

Structure and rheology of recycled PET modified by reactive extrusion

L. Incarnato^{a,*}, P. Scarfato^a, L. Di Maio^a, D. Acierno^b

^aDepartment of Chemical and Food Engineering, University of Salerno, Via Ponte don Melillo, 84084 Fisciano (SA), Italy

^bDepartment of Materials and Production Engineering, University of Naples, P.le Tecchio 80, 80125 Napoli, Italy

Received 16 September 1999; accepted 6 December 1999

Abstract

In this work pyromellitic dianhydride (PMDA) was used as a chain extender to increase the molecular weight of polyethylene-terephthalate (PET) industrial scraps with low intrinsic viscosity ($IV = 0.48$ dl/g), coming from a PET processing plant. The reaction was performed in a single step through reactive extrusion. Different percentages of chain extender were used in order to investigate the effect of PMDA content on the molecular structure (average molecular weight, molecular weight distribution, branching) of PET. Rheological and thermal characterizations were performed on treated PET extruded samples. In particular, the increase in the dynamic viscosity at low frequencies and the high pronounced shear thinning behavior observed in the PMDA-treated PET samples were correlated to the broadening of the M_w/M_n and to the long chain branching. These structural changes are also responsible for the decrease in the T_{mc} and ΔH_{mc} and the increase in the T_{cc} values increasing the PMDA content in the PET samples. The study was performed also on bottle grade PET ($IV = 0.74$ dl/g) for comparison purpose. The results have pointed out that with an amount of PMDA included between 0.50 and 0.75% the chain extending reaction produces an increase of M_w , a broadening of M_w/M_n and branching phenomena, that modify the PET scraps in order to make the recycled polymer suitable for film blowing and blow molding processes. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Reactive extrusion; Rheology; Gel permeation chromatography

1. Introduction

It is known that chain extenders are low molecular weight compounds that can be used to increase the molecular weight of polymers [1–5]. In the case of polyethylene-terephthalate (PET), chain extension is represented mainly by a polyaddition between the PET end groups (carboxyl and hydroxyl groups) and the reagent, which should have at least two reactive sites. The polyaddition can happen in the solid state (SSPA) and in the melt phase (reactive extrusion). Both operations have their own advantages and inconveniences related to the control of the reaction or to the complexity of the system. In particular, SSPA is slow and requires special equipment for large-scale operation. On the contrary the reactive extrusion process is faster and can be easily applied during the ordinary melt processing. In this case the main problem is to control the extent of polyaddition optimizing the working parameters. These are, in particular, the concentration of the chain extender, the residence time of the polymer in the extruder and the working temperatures [6–12].

The reactive extrusion process can be used to increase the molecular weight of industrial scraps coming from PET processing plants. In many cases these scraps are uncontaminated but their viscosity is lowered by the first extrusion. This is certainly true in the case of fiber production where refuse PET has an intrinsic viscosity of about 0.4 dl/g. In this instance the use of some of the so-called chain extenders has been pointed out in specific works as a good method of enhancing material viscosity [1–10]. Depending on the structure of the chain extender used, the addition reaction can be accompanied by branching or even cross-linking, thus leading to a polymer with a higher molecular weight and significantly different properties.

The aim of this work was to increase the melt viscosity and the melt strength of PET scraps with a low intrinsic viscosity ($[\eta] = 0.48$ dl/g), coming from the fiber production of a national company, to obtain a grade suitable for film blowing or blow molding. For this purpose pyromellitic dianhydride (PMDA) was used as a chain extender to increase the molecular weight of the PET scraps. PMDA was selected since it has a melting point (about 283°C) near to that of PET and reacts within a few minutes in the ordinary PET processing conditions. Moreover PMDA is a tetrafunctional reactive which depending on the reaction

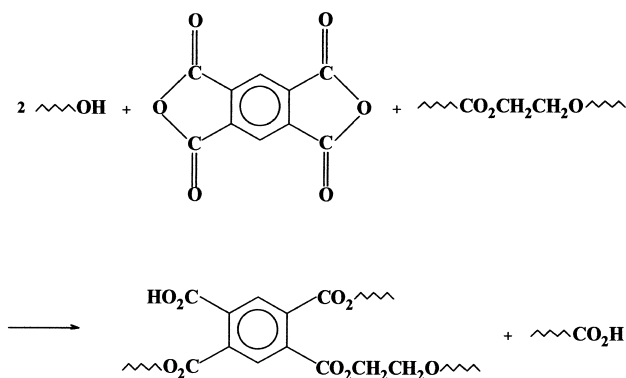
* Corresponding author. Tel.: + 39-089-964144; fax: + 39-0-89-964057.
E-mail address: incarnat@post.dica.unisa.it (L. Incarnato).

conditions, can lead to branching [2,13]. The presence of chain branches produces a remarkable enhancement in the melt viscosity and in the melt strength of the modified PET scraps that can become processable again even in processing operations when stretching is needed. PMDA content and reaction time were varied to study their effect on the molecular weight (M_w) and molecular weight distribution (M_w/M_n) which in turn influence the properties of the final product. In this regard rheological and thermal characterizations were performed on the PET extruded samples and the results were correlated to the structure parameters determined by GPC and intrinsic viscosity measurements. The same experiments were performed on a linear bottle grade PET ($[\eta] = 0.74$ dl/g) for comparison purpose. Optimizing the processing conditions and the PMDA content we have obtained a modified PET with a grade suitable for processing technologies such as film blowing or blow molding which require a high level of viscosity and melt strength.

2. Experimental

2.1. Materials

The study was conducted on PET scraps with a low intrinsic viscosity ($[\eta] = 0.48$ dl/g), coming from refuses of the fiber production of a national company (Montefibre, Italy), added with different percentages of PMDA supplied by Aldrich. PMDA is a tetrafunctional reactive that can lead to branching according to the reaction scheme reported below [13].



Samples of untreated PET and PET treated with 0.25, 0.50, 0.75 and 1.00% (w/w) of PMDA were prepared and reported as UT, T25, T50, T75 and T100, respectively. The linear bottle grade PET, used as a reference material, was reported as BG.

2.2. Reactive processing

Continuous blending of PET and PMDA was performed with a GIMAC extruder ($D = 12$ mm, $L/D = 20$) and a Ross type [14] static mixer to achieve polyaddition reaction of the refuse PET with the chain extender. The extruder

screw rotation speed determines the residence time of the polymer and the reactive blending effectiveness of the system. This parameter was chosen on the basis of preliminary torque measurements as a function of the reaction time.

Torque measurements were performed using a Brabender torque rheometer (Do-corder E330). The torque growth was monitored as a function of time for the untreated PET scraps (UT) and for the scraps added with 0.50 and 1.00% by weight of PMDA (T50, T100) at $T = 290^\circ\text{C}$ using a screw rotation speed of 40 rpm.

Dry blends of PET chips and PMDA powder were prepared with different amounts of PMDA (0.25, 0.50, 0.75 and 1.00% by weight). These were vacuum dried for 12 h at 110°C and were extruded with the system described above in the following conditions.

Extruder temperature: 280°C .

Mixer temperature: 290°C .

Screw speed: 40 rpm.

Extrusion die: slit die (30×1 mm²).

Die temperature: 270°C .

In these conditions the average residence time was approximately 150 s. The average residence time in the apparatus was evaluated by means of some preliminary experiments using a colored polymer as a tracer. For each extrusion speed, the tracer was fed and the time required to find the maximum intensity of color in the outlet stream was recorded.

2.3. Methods

Gel permeation chromatography (GPC) was the technique used to provide information about the average molecular weights M_n and M_w and the molecular weight distribution M_w/M_n of the PET samples. The GPC system used in this work was the Waters 150-C ALC/GPC (Millipore) fitted with four PLgel 20 μm MIXED-4 columns of dimensions 300×7.5 mm². The samples were dissolved in 1,1,1,3,3,3-hexafluoro-2-isopropanol at 30°C . The volume of injected sample was 1 μl at a flow rate of 1 ml/min.

Intrinsic viscosity determinations on UT, T25, T50 and T75 samples, solved at 100°C , were carried out with a Schott-Gerate viscometer in *ortho*-chlorophenol at 35°C .

The dynamic flow properties of the molten materials were measured with a Rheometrics Dynamic Spectrometer Mod. RDS-II (Rheometrics, Inc.) using a parallel plates geometry (plate radius = 25 mm, gap = 2 mm). The samples for testing were dried at 120°C in a vacuum oven for 12 h. Frequency sweep tests ($\omega = 0.1 \div 100$ rad/s) were made at 280°C at a constant strain amplitude (10% strain) under a nitrogen gas purge in order to minimize thermo-oxidative degradation phenomena.

Experimental runs in non-isothermal elongational flow have been carried out with a capillary rheometer (Rheoscope 1000, CEAST) equipped with a tensile module. The measurements have been performed employing a capillary

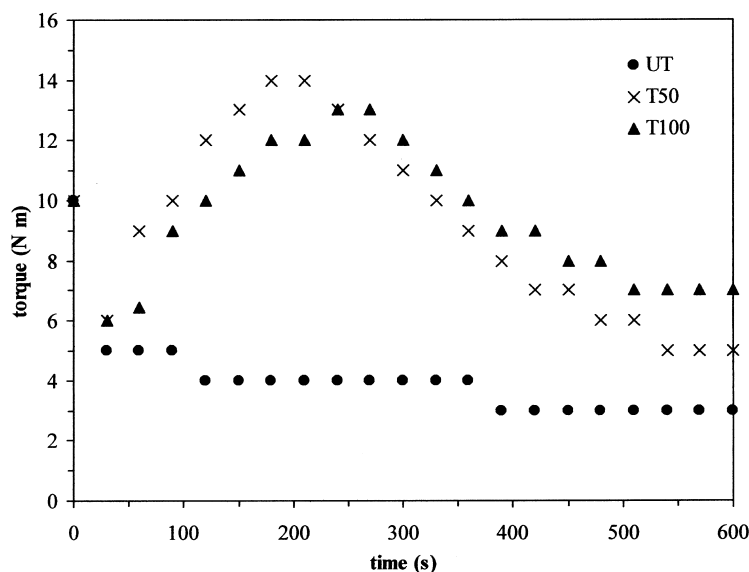


Fig. 1. Torque vs. residence time for untreated PET (UT) and for PMDA-treated PET (T50, T100) samples.

die of diameter 1 mm ($L/D = 20$) with the tensile module situated about 20 cm from the extrusion die. The extrusion temperature has been 280°C in all the cases while a wall shear rate of 125 s^{-1} was employed. The tests allowed determination of the melt strength i.e. the force acting on the filament at breaking and the breaking stretching ratio (BSR) which is the ratio between the drawing speed at breaking and the extrusion velocity at the die. Filament tension was measured at varied extensional strain rates corresponding to varied take-up wheel speeds. The initial take-up pulley speed (pulley diameter 120 mm) was fixed at 100 rpm.

Calorimetric measurements were performed with a Mettler Differential Scanning Calorimeter mod. DSC30 calibrated for temperature and enthalpy with metallic standards (indium and zinc). DSC thermograms were obtained from 12–15 mg samples, sealed in standard aluminum pans. The samples were first heated at a rate of $10^{\circ}\text{C}/\text{min}$ from 0 to 300°C and held at this temperature for 3 min to allow the complete melting of the crystallites; then, they were cooled at $10^{\circ}\text{C}/\text{min}$ from 300 to 0°C and re-heated up to 300°C at the same scan rate. The values of cold crystallization temperature T_{cc} and enthalpy ΔH_{cc} obtained from the

first scan are reported. The glass transition temperature T_{g} , melting temperature T_{m} and enthalpy of melting ΔH_{m} are referred to the second heating run. The melt crystallization temperature T_{mc} and enthalpy ΔH_{mc} were calculated from the cooling scan.

3. Results and discussion

Initial screening studies using a torque rheometer were performed to optimize the reaction time of PET–PMDA blends. As known the torque response is not a well-defined rheological property but this instrument offers the possibility of introducing and mixing into the melt polymer different amounts of PMDA and observing the response of the material with time. The torque values were measured as a function of time for the untreated PET scraps (UT) and for the scraps added with 0.50 and 1.00% by weight of PMDA (T50, T100) at $T = 290^{\circ}\text{C}$ and with a screw rotation speed of 40 rpm. The obtained results are reported in Fig. 1. As expected, the untreated PET shows a continuous decrease in the torque values, because of the occurrence of thermal and mechanical degradation phenomena during the processing. On the contrary, for the T50 and T100 samples a maximum in the torque curves can be observed, as a consequence of the chain extension reaction due to PMDA. The torque grows within $150 \div 250$ s then decreases again, since the thermo-mechanical degradation prevails on the poly-addition reaction. On the basis of these preliminary results and considering the geometry of the extruder and the connected static mixer used in this work we have chosen a screw speed of 40 rpm in order to obtain an average residence time of the blends in the apparatus of 150 s.

In order to investigate the effect of the chain extender amount on the molecular structure of PET, dilute solution

Table 1
Molecular structure parameters and intrinsic viscosity for untreated PET (UT), for PMDA-treated PET samples (T25, T50, T75) and for bottle grade PET (BG)

PET sample	M_w	M_n	M_w/M_n	$[\eta]$ (dl/g)
UT	38 834	18 649	2.08	0.49
T25	52 503	20 805	2.52	0.59
T50	65 802	23 303	2.82	0.67
T75	66 653	22 365	2.98	0.77
BG	67 891	38 504	1.76	–

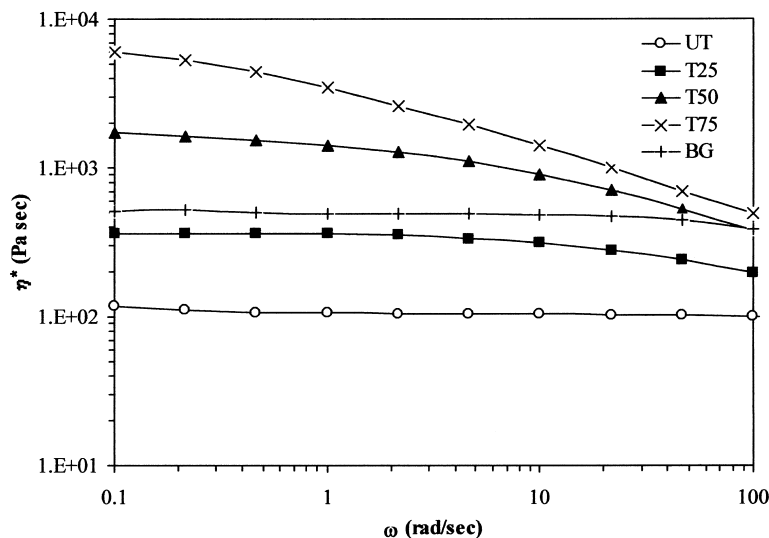


Fig. 2. Flow curves vs. frequency for untreated PET (UT), for PMDA-treated PET samples (T25, T50, T75) and for bottle grade PET (BG).

techniques such as GPC analysis and intrinsic viscosity measurements were performed on samples of untreated PET scraps and PMDA-treated PET obtained after the reactive extrusion. In Table 1 the weight average molecular weight M_w , the number average molecular weight M_n , the molecular weight distribution M_w/M_n and the intrinsic viscosity are reported for all samples analyzed. As it can be seen, even the lowest amount of PMDA used (0.25% by weight) produces a considerable increase in the M_w value. On increasing the PMDA content up to 0.5% (w/w) a further increase in the molecular weight parameters is obtained; then, passing from T50 to T75 sample, the growth of M_w and M_n is more contained. These results indicate that PMDA was an effective chain extender in the processing conditions fixed in this work. Moreover, it is important to point out that some gel formation, indicative of cross-linking, was revealed in the extruded samples when the quantity of the chain extender used was higher than 0.75% (w/w). For this reason the GPC data of the sample T100 were not reported. With regard to the molecular weight distribution M_w/M_n , it appears that a broadening of distribution is obtained on increasing the chain extender content in the blends. This result can be attributed to the chain extension reaction and branching occurring during the reactive processing. In fact, PMDA has four reactive sites and can add up to four polymeric molecules. As a consequence, besides chain extension some branching can occur and the MWD of the polymer becomes broader. Moreover, it must be considered that uncertainties in the GPC measurements can arise, the GPC data being hydro-dynamically equivalent to the molecular weight of linear polymers. Therefore the exact nature of branches formation and absolute quantification of molecular weight averages cannot be provided by this technique.

Intrinsic viscosity measurements were also performed and the results are reported in Table 1. These data do not lead to a quantitative determination of the average

molecular weight directly, but they provide a clear evidence of an increase in M_w with the PMDA amount, in agreement with the GPC analysis.

In Table 1 the molecular structure parameters of bottle grade PET are also reported for comparison. As it can be seen the M_w of such PET is close to those of T50 and T75 samples, but, as expected, the M_w/M_n value is lower for the linear bottle grade PET.

All these results obtained using dilute solution characterization techniques indicate that relevant changes in the molecular structure of the polymer occur due to the chain extension reaction. Moreover caution has to be devoted to these measurements because chain branching affects both the GPC elution volume and the intrinsic viscosity. Comparison of a variety of measurements is therefore required to establish the existence of chain branches. Since the rheological properties are strongly dependent on the structure the knowledge of the rheological behavior can be very useful for determining the effect of a change in the PMDA content and for evaluating the PMDA-treated PET samples processability. In this regard dynamic tests were performed at 280°C on samples of untreated and PMDA-treated PET in the frequency region of 0.1–100 rad/s where the sensitivity of the rheological parameters to structural variations is higher than in the power-law region. Only the T100 blend was not tested because some gel formation was observed in the extruded material. Fig. 2 shows the frequency (ω) dependence of the complex viscosity (η^*) for all analyzed samples. It clearly appears that the UT and the BG PET curves are Newtonian in the whole frequency range examined. Moreover, the BG PET, having an average molecular weight higher than the UT PET, also shows a higher viscosity. With regard to the PMDA treated PET samples, they show a complex viscosity higher than that of UT PET and display a Newtonian behavior only at low frequencies becoming shear thinning at high frequencies.

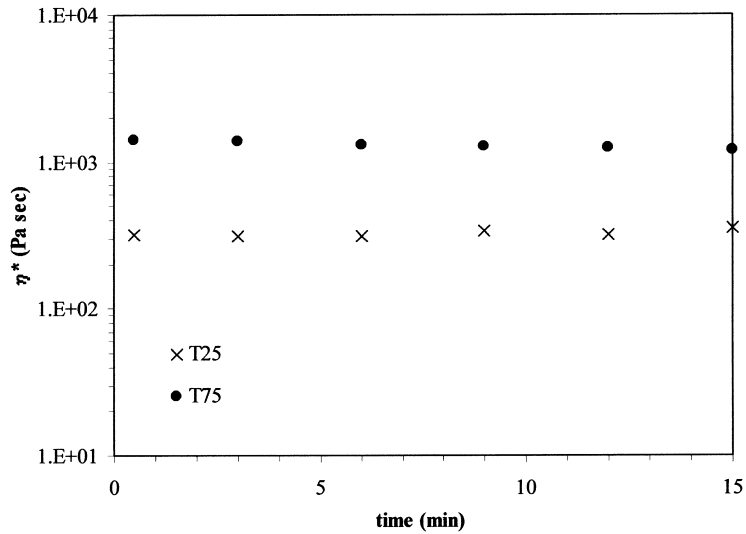


Fig. 3. Complex viscosity vs. time at frequency of 5 rad/s for untreated PET (UT), PMDA-treated PET samples (T25, T50, T75) and for bottle grade PET (BG).

The decrease of the viscosity with the shear rate begins at lower shear rate with the increase of the PMDA percentage in the blends. In particular, the flow curves of the T50 and T75 samples are highly shear thinning and the shape is very similar to that of commercial polymers (as LDPE) used in blow molding [15,16] that have long chain branches. The high pronounced shear thinning behavior of the treated-PET samples can be attributed to the broadening of the molecular weight distribution M_w/M_n and the introduction of long chain branches in the PET molecules during the reactive extrusion with the PMDA [15,17]. The effects of these two factors are difficult to separate. It is evident from the comparison of η^* at very low ω that the T50 and T75 samples have a higher viscosity than the BG PET sample even though the M_w values, calculated by GPC curves, of these materials are very close to each other. It is known from

the literature [15,17] that the occurrence of long chain branching produces entanglement networks that reduce the mobility of the macromolecules and strongly affect the polymer rheology. In particular, the low frequency viscosity may be orders of magnitude higher than that of a linear polymer at the same M_w and the slope of the flow curve increases.

With the aim to verify if structural modifications occur during the tests, time sweep measurements were performed. In Fig. 3 melt viscosity as a function of time was reported for the T25 and T75 samples. As it can be observed, at the condition fixed for the test η^* is almost constant up to 15 min, indicating that no significant structural changes occur during the rheological tests.

Analysis of the viscosity data shows that the chain extension reaction leads to an increase in the M_w and M_w/M_n

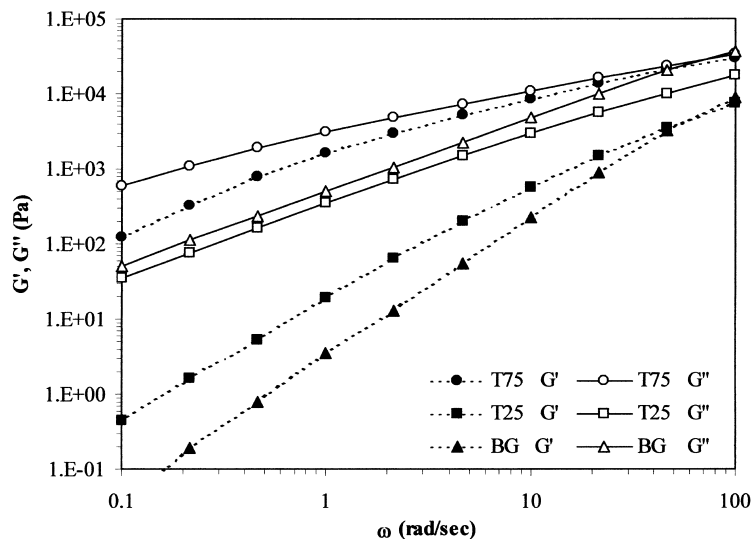


Fig. 4. Dynamic moduli vs. frequency for PMDA-treated PET samples (T25, T75) and for bottle grade PET (BG).

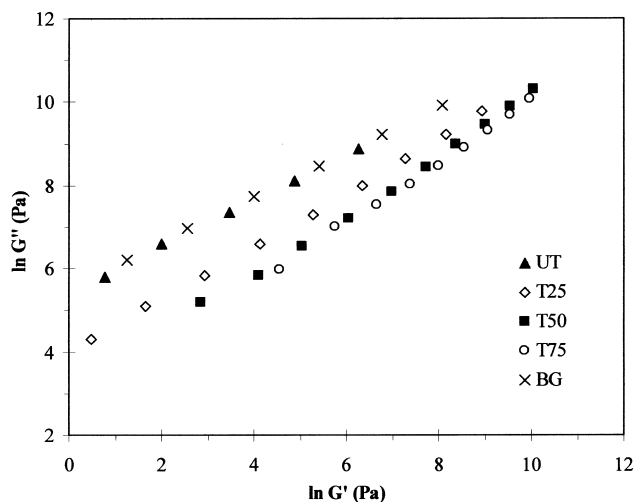


Fig. 5. Loss modulus G'' vs. storage modulus G' for untreated PET (UT), PMDA-treated PET samples (T25, T50, T75) and for bottle grade PET (BG).

values of the PMDA-treated PET, in accordance with the GPC data.

In Fig. 4 the G' and G'' curves for the BG, T25 and T75 samples were compared. It clearly appears that for all the materials analyzed the loss G'' moduli dominate with respect to the storage G' moduli in the whole frequency range investigated. Nevertheless, the examination of the low frequency region reveals that the contribution of the G' response to the total response is lower in the linear BG PET than in the treated PET and increases with the percentage of PMDA in the blends. These results can be explained as a consequence of some branching of PET molecules occurring during the reactive extrusion. Similar results were observed by Harrel and Nakajima for other long chain branched systems [18]. A better tool of comparing the differences in viscoelastic behavior resulting from

Table 2

Melt strength and BSR for untreated PET (UT), for PMDA-treated PET samples (T25, T50, T75) and for bottle grade PET (BG).

PET sample	Melt strength (10^{-2} N)	BSR
UT	Not measurable	Not measurable
T25	0.005	80
T50	0.012	120
T75	0.054	92
BG	0.010	320

Table 3

Thermal parameters for untreated PET (UT), for PMDA-treated PET samples (T25, T50, T75) and for bottle grade PET (BG)

PET sample	T_g ($^{\circ}$ C)	T_{mc} ($^{\circ}$ C)	ΔH_{mc} (J/g)	T_m ($^{\circ}$ C)	ΔH_m (J/g)	T_{cc} ($^{\circ}$ C)	ΔH_{cc} (J/g)
UT	83	201	46	255	49	124	31
T25	81	197	45	252	47	127	29
T50	83	194	43	251	46	127	28
T75	83	193	41	250	44	128	26

variations in the branched structure of polymers is the $\log G' - \log G''$ plot (or logarithmic Cole–Cole plots). Han et al. reported that such plots are independent of molecular weight but strongly dependent upon the M_w/M_n and the side-chain branching [19, 20]. The plots of all the materials analyzed are reported in Fig. 5. In general a single molecular weight curve is formed for each linear polymer species type and the introduction of branching shifts the Cole–Cole plot to higher values of G' at a constant value of G'' as revealed upon increasing the PMDA content.

In order to verify if the modified PET possesses melt properties are suitable for film blowing or blow molding processes, melt strength measurements were performed. The tests have shown that the reaction of the PET scraps with PMDA produces an enhancement of the melt strength of the polymer (Table 2). The increase is related to the content of chain extender and can be attributed not only to the rise in the M_w values but essentially to the introduction of chain branches due to chain extending reactions. In fact the T75 sample has a melt strength higher than the BG PET although they have similar M_w . On the contrary, as expected, the occurrence of branching also has the effect of reducing the BSR, which is lower for the PMDA treated PET than that for the linear BG PET.

Differential scanning calorimetric measurements were carried out on PMDA-treated PET and untreated PET. In particular, non-isothermal crystallization runs were performed at a cooling rate of 10° C/min. In order to erase all previous thermal history, the samples were heated up to 300° C and held at this temperature for 3 min to allow the complete destruction of the crystals. In Table 3 the numerical data are listed. The values of T_g , T_m and ΔH_m are referred to the heating traces obtained after the cooling runs, while the T_{cc} and ΔH_{cc} are referred to the crystallization peak that appears in the first scan.

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_{mc} 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.

4. Conclusions

In this work the effect of the PMDA on the molecular structure (M_w , M_w/M_n) and on the rheological and thermal properties of a refuse PET has been analyzed. The study has shown that the PMDA is an effective chain extender in the reactive extrusion of PET. By selecting the appropriate processing conditions and controlling the PMDA amount structural changes can occur to obtain polyester with pre-determined properties. In particular, the GPC, rheological and thermal results have pointed out that with an amount of PMDA included between 0.50 and 0.75% the chain extending reaction produces an increase of M_w , a broadening of M_w/M_n and branching phenomena, that modify the PET scraps so as to make them suitable for film blowing or blow molding processes.

References

- [1] Hinata H, Matsumura S. J Appl Polym Sci 1985;30:3325.
- [2] Hinata H, Matsumura S. J Appl Polym Sci 1986;32:4581.
- [3] Hinata H, Matsumura S. J Appl Polym Sci 1986;32:5193.
- [4] Hinata H, Matsumura S. J Appl Polym Sci 1987;33:3069.
- [5] Hinata H, Matsumura S. J Appl Polym Sci 1987;34:2769.
- [6] Cardi N, Po R, Giannotta G, Occhiello E, Garbassi F, Messina G. J Appl Polym Sci 1993;50:1501.
- [7] Karayannidis GP, Kokkalas DE, Bikiaris DN. J Appl Polym Sci 1995;56:405.
- [8] Bikiaris DN, Karayannidis GP. J Polym Sci: Part A Polym Chem 1995;33:1705.
- [9] Bikiaris DN, Karayannidis GP. J Polym Sci: Part A Polym Chem 1996;34:1337.
- [10] Loontjens T, Pauwels K, Derks F, Neilen M, Sham CK, Serné M. J Appl Polym Sci 1997;65:1813.
- [11] Guo B, Chan C-M. J Appl Polym Sci 1999;71:1827.
- [12] Rosales C, Perera R, Gonzalez J, Ichazo M, Rojas H, Sánchez A. J Appl Polym Sci 1999;73:2549.
- [13] Dijkstra AJ, Goodman I, Reid JAV. US Pat. No. 3,553,157, 1971.
- [14] Rauwendaal C. Polymer extrusion. Munich: Hanser Publishers, 1986 (p. 330).
- [15] Dealy JM, Wissbrun KF. Melt rheology and its role in plastics processing—theory and applications. New York: Van Nostrand Reynold, 1990.
- [16] Yan D, Wang W-J, Zhu S. Polymer 1999;40:1737.
- [17] MacOsco CW. Rheology: principles, measurements, and applications. New York: VCH Publishers, 1994.
- [18] Harrel ER, Nakajima N. J Appl Polym Sci 1984;29:995.
- [19] Han CD, Chuang HK. J Appl Polym Sci 1985;30:4431.
- [20] Han CD. J Appl Polym Sci 1988;35:167.