Influence of Water Content, Time, and Temperature on the Rheological Behavior of Polyethylene Terephtalate

A. M. C. Souza,[1] D. S. Leprêtre,[2] N. R. Demarquette,[1] M. F. Lacrampe,[2] P. Krawczak[2]

[1]Metallurgical and Materials Engineering Department, Escola Politécnica - São Paulo University, Av. Prof. Mello Moraes, 2463 CEP, São Paulo 05508-900, SP, Brazil
[2]Département Technologie des Polymères et Composites et Ingénierie Mécanique, Ecole des Mines de Douai, 941, rue Charles Bourseul BP 10838, Douai Cedex 59508, France

ABSTRACT: In this work, the main factors affecting the rheological behavior of polyethylene terephtalate (PET) in the linear viscoelastic regime (water content, time delay before test, duration of experiment, and temperature) were accessed. Small amplitude oscillatory shear tests were performed after different time delays ranging from 300 to 5000 s for samples with water contents ranging from 0.02 to 0.45 wt %. Time sweep tests were carried out for different durations to explain the changes undergone by PET before and during small amplitude oscillatory shear measurements. Immediately after the time sweep tests, the PET samples were removed from the rheometer, analyzed by differential scanning calorimetry and their molar mass was obtained by viscometry analysis. It was shown that for all the samples, the delay before test and residence time within the rheometer (i.e. duration of experiment) result in structural changes of the PET samples, such as increase or decrease of molar mass, broadening of molar mass distribution, and branching phenomena. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 3525–3533, 2010

Key words: molecular weight distribution/molar; rheology; viscosity; viscoelastic properties

INTRODUCTION

Polyethylene terephtalate (PET) is a thermoplastic polyester that can be used in several applications such as textile and packaging industries (beverages and food) because of its interesting mechanical (good impact resistance) and barrier properties and although it is an engineering polymer, its production is very large.[1] However, PET presents a relatively low molar mass compared with the one of other thermoplastics and relatively narrow molar mass distribution resulting in a low viscosity in the melt state. To increase the melt viscosity of PET, several solutions have been suggested in the literature: use of chain extenders to increase its molar mass,[2–5] it has been blended to other polymers[6–9] and nanocomposites with different types of nanoparticles have been obtained.[10,11]

The study of rheological properties, in the linear viscoelastic behavior, of thermoplastics can be a nice tool to infer some information of their microstructure (molar mass, blend morphology, state of dispersion in the case of nanocomposites).[12–16] In the case of PET, rheology has been used to obtain some information about the increase of molar mass when a chain extender was added[2–5]; to evaluate the interfacial tension between the components of blends involving PET[8] and the state of exfoliation in clay containing PET matrix nanocomposites.[10,11] It has been shown that an increase of molar mass, a broadening of molar mass distribution and the presence of branching in PET chains implies in an enhancement of elasticity, resulting in an increase of storage modulus, a decrease of slope of the storage modulus at high frequencies and a displacement of terminal zone to lower frequencies.[2–6]

However, the evaluation of rheological properties of PET is not simple due to its particular molecular chain characteristics. PET chains present ester groups, which are extremely hygroscopic and a dimethylene sequence, which is highly reactive with oxygen above the PET melting temperature. This chemical structure of PET is responsible for a possible hydrolysis or polycondensation (according to the water content within the sample), thermal degradation, and oxidation process[17] during the rheological measurement affecting therefore directly the results to be obtained. PET hydrolysis involves the chemical scission of an ester linkage in the main chain by water, resulting in an increase of carboxylic and alcoholic end groups

and in a decrease of molecular weight. It occurs if the initial water content within the sample is higher than a certain critical concentration.[18–20] If the initial water content within the sample is lower than this critical concentration, polycondensation occurs resulting in an increase of molecular weight. At high temperatures, trans-esterification can also occur resulting in changes of molar mass distribution until an equilibrium distribution is reached. In the absence of oxygen, which is the case when performing rheological measurements in nitrogen atmosphere, PET chains degrade essentially by a nonradicalar mechanism involving a rearrangement of the ethylene ester. This process is very slow and predominates only in the long term when the hydrolysis/polycondensation reactions have reached their equilibrium.[17]

In spite of the difficulties encountered during the rheological measurements, the preparation of PET samples to be tested rheologically and the way the rheological tests are conducted differ considerably from one study to another. The drying conditions before rheological evaluation, delays before experiments, ranges of frequencies covered, number of points per decade in small amplitude oscillatory shear tests and consequently duration of experiments vary.[2–10,21]

Carrot et al.[8] attended to the fact that the thermal stability in the melt of PET is a key limitation of the measurement time, and consequently, the frequency range reached for PET and their blends with polycarbonate (PC). The authors also observed that a prethermal treatment of PET samples and their blends, before rheological experiments, results in more reproducible data. All samples had been dried under vacuum at 120°C for 24 h. Hatzikiriakos et al.[21] observed that PET samples dried under vacuum at 160°C for 6–10 h or at 130°C for 18–24 h present more reproducible results than nondried PET samples. The authors also observed that, even for dried PET samples, for four consecutive small amplitude oscillatory shear experiments carried out from 500 to 1 rad/s, the storage and loss modulus change continuously, indicating that degradation reactions occur even in the presence of nitrogen.

In view of the earlier, the effect of water content, time delay before rheological tests, and duration of experiment on the rheological behavior of PET samples during small amplitude oscillatory shear was studied in this work. This study focuses on obtaining dynamic frequency sweep tests with a wider range of frequencies as compared to other studies on rheological behavior of PET.

EXPERIMENTAL

Commercial PET from Acordis Industrial Fibers BV. was used in this study. Disks of 25 mm diameter and 1 mm thickness were compression molded at a

TABLE I
Water Content (wt %) of PET Samples Dried, for Different Times and Temperatures, and Complex Viscosity (Pa.s) at the Beginning of Time Sweep Tests at 270°C

Drying time(h)/ temperature(°C)	Water content (wt %)	Complex viscosity at the beginning of time sweep tests at 270°C (Pa.s)
0	0.45	15
1/120	0.20	44
4/120	0.12	77
24/120	0.02	97
6/150	0.02	96

temperature of 270°C, under isostatic pressure of 18 MPa for 3 min, using pellets dried at 120°C for 2 h in a vacuum oven at approximately 10 m bar. These disks were dried for different times (0, 1, 4, and 24 h) at a temperature of 120°C and for 6 h at a temperature of 150°C, in a vacuum oven at approximately 10 m bar. Table I shows the water content of the samples, which were evaluated by Karl Fisher titration at a temperature of 250°C. It varied from 0.02 to 0.45 wt %. Similar water content was observed for PET samples dried 24 h at 120°C and 6 h at 150°C.

The rheological characterization of PET was carried out using a controlled strain rheometer ARES. The experiments were conducted under dry nitrogen atmosphere to avoid oxidation of the samples. A parallel-plate configuration was used with a gap size of 0.7 mm and a plate diameter of 25 mm.

Time sweep tests were performed at 270°C for up to 10,800 s for PET samples with different water content 0.45, 0.20, 0.12, and 0.02 wt %. Time sweep tests were also performed at 285 and 300°C for up to 10,800 s for PET samples with water content 0.02 wt %. The time delay before tests used was 60s to remove the residual stresses within the sample before rheological measurements. Such a delay was optimized monitoring the first normal stress before test. Immediately after the time sweep tests, the PET samples were removed from the rheometer. The viscosity average molar mass was obtained by viscometry analysis using a capillary Ubbelohde IC viscometer according to NF En ISO 1628-1. PET samples were dissolved in a solvent mixture of phenol to 1,1,2,2-tetrachloroethane (60/40) at a temperature of 25°C under magnetic stirring overnight. The concentrations of PET samples for the specific viscosity measurements were 5, 4, 2, and 1 g/L. The viscosity average molar mass (M_v) of the samples was calculated on the basis of the viscosity data using Mark-Houwink equation: $\eta = KM_v^a$, where η is the intrinsic viscosity and K and a are Mark-Houvink constants ($K = 7.44 \times 10^{-4}$ dL/g and $a = 0.648$ at 25°C).[22]

Dynamic frequency sweep tests were also performed in the linear viscoelastic regime at a temperature of 270°C for PET samples with low water content (0.02 wt %). Two types of tests were performed: decreasing the frequency from 100 to 0.1 rad/s (first frequency scan) and increasing it again to 100 rad/s immediately after (second frequency scan), or decreasing the frequency from 100 to 0.1 rad/s (first frequency scan) and repetition of frequencies scan from 100 to 0.1 rad/s (second frequency scan). The time delay before rheological test (first frequency scan) ranged from 300 to 5000 s. Both types of experiment had a duration of 12 min (approximately 6 min for the first frequency scan and 6 min for the second frequency scan). Also, dynamic frequency sweep tests were performed in the linear viscoelastic regime at a temperature of 270°C, decreasing the frequency from 100 to 0.01 rad/s, with five points per decade, resulting in a duration of experiment of approximately 60 min. These tests were carried out for PET samples with different water content. Time delays before tests varied from 300 to 5000 s. To avoid phase angle problems,[23] all experiments were conducted using the maximum strain value of the linear viscoelastic range.

To study possible structural changes such as branching and broadening of molar mass distribution of the PET samples, differential scanning calorimetric (DSC) analyses were carried out on PET samples removed from the rheometer after 1000 and 5000 s during the time sweep tests conducted at 270°C, for the different water content using a PerkinElmer DSC-7. Two analyses were carried out: nonisothermal crystallization and isothermal crystallization runs. Nonisothermal crystallization runs were carried out at a cooling rate of 10°C/min. The samples were first heated up to 300°C at the rate of 10°C/min and kept for 3 min at this temperature, then cooled at the same rate (10°C/min) following the procedures of Li et al.,[24] Oh and Kim[25] and Jayakannan and Ramakrishanan.[26] Although these procedures are not standard, all the samples suffered the same thermal treatment. For the isothermal crystallization runs, the samples were first heated up to 300°C at the rate of 10°C/min and kept for 3 min at this temperature, then the samples were quenched to 220°C at the rate of 50°C/min and the enthalpy changes as a function of time was observed.

RESULTS AND DISCUSSION

Time sweep tests

Influence of water content and time

Figure 1 shows the evolution of complex viscosity (frequency 1 rad/s) as a function of time for PET
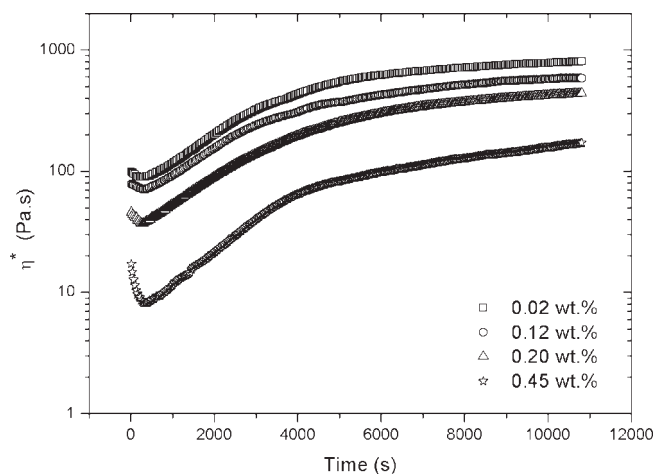

Figure 1 Evolution of complex viscosity (frequency 1 rad/s) as a function of time for PET samples with different water contents (temperature = 270°C and time delay before test = 60s).

samples with different water content (0.45, 0.20, 0.12, and 0.02 wt %) for experiments conducted at 270°C for up to 10,800 s. The values of complex viscosity at the beginning of time sweep test for the different samples tested are reported in Table I. It can be seen that the complex viscosity is a decreasing function of water content indicating that the water acts as a plasticizer for PET at the beginning of the tests. It can also be seen from Figure 1 that for PET samples with different water contents, the complex viscosity of PET decreases in the initial stages. This decrease is larger for PET samples with higher water content. After approximately 500s, the complex viscosity of PET samples with different water contents increases quickly until an equilibrium value. This equilibrium value seems to be reached faster for PET with lower water content: approximately 5000 s.

Figure 2 shows the viscosity average molar mass of PET samples removed from the rheometer at different times during the time sweep tests conducted at 270°C, for different water content. The molar mass was obtained by viscometry analysis dissolving the polymers in a solvent mixture of phenol to 1,1,2,2-tetrachloroethane (60/40) at a temperature of 25°C in different concentrations. All the samples dissolved readily, indicating that the samples did not present any crosslinking. It can be seen that the viscosity average molar mass of all PET samples decreases with time until 500s approximately, indicating that hydrolysis occurred during the initial stages of the time sweep tests. The hydrolysis was more important for samples with higher water content, resulting in a lower molar mass. After 500 s approximately, the viscosity average molar mass of all PET samples increases, indicating that
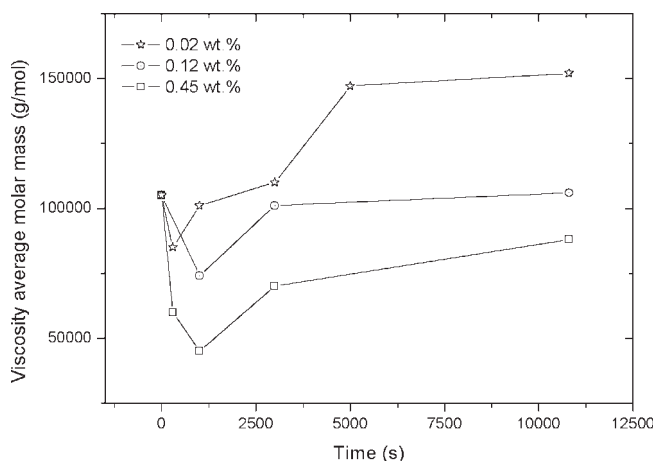
Figure 2 Evolution of viscosity average molar mass as a function of time for PET samples with different water contents.

Figure 3 Evolution of complex viscosity (frequency 1 rad/s) and viscosity average molar mass as a function of time for PET samples with 0.02 wt % water content at two temperatures (270 and 300°C).

polycondensation occurred during the time sweep tests. The viscosity average molar mass of PET shows to be larger for lower initial water content. This can be easily explained, if we consider that hydrolysis predominates if the initial water content is higher than the equilibrium concentration, whereas polycondensation predominates if the initial water content is lower than the equilibrium concentration.[17] In the case of PET samples with water content of 0.02 wt %, the initial water content is lower than the equilibrium concentration and polycondensation predominates, although a small hydrolysis seems to occur at the beginning of the experiment. In the case of PET samples with water content of 0.45 wt %, the initial water content is higher than the equilibrium concentration and hydrolysis predominates until 500s. After 500s, the water content may decrease and the polycondensation process becomes predominant. The results presented in Figure 1 show that the complex viscosity increases with the water content decreasing, indicating that the water regulates the kinetics of polycondensation: the equilibrium of the complex viscosity of PET seems to be reached at lower times for lower water content. The lower the water content is, the lower hydrolysis rate is, resulting in an increase of the polycondensation rate.[17] Similar behavior was observed by Acierno and Van Puyvelde[27] with Polyamide 11.

Influence of temperature

Figure 3 shows the evolution of complex viscosity (frequency 1 rad/s) as a function of time for PET samples with water content of 0.02 wt % for experiments conducted at 270 and 300°C. In this Figure, it is also shown the evolution of viscosity average
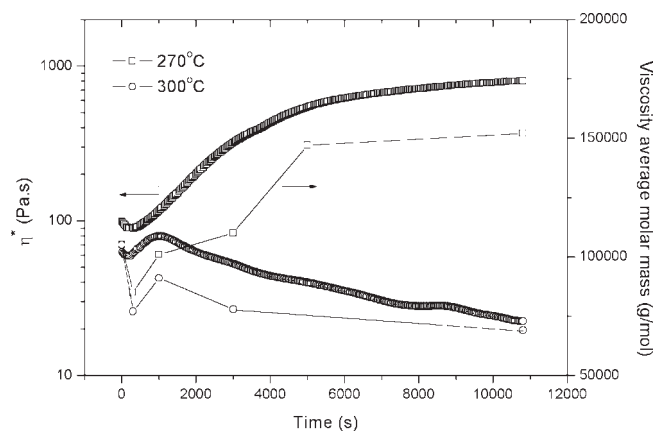
molar mass as a function of time. It can be seen that the temperature affects dramatically the evolution of complex viscosity as a function of time of PET. As shown earlier, for experiments conducted at 270°C, the complex viscosity increases and then levels off, indicating that the process of polycondensation prevails at this temperature. For experiments conducted at 300°C, the complex viscosity initially increases and then begins to decrease drastically. Initially, until 1000 s approximately, polycondensation prevails while thermal degradation prevails in a second stage. Similar behavior was observed for experiments conducted at 285°C although the thermal degradation undergone by the samples was lower as shown by the viscosity average molar mass results shown Table II.

Similar changes of molar mass undergone by the samples studied in this work were observed by Paci and La Mantia[28] during processing of PET in an internal mixer under nitrogen atmosphere during 60 min. The authors observed that increasing the processing temperature resulted in a decrease of molar mass at temperatures higher than 270°C, indicating that thermal degradation is present at higher temperatures. No crosslinking of the samples was observed by Paci and La Mantia.[28]

TABLE II
Viscosity Average Molar Masses of PET Samples with 0.02 wt % Water Content after 10,800 s During Time Sweep Tests at Different Temperatures

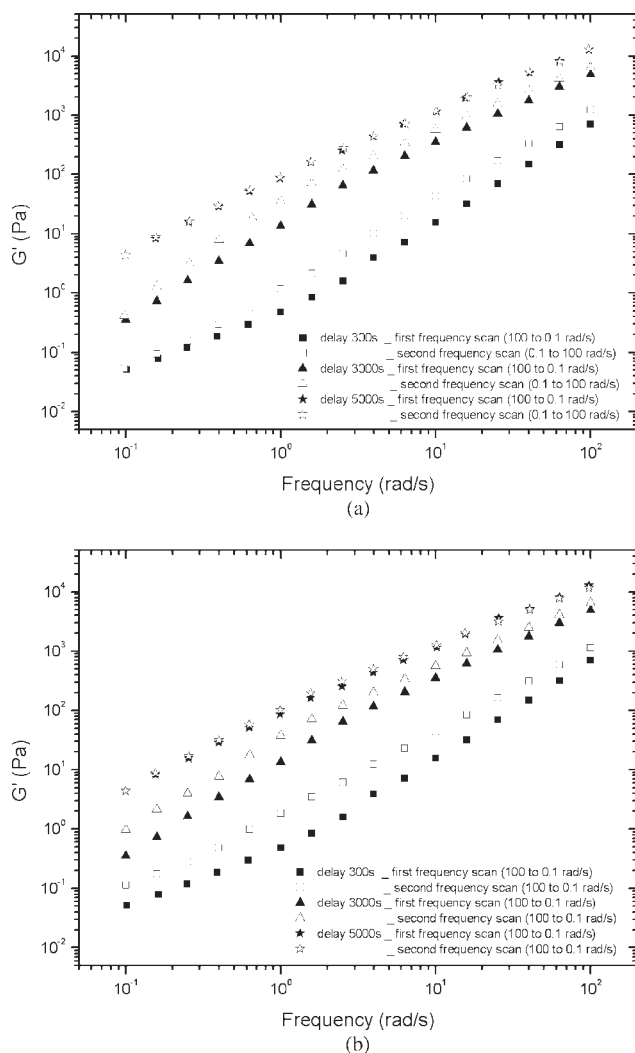| Temperature (°C)	Viscosity average molar mass (g/mol)
270	153,000
285	96,000
300	69,000

Figure 4 Superposition of two frequency scans for PET samples with 0.02 wt % water content after different time delays before first frequency scan at 270°C: (a) the frequency was decreased from 100 to 0.1 rad/s (first frequency scan) and increasing it again to 100 rad/s immediately after (second frequency scan); (b) the frequency was decreased from 100 to 0.1 rad/s (first frequency scan) and repetition of frequencies scan from 100 to 0.1 rad/s (second frequency scan).

Dynamic frequency sweep tests

Influence of time delay before rheological test

To study the influence of experimental time and time delays before experiment, on the rheological behavior of PET, dynamic frequency sweep tests were performed at 270°C for PET samples with low water content (0.02 wt %). Two types of tests were performed as mentioned in the experimental section. The results for both types of tests are shown Figure 4(a,b), respectively. The tests were repeated three times and the curves shown represent the average of the three tests. The standard deviation was approxi-

mately 5%. Similar type of experimental error was observed for all the rheological experiments reported in this manuscript. It can be seen that for time delays of 300 and 3000 s, the storage modulus curves obtained in the first (decreasing frequency) and second (either increasing or decreasing frequency) frequency scan differ from each other drastically even at low water content (0.02 wt %). The storage modulus for the second frequency scan is larger than the one for the first frequency scan indicating that the molar mass of the sample may have increased during rheological measurement due to polycondensation or that the polymer suffered structural changes such as branching. Similar behavior was observed for time delay of 1000 s. Hatzikiriakos et al.[21] also observed structural changes of PET during rheological experiments. In their case, the storage modulus of PET dried 24 h at 130°C decreased from one consecutive test to another performed decreasing the frequency from 500 to 1 rad/s. It can also be seen from Figure 4(a,b) that for time delays of 300 and 3000 s, the second frequency scan obtained increasing frequency [Fig. 4(a)] differ from the second frequency scan obtained decreasing frequency [Fig. 4(b)] mainly at low frequencies. The main reason for that relies in the fact that the time at which the second measurement for a same frequency was taken for either protocol was different. In the case of Figure 4(a) the second measurement at a frequency of 0.1 rad/s was taken 35 s after the first one, whereas in the case of Figure 4(b) it was taken 320 s after the first one.

The behaviors observed for time delays of 300, 1000, and 3000 s were not observed for a time delay of 5000 s. In that case, the storage modulus data obtained for the two frequency scans superposed, for either type of experiment, indicating that the structural changes undergone by the material reached an equilibrium. This time (5000 s) corresponds to the time for which the viscosity obtained during time sweep tests (Fig. 1), and the molar mass, obtained by viscometry analyses (Fig. 2) reached an equilibrium.

Influence of water content

To study the influence of water content, on the rheological behavior of PET, dynamic frequency sweep tests were performed at 270°C for PET samples with different water content (0.45, 0.20, 0.12, and 0.02 wt %), after different time delays before rheological test ranging from 300 to 5000 s. The tests were performed decreasing the frequency from 100 to 0.01 rad/s.

The dynamic curves of PET samples with 0.45 wt % of water content were irregular. The presence of water resulted, in this case, in the presence of many
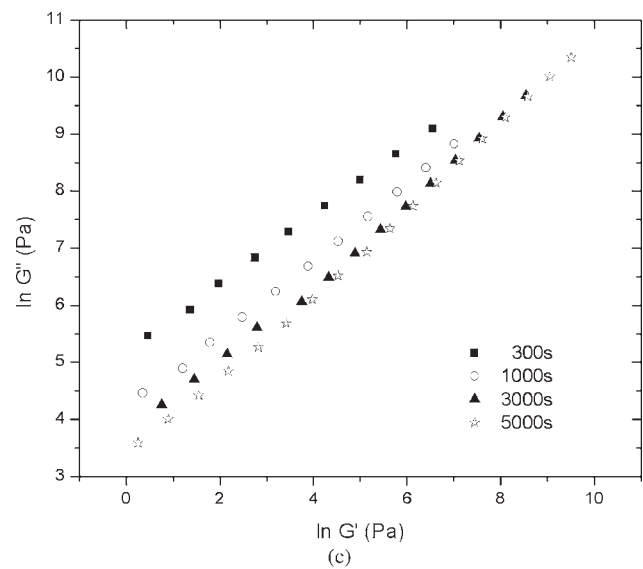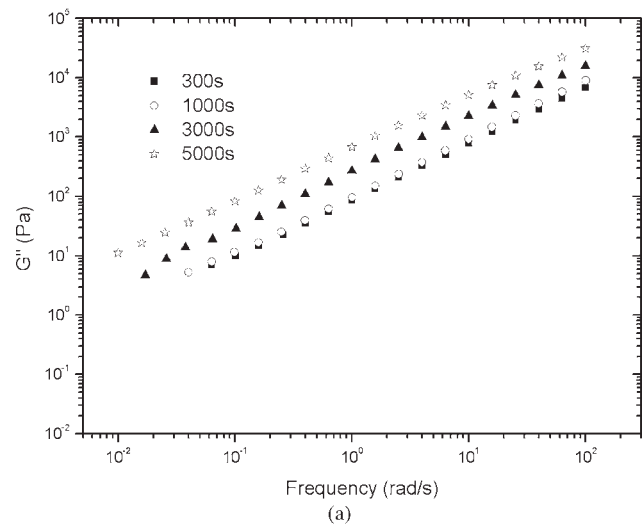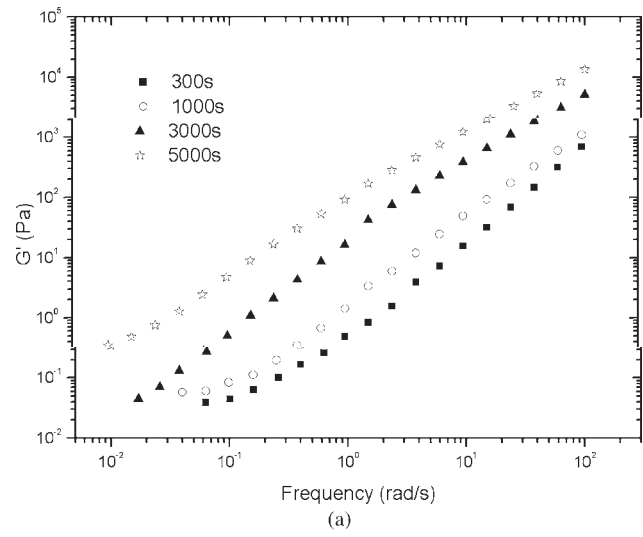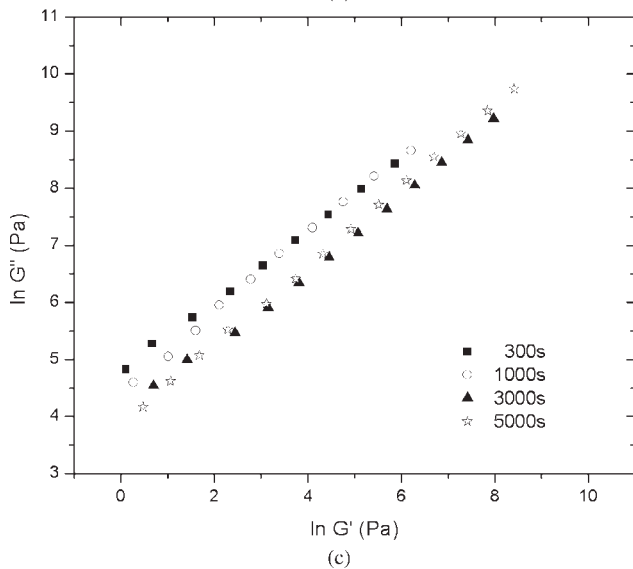
Figure 5 Storage moduli (a), loss moduli (b) as a function of frequency and Cole-Cole plot (c) for PET samples with 0.20 wt % water content, after different time delays before rheological test ranging from 300 to 5000 s (temperature = 270°C).
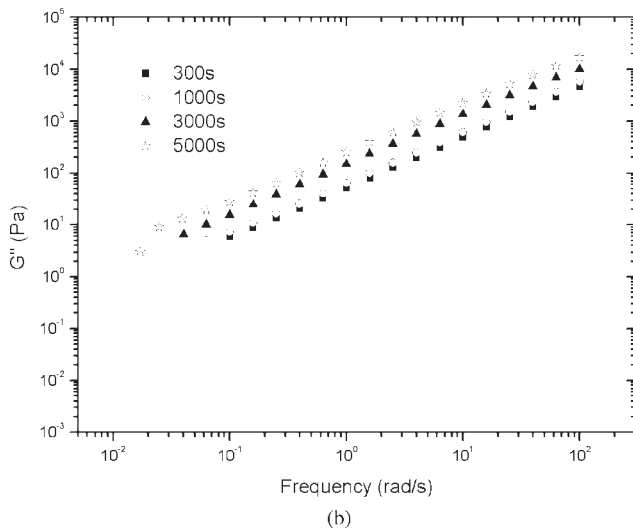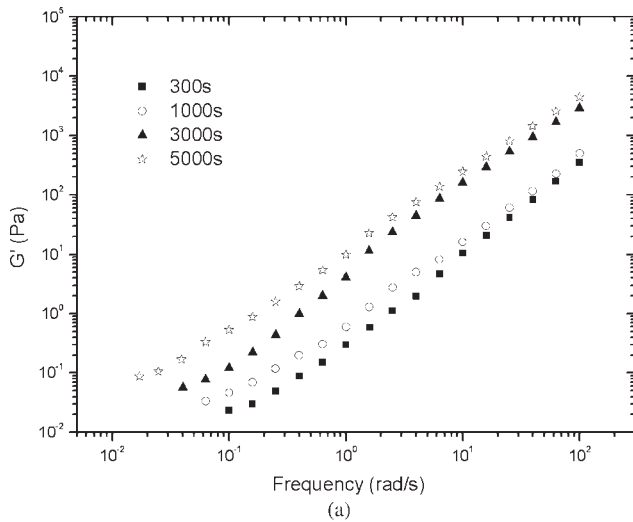
Figure 6 Storage moduli (a), loss moduli (b) as a function of frequency and Cole-Cole plot (c) for PET samples with 0.02 wt % water content, after different time delays before to rheological test ranging from 300 to 5000 s (temperature = 270°C).

Slopes of Storage Modulus G′(ω) curves and the Minimum Frequency Reached for PET Samples with Different Water Content (0.20, 0.12, and 0.02 wt %)

Water content (wt %)	0.02		0.12		0.20	
Delay time (s)	Slope of the curve G′(ω) x freq.	Minimum frequency reached (rad/s)	Slope of the curve G′(ω) x freq.	Minimum frequency reached (rad/s)	Slope of the curve G′(ω) x freq.	Minimum frequency reached (rad/s)
300	1.54	0.15	1.59	1.0	1.63	2.5
1000	1.46	0.10	1.57	0.25	1.53	0.4
3000	1.24	0.015	1.51	0.06	1.50	0.1
5000	1.08	0.01	1.24	0.04	1.33	0.1

bubbles within the sample affecting greatly the rheological measurements.

Figures 5(a,b) and 6(a,b) show the storage and loss moduli as a function of frequency for PET samples with 0.20 and 0.02 wt % of water content, respectively after different time delays before rheological test. No bubbles were observed within those samples. It can be seen that the storage G′(ω) and loss G″(ω) moduli of the sample with 0.20 wt % water content are lower than the one with 0.02 wt %. It can be also seen that for both water contents the storage modulus (G′(ω)) of PET increases with increasing time delay before experiment and that reliable data at low frequencies are only obtained for larger time delays and lower water content. The rheological experiments were carried out using the maximum strain value of the linear viscoelastic range indicating that this increase of storage modulus could not be attributed to phase angle problems.[23] Table III shows the slopes of storage modulus, G′(ω) curves (calculated taking into account frequency points from 300 to 0.6 rad/s) and the minimum frequency reached for PET samples with different water content (0.20, 0.12, and 0.02 wt %). It can be seen that for PET samples containing different water content, the slope of G′(ω) curve and the minimum frequency reached, decrease with increasing time delay before rheological test. The decrease of slope and, consequently, the displacement of the terminal zone to lower frequencies, could indicate that both the molar mass and the molar mass distri-

bution of the PET sample increase.[29] However, no gel point was observed for any of the samples as no cross over of (G′(ω)) and (G″(ω)) curves were observed in this work. Figures 5(c) and 6(c) show the Cole-Cole plot for samples with 0.20 and 0.02 wt % water content, respectively, after different time delays before rheological tests. It can be seen that for both water contents, the samples are more elastic as the time delay before experiment increases: at a constant value of loss modulus (G″(ω)), the storage modulus (G′(ω)) shifts to higher values with increasing time delay before experiment. This increase of elasticity is normally observed when the number of branches and the molar mass distribution increases, but does not seem to be affected by increase of molar mass.[2–4]

Differential scanning calorimetric analyses

DSC analyses were carried out on PET samples removed from the rheometer after 1000 and 5000 s during the time sweep tests conducted at 270°C, for the different water contents. Table IV shows the experimental results obtained during the nonisothermal runs. These tests were carried out at a cooling rate of 10°C/min. The samples were first heated up to 300°C at the rate of 10°C/min and kept for 3 min at this temperature, then cooled at the same rate (10°C/min). The glass temperature (T_g), the heating crystalline temperatures (T_{cc}), the melting temperature (T_m), and the enthalpy of melting (ΔH_m) were

TABLE IV
DSC Analyses of PET Samples

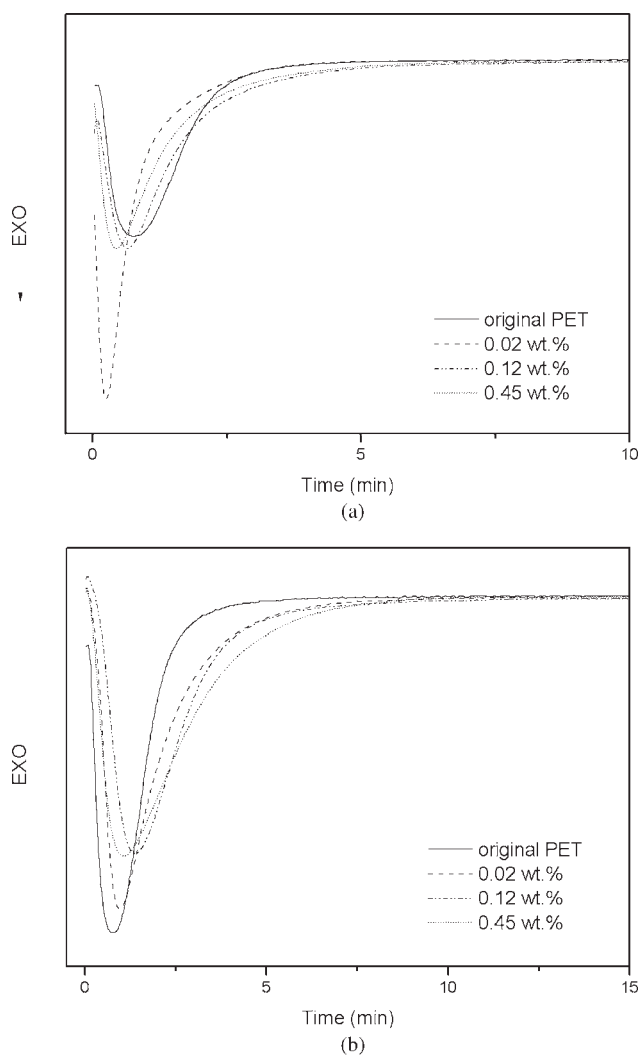| Water content (wt %)	Time delay (s)	T_g (°C)	T_{cc} (°C)	T_c (°C)	T_m (°C)	ΔH_m (J/g)
0.20	1000	70	130	219	260	47
	5000	72	142	207	259	46
0.12	1000	73	129	214	258	45
	5000	73	138	210	258	41
0.02	1000	70	128	215	263	41
	5000	72	137	211	259	42
Original PET		75	132	213	261	41

Figure 7 Experimental crystallization exothermic curves for PET samples removed from the rheometer after 1000 s (a) and 5000 s (b) (temperature = 220°C).

obtained from the first run (heating run) while the cooling crystalline temperatures (T_c) were obtained from the second run (cooling run). T_g was measured from the "center point" of the inflection points.

It can be seen that the glass temperature (T_g) of all samples removed from the rheometer present a slight decrease when compared to the one of the original PET sample. This decrease indicates that the motion of the chain segments of the samples got easier compared to initial one most likely due to an increase of molar mass distribution or occurrence of branching within the samples. The cooling crystalline temperatures (T_c) for PET samples removed from the rheometer after 1000 s (for all water contents) are larger than the one of the original PET sample while their heating crystalline temperatures (T_{cc}) are smaller. An opposite behavior was observed for PET samples removed from the rheometer after 5000 s (for all water contents): T_c decreased

while T_{cc} increased after thermal treatment. The melting enthalpy (ΔH_m) presents a slight increase for PET samples removed from the rheometer after 1000 s and almost no change for PET samples removed from the rheometer after 5000 s, except for the sample with 0.20 wt % water content. This behavior could indicate that PET samples removed from the rheometer after 1000 s crystallize in an easier fashion than the initial PET and that the crystallization of PET samples removed from the rheometer after 5000 s is more difficult.

Isothermal crystallization runs were carried out at 220°C. Figure 7(a,b) shows the experimental crystallization exothermic curves for PET samples removed from the rheometer after 1000 s and 5000 s, respectively. It can be seen that for the samples removed after 1000 s, the crystallization peak is sharper and that total crystallization finishes at smaller times. The same cannot be said for the samples removed after 5000 s: in that case, the crystallization peak is larger and the total crystallization finishes at larger times for the samples that underwent thermal treatment.

A review of the literature[24–26] indicates that both molar mass and amount of branching affect the crystallization behavior of PET. The studies indicate that a small amount of branches increases the crystallization temperature and the rate of crystallization of PET.[24,26] When the amount of branches increases, for a constant molar mass of PET, the presence of branching slows down the crystallization and results in a smaller crystallization temperature.[25] Also, the studies of the literature show that an increase of molar mass for a fixed number of branches has the same effect. The results presented in this work indicate that the samples that underwent thermal treatment suffered structural changes: change of molar mass (see viscosity average molar mass results) and occurrence of branches or increase of molar mass distribution (Cole-Cole plots). The DSC results shown in Figure 7(a,b) confirm these structural changes. For the samples that underwent 1000 s of thermal treatment, a sharper crystallization peak and faster crystallization was observed. This can be explained by the decrease of molar mass. However, as mentioned earlier, for those samples, the storage modulus was shown to be larger than the one of the original PET. This fact cannot be explained by the decrease of molar mass. Consequently, an increase of the molar mass distribution or branching occurred. It is unlikely, however, that a large amount of branches occurred in those samples as the crystallization peak was sharper and crystallization was faster. For the samples that underwent 5000 s of thermal treatment, the crystallization peak was broader and crystallization was slower due to the increase of molar

mass and probably due to an increase of molar mass distribution and presence of branching.

CONCLUSIONS

The results obtained in this work indicate that the rheological behavior of PET is complex, due to its particular molecular chain characteristics, being strongly dependent on water content, time delay before test, duration, and temperature of experiment. During the experiments, PET chains suffer structural changes, such as increase or decrease of molar mass, broadening of the molar mass distribution, and branching, even at low water content.

It was observed that for all water contents the storage modulus ($G'(\omega)$) of PET increases with increasing time delay before experiment. Nevertheless, reliable data at low frequencies can be obtained for larger time delays before experiments (about 5000 s) and low water content (around 0.02 wt %).

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