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PET recycling and chain extension during reactive processing in the presence of pyromellitic dianhydride (PMDA)

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ABSTRACT

In this study, poly(ethylene terephthalate)(PET) industrial scraps with low intrinsic viscosity $[\eta]$, coming from a PET bottle processing plant was chain extended with pyromellitic dianhydride(PMDA). The reaction was performed in a single step through reactive extrusion. ^{13}C NMR spectroscopy, Differential Scanning Calorimetry(DSC), Intrinsic Viscosity and Melting Flow Index(MFI) measurements were carried out to study the chemical structure, the thermal properties(glass transition, melting point and crystallinity) and the molecular characteristics of different PET samples. Properties of recycled poly(ethylene terephthalate) (PET-R) were compared with those of the virgin polymer(PET-V). The effect of the chain extension process on the properties of PET-R was then evaluated. Modified PET(PET-M) samples were tested based on two different PMDA concentrations(0,3 and 1% wt). The PMDA concentration was varied with the intention of reaching a higher recycled PET intrinsic viscosity and to investigate the effect of PMDA content on the chemical structure and properties of recycled PET.

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KEYWORDS

PET;
PMDA;
Reactive extrusion;
Recycling;
 ^{13}C NMR.

INTRODUCTION

The recycling of plastic wastes has attracted much interest in recent year's. It is of no doubt that the wide variety of applications of plastics in industry and the continuing increase in household plastics consumption has led to serious waste disposal problems. The recycling of plastic wastes coming from a separate collection of municipal solid waste can be a convenient way to solve the problem of landfilling this large amount of material and has therefore become not only desirable but also increasingly mandatory. PET recycling represents one

of the most successful and widespread examples of polymer recycling. The main driving force responsible for the increase in recycling of post-consumer PET is its widespread use, particularly, in the beverage industry which has made PET the main target for plastic recycling. However, bottle-to-bottle recycling is prevented due to lack of desirable mechanical properties and high melt strength, which depends on the molecular characteristics, such as average molar mass, molar mass distribution and chain branching.

During its life cycle PET comes in contact with degrading agents such as oxygen, light, high

temperatures, shearing, and water (not only as a residue of the washing process but also due to short storage periods). These factors cause degradation through chain scission, which leads to the decrease in intrinsic viscosity (η) by formation of low molar mass PET with a significant increase of carboxyl and hydroxyl end groups^[1-3].

In order to raise the intrinsic viscosity of the PET to a higher desired level, reactive blending of virgin PET with potential chain extenders was investigated by different authors^[4-11]. They showed that additive type di- or polyfunctional chain extenders were the preferred chain extenders because of their high reaction rate without generating by-products. Pyromellitic dianhydride PMDA has previously been reported as an efficient chain extender and branching agent^[12,13]. It is thermally stable, produces no by products on reaction with PET, and is commercially available, and economical. The influence of variables such as the chain extender concentration and the reaction time on the virgin and recycled PET chain extension process has also been investigated^[4,12-21]. Khemani^[12] showed that when 0.2 to 0.3 wt% PMDA was used with virgin PET, a significant increase in melt strength was obtained. Otherwise, the author found that a high PMDA concentration produced chemical, thermal and rheological instability in the system, causing crosslinking reactions and gel formation. PMDA was the selected chain extender in this study; its concentration was chosen to be the process variable. Properties of modified recycled PET (PET-M) at different PMDA concentrations were compared with those of recycled and virgin PET. Thus, ¹³C NMR spectroscopy, Differential Scanning Calorimetry (DSC), Intrinsic Viscosity and Melting Flow Index (MFI) measurements were investigated.

EXPERIMENTAL

Virgin PET was supplied by Texpet (TexPet® 874-C80). It comes in pellet form and is used for soft-drink bottle manufacture. TABLE 1 represents its properties

The recycled material was PET from colorless softdrink bottles, supplied by Flacotec S.A., Tunisia. PMDA (pyromellitic dianhydride), was obtained from Fluka, Switzerland with a purity of 99.7%. It showed

TABLE 1: Properties of virgin PET (PET-V)

Properties	Values
Density ASTM D792	1,39±0,01 sp gr 23 ⁰ C
Melting point (DSC)	248±5 ⁰ C
Intrinsic viscosity	0,8±0,02dl/g
Acetaldehyde	1,0 max ppm
Moisture contents	0,2 max wt%

TABLE 2: Terminology used for the materials during the work

Terminology	Description
PET-V	Virgin PET
PET-R	Recycled PET
PET-RM0,3	Modified recycled PET with 0,3% PMDA
PET-RM1	Modified recycled PET with 1% PMDA

very sharp melting points at 285-286⁰C^[22].

Recycled PET was subjected to intensive drying at 140⁰C during 24 hours in a vacuum oven before being fed to the extruder. Chain extension was performed in a single-screw extruder (YVROUD: D=25mm, L/D=28). The thermal profile was 255-255-260-260⁰C and the rotational speed was 45 rpm.

To facilitate interpretation and identification throughout this work, the samples were named as shown in TABLE 2.

The ¹³C NMR experiments were carried out at room temperature on a BRUKER 300MHz Ultra Shield spectrometer at the National School of Engineering of Sfax, Tunisia, operating at a frequency of 75.47MHz for 13⁰C. The solid-state high-resolution ¹³C NMR spectra were obtained by the combined use of cross-polarisation CP, high-power proton decoupling (DD) and magic angle spinning (MAS). A solid CP/MAS 4-mm diameter probe was used with ZrO₂ rotor and Kel-F lid at 11kHz rotation speed. tetramethylsilane (TMS) was used as a reference. The contact time of CP was 12 ms in all CP experiments. The recycle delay was 5s. The accumulation number was 5000–10000, depending on the signal to noise ratio.

A Mettler TA 3000 DSC calorimeter was used to obtain thermograms of virgin recycled and modified PET. The temperature used was 20-300⁰C with a helium atmosphere and the samples (10-20mg) were heated and cooled at 10⁰C/min. Glass transition temperature, T_g , crystallization temperature, T_c , melting temperature, T_m , enthalpy of crystallization, ΔH_c , and enthalpy of melting, ΔH_m , of samples were calculated. The percent of crystallinity (χ_c) of PET was calculated from the Eq. (1).

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$$\chi_c (\text{Wt.}\%) = 100 \frac{\Delta H_m - |\Delta H_c|}{\Delta H_m^0} \quad (1)$$

Where ΔH_m^0 is the heat of fusion of 100% crystalline PET ($\Delta H_m^0 = 135.8 \text{ J.g}^{-1}$)^[23].

Melt flow index (MFI) measurements were performed according to ASTM D1238-99 (load 2.16kg, $T=260^\circ\text{C}$, capillary $L/D=4$) by using an equipment CEAST mod 6243/0000.

Solution viscosity measurements were carried out in a viscosimeter equipped with Ubbelohde capillaries in a mixture of phenol and 1,1,2,2-tetrachloroethane (60/40 by volume) at 25°C . The intrinsic viscosity, $[\eta]$ was determined by extrapolation using the Huggins equation. The efflux time (t) is proportional to the absolute viscosity:

$$t = A\eta$$

The inherent viscosity is given by the following relation:

$$\eta_{\text{inh}} = \left(\frac{1}{C}\right) \log\left(\frac{\eta}{\eta_0}\right)$$

With: η : absolute viscosity of PET in the solvent; η_0 : viscosity of the pure solvent; C : concentration of the solution.

From where:

$$\eta = \left(\frac{1}{C}\right) \log\left(\frac{t}{t_0}\right)$$

25mg PET samples were dissolved in 15ml solvent during 4 hours at 120°C . The tests are carried out at the ambient temperature.

The mass average molar mass, M_w , was determined from the Mark Houwink relation:

$$[\eta] = KM_w^\alpha$$

Where $[\eta]$ is the intrinsic viscosity, K and α are constants the values of which depend on the nature of the polymer and solvent as well as on temperature.

In the case of PET, at a temperature of 25°C $K_{\text{PET}} = 2,75 \cdot 10^{-4}$ and $\alpha_{\text{PET}} = 0,77$ ^[24].

RESULTS AND DISCUSSION

The NMR spectra of PET-V and PET-R are shown in figure 1 and the assignment of the peaks in the spectra of the two polymers is given in TABLE 1. In the 75.46MHz noise decoupled ^{13}C NMR spectrum of PET-V, carbonyl signals ($\delta=163,51\text{ppm}$) and the

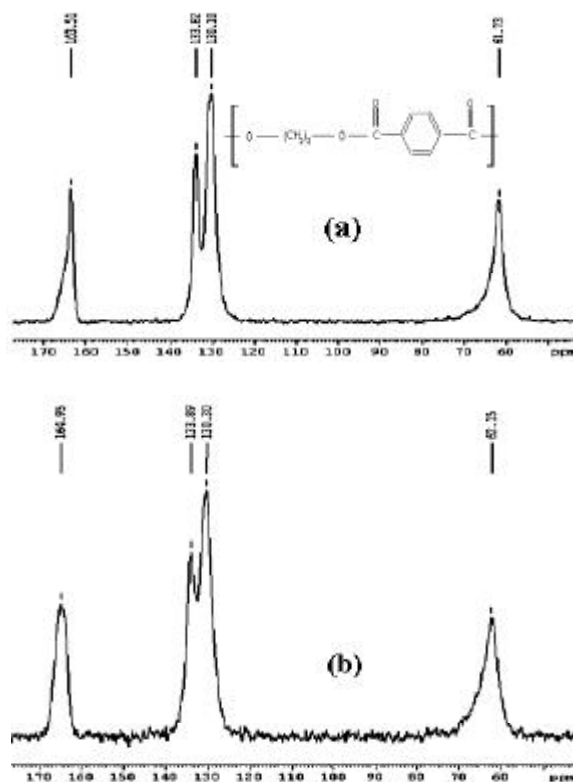


Figure 1: ^{13}C NMR of PET-V (a) and PET-R (b)

TABLE 3: Chemical shifts (δ) for carbon resonance: protonated aromatic (C1); deprotonated aromatic (C2); ethylene (C3); carbonyl (C4) for PET-V and PET-R

Nucleus	$\delta(\text{ppm})$	
	PET-V	PET-R
Protonated aromatic (C1)	130,10	130,30
Deprotonated aromatic (C2)	133,82	133,89
CH_2O (C3)	61,73	62,15
CO (C4)	163,51	164,95

resonances from carbonyl and phenyl were present (the signal respectively at $\delta=133.82\text{ppm}$ and 163.51ppm). A signal of weak resonance at 61.73ppm characteristic of the superposition of two signals of the carbons symmetrical methylenes.

From TABLE 3 we note that chemical shifts of the aromatic quaternary and the carbonyl carbon atoms are sensitive to the nature of the alkyl group in close proximity to the phenylene ring. All of the peaks noted in TABLE 3 are observed in the spectrum of virgin and recycled PET shown in figure 1 The chemical shifts due

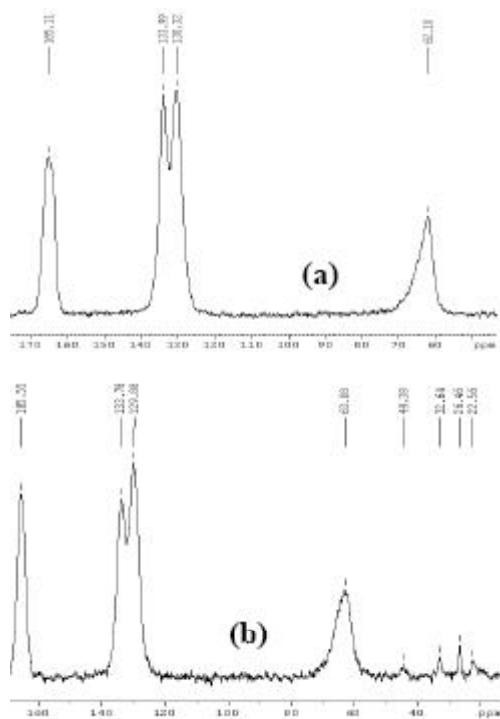


Figure 2: ^{13}C NMR of PET-M0,3% (a) and PET-M1% (b)

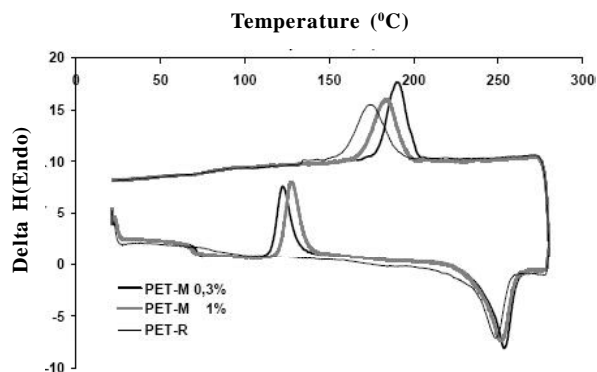


Figure 3: DSC melting curves of PET-V and PET-R

TABLE 4: Rheological properties of PET-V, PET-R and PET-M0, 3%

	PET-V	PET-R	PET-M0,3%
MFI (g/10min)	38,2	106	64,3
$[\eta]$ g.dl $^{-1}$	0,81	0,39	0,68
M_w (dl/g)	32000	10000	25000

TABLE 5: Thermal properties of PET-V and PET-R

	T_g (°C)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	χ_c
PET-V	76	244	60,8	-	-	44,7
PET-R	85	249	37,3	173	40,58	27,7

to the quaternary carbon and carbonyl carbon atoms are diagnostics of their environment and are sufficient to characterize and quantify changes in chain structure

(particularly sequence lengths) due to trans reaction.

There are no additional peaks due to PET degradation products.

^{13}C NMR of PET-M0, 3% (figure 2a) shows 4 signals which are close to those of the PET-V and PET-R but with larger intensities for the carbonyl, carboxyl and phenyl groups. This is due to the addition of PMDA which comprises these three groups. To confirm chain ramification when a percentage higher than 0,3% is added, we prepared modified recycled PET with 1% of PMDA. The product was analyzed by solid NMR under the same operating conditions. The obtained ^{13}C NMR spectrum contains the same four signals present in the PET-V, PET-R and PET-M. Spectrums. But the spectrum of PET-R-M1% (figure 2b) contains other aliphatic peaks which could be a result of chain ramification.

The comparison between PET-R and PET-V (TABLE 4) shows the reduction in intrinsic viscosity $[\eta]$ and the molecular mass M_w it generated an increase of the melt flow index MFI. The occurrence of thermal and hydrolytic degradation reactions during recycled PET melt processing is responsible for the reduction in $[\eta]$ or molar mass of the PET^[25-27].

TABLE 4 gives the intrinsic viscosity $[\eta]$, and the mass average molar mass, M_w , of virgin PET, recycled PET and modified PET with 0,3% PMDA. Before processing at a high temperature, virgin PET possesses a value of $[\eta]$ equal to 0.81 dl.g $^{-1}$. The decrease in $[\eta]$ and M_w of virgin PET after recycling is important, whereas this effect is strongly reduced for modified PET

Figure 3 shows the DSC heating curves of PET-V and PET-R over the temperature range 20 to 300°C and TABLE 5 lists the DSC characteristics of both virgin and recycled polymers. PET-V displayed two peaks: a sharp endothermic melting process of PET 244°C (T_m) and a second peak indicating a glass transition at about 76°C. The PET-R curve shows three peaks: the first heating run has a strong step at the glass transition temperature process is followed. The melting peak

TABLE 6: Thermal properties of PET-R, PET-M0,3% and PET-M1%

	T_g	T_{cc}	ΔH_{cc}	T_f	ΔH_f	T_c	ΔH_c	χ_c
PET-R	85	-	-	24937	-	28	28	
PET-R-M0,3%	71	123	28	25446	189	43	34	
PET-R-M1%	68	128	28	25244	182	39	32	

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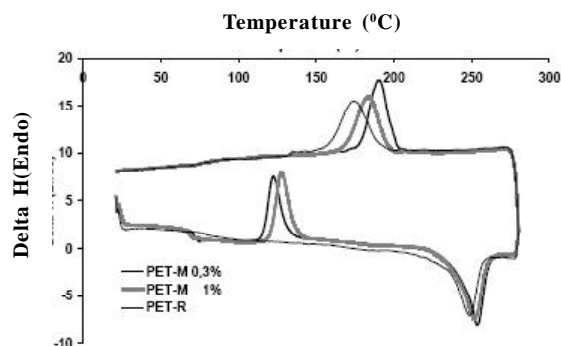


Figure 4: DSC melting curves of PET-R, PETR-M,3% and PETR-M1%

contains one broad peak with a single peak melting temperature at 249°C range. The slow cooling results in crystallisation of the PET samples therefore there is no cold crystallisation on the curve.

Figure 4 and TABLE 6 represent the DSC thermograms of PETR, PETR-M0,3% and PETR-M1%. As it can be seen, the glass transition temperature of PET is not significantly affected by the PMDA content. On the contrary the analysis of melting and crystallization enthalpy appears strictly dependent on the PMDA amount. The area under the exothermal crystallization peak is a measure of the amount of PET crystallinity, so the reduction of ΔH_c with the increase of the chain extender percentage suggests that a lower amount of PET crystallinity is present in the treated PET samples. Moreover the T_{mc} values also decrease on increasing the PMDA content. Both results can be attributed to structural changes occurring during the chain extension reaction: increase of M_w ; broadening of M_w/M_n ; and branching phenomena. On the contrary the data obtained in the first scan in terms of cold crystallization temperatures T_{cc} increase as the PMDA amount increases, confirming that the crystallization of treated samples becomes more difficult.

CONCLUSION

In this study, we compared the chemical structure, the thermal properties (glass transition, melting point and crystallinity), the intrinsic viscosity and the molecular characteristics of recycled PET with those of the virgin resin. Recycled PET is an industrial scrap and it is arising from homogeneous non contaminated deposits of

colourless bottles.

The different thermal and mechanical history of the virgin and recycled PET leads to different thermal and molecular properties but the chemical structure is not affected.

To develop new applications of recycled PET arising from post-consumer bottles other than that of the fibers which require a low intrinsic viscosity, it should be interesting to modify chemically recycled PET by adding a coupling agent (PMDA) to increase its intrinsic viscosity.

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