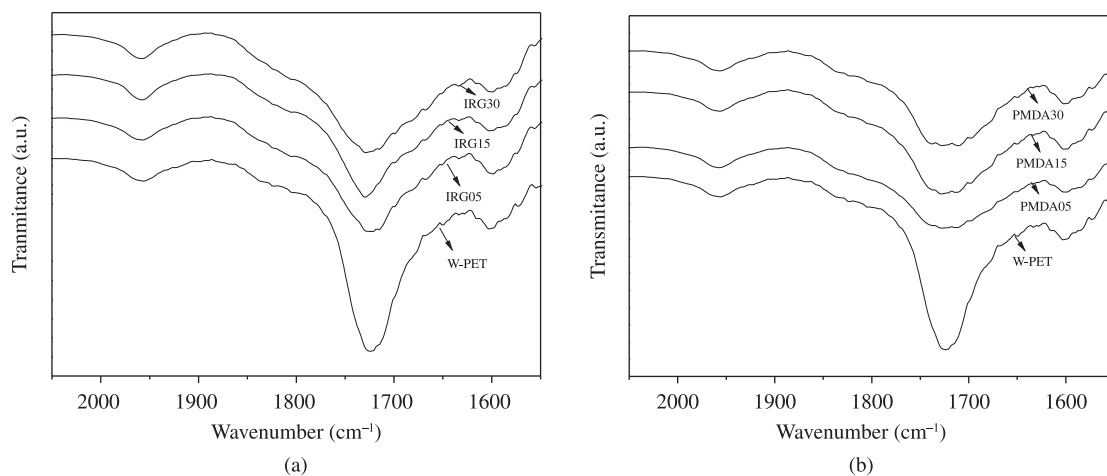


Figure 6. FTIR spectra of the carbonyl region: a) W-PET containing Irgafos 126; b) W-PET containing PMDA.

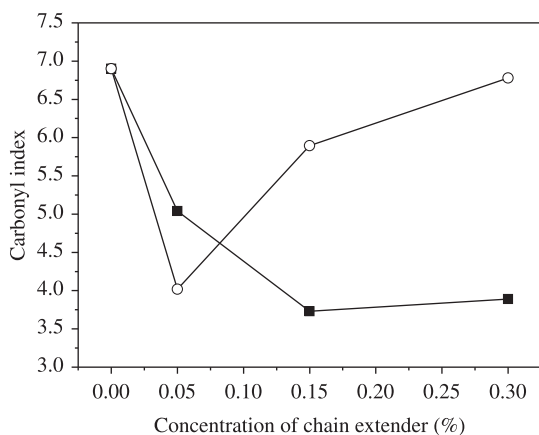


Figure 7. Carbonyl index: W-PET containing Irgafos 126 (■-) and W-PET containing PMDA (○-).

decrease accentuated of carbonyl index for concentration of 0.05% and increase for higher concentrations. This effect shows that carbonyl groups can also actively participate in extension reaction with Irgafos 126 and PMDA. Oxidation-reduction mechanism should be to more likely to occur to the Irgafos 126, which this chain extender acts as reduction agent and carbonyl groups as oxidation agent.

4. Conclusions

The secondary stabilizer Irgafos 126 act as a chain extender to the polymer when incorporated to post industrial PET wastes by extrusion molding, similarly to the traditional chain extender PMDA. The molecular weight of polymer increases as a function of the concentration of Irgafos 126, as well as to PMDA, while crystallinity tends to lower values. Chain extender reaction should occur when

hydroxyl groups react with active sites of the chain extender molecule, which correspond to the two phosphorus atoms in the molecule. The use of Irgafos 126 such as a chain extender can represent a new application for this additive and an alternative to recover several mechanical properties of PET that were depreciated by degradation, favoring the mechanical recycling of PET wastes.

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