

Effects of hygrothermal aging on the molar mass and thermal properties of recycled poly(ethylene terephthalate) and its short glass fibre composites

Alessandro Pegoretti*, Amabile Penati

Department of Materials Engineering and Industrial Technologies, University of Trento, via Mesiano 77, 38050 Trento, Italy

Received 27 February 2004; received in revised form 16 April 2004; accepted 1 May 2004

Abstract

This paper reports on the effects of hygrothermal aging at 70 °C in water, and at 80% relative humidity, on the molar mass and thermal properties of recycled poly(ethylene terephthalate) and its short glass fibre composites.

During the initial period of exposure, water uptake increases linearly with the square root of time and apparent diffusivity decreases as fibre content increases and as relative humidity decreases. Samples exposed to 80% RH reach an equilibrium water content, while samples immersed in water do not. Composites absorb more water than expected on the basis of matrix sorption behaviour, thus suggesting that other mechanisms, like capillarity and/or transport by microcracks, are active.

The observed molar mass decrease has been successfully modelled as a pseudo first-order reaction whose rate constant depends on the humidity conditions.

Due to a chemocrystallization process the crystallinity of rPET and its composites increases during aging. The glass transition temperature, as measured on the second DSC scan, depends on the number-average molar mass reached during hygrothermal aging. © 2004 Elsevier Ltd. All rights reserved.

Keywords: PET; Hygrothermal aging; Molar mass; Thermal properties

1. Introduction

Poly(ethylene terephthalate) (PET) separation from municipal wastes represents one of the most successful examples of polymer recycling. In 2000, 187.4 ktons of PET were recycled in Europe, and most of them (70 ktons) in Italy [1]. In fact, as a result of the diversity of its applications in large volume products such as fibres, yarns, films, and bottles, the total consumption of PET is comparable to that of commodity polymers [2]. Due to the possible loss of properties induced by reprocessing [3–11], recycling is usually based on the reutilization of the recovered PET for production of articles having less demanding performance requirements than the original products (mostly fibres) [12–14].

On the other hand, the availability of large amounts of recycled poly(ethylene terephthalate) (rPET) is stimulating an in depth investigation of the properties of new products based on it. The most challenging opportunity is a possible usage of rPET for highly demanding applications, for which virgin reinforced PET is already used, like windshield wiper arms, brake systems, motor end frames, microswitches, coil formers, lamp sockets, oven handles, iron skirts, etc [15]. In most engineering applications a key point for a successful use of a polymeric material is the knowledge of how a given property changes with selected environmental variables. In the case of thermoplastic polyesters, such as poly(butylene terephthalate) (PBT) and PET (or rPET), an important feature is the stability of the material in the presence of water. Several studies have been published on the hygrothermal behaviour of PBT and its short glass fibre composites [16–22] and of virgin PET [23–31] but, to our knowledge, quite limited information is available on

* Corresponding author. Tel.: +39-0461-882452; fax: +39-0461-881977.

E-mail address: Alessandro.Pegoretti@ing.unitn.it (A. Pegoretti).

the hydrothermal stability of PET (or rPET) glass fibre composites under accelerated aging conditions [32,33]. On the other hand, a large amount of literature information is available on the hydrolytic degradation of PET (and rPET) during processing, i.e. in the molten state [3–11], or at the high temperature and pressure conditions adopted for chemical recycling by hydrolytic depolymerisation [34–40].

The aim of this paper is to report on the effects of hydrothermal aging at 70 °C in water or at 80% relative humidity on the molar mass and thermal properties of recycled poly(ethylene terephthalate) and its short glass fibre composites.

2. Experimental

2.1. Materials and processing

Recycled poly(ethylene terephthalate) (rPET) pellets (density ISO 1183(A): 1.328 g/cm³; MVR ISO 1133 = 115 ml/10 min; intrinsic viscosity ISO 1628-5 = 0.70 dl/g) were produced by Eco Selekt Europa Srl (Salorno-BZ, Italy) starting from beverage bottles recovered from municipal wastes and crushed into flakes. Tests of contaminants performed on rPET flakes in accordance with UNI 10667 standard, indicated the presence of about 40 ppm of PVC and less than 20 ppm of polyolefins, respectively. Chopped strand E-glass fibres type 952, produced by Saint Gobain–Vetrotex, were used as reinforcing agents in percentages of 15 and 30 by weight (samples rPET–15GF and rPET–30GF, respectively). All components, i.e., rPET, nucleating agent, and short glass fibres were mixed in a single screw extruder (model EEGT/35/L-D36/ESI) working at 160 rpm and at temperatures in the range 280–310 °C. The pellets produced were used for feeding a Sandretto injection moulding machine, model 310/95, (average barrel temperature range: 270–300 °C; injection pressure: 20 MPa; mould temperature: 130 °C) to obtain rectangular test bars (length: 127 mm; width: 12.7 mm; thickness: 3.3 mm). Before melt processing all components were carefully dried at temperatures in the range 100–130 °C for at least 4 h in order to reduce their hydrolytic degradation during processing.

2.2. Conditioning of specimens

After moulding, all samples were conditioned for three months under laboratory conditions (23 °C, 40% RH) until a constant weight was reached. The initial water content of samples reported in Table 1 was determined by evaluating their mass loss after drying at 120 °C under vacuum for 84 h. These annealing conditions have been proven to be suitable to completely remove the excess of water from a 3.2 mm thick plate [41].

Table 1

Water content of samples before hydrothermal aging treatments

Material	Water content (wt%)	Water content related to matrix weight fraction (wt%)
rPET	0.192 ± 0.004	0.192 ± 0.004
rPET–15GF	0.176 ± 0.004	0.207 ± 0.004
rPET–30GF	0.156 ± 0.001	0.223 ± 0.002

Specimens were then hydrothermally aged at 70 °C under two different conditions, i.e. (i) exposure to a humid environment (80% RH), and (ii) direct immersion in water (100% RH). The first condition was achieved by an ATS-FAAR mod. CU/220-35 humidostatic chamber set at 70 °C and 80% relative humidity. In the second condition, the specimens were totally immersed in a large surplus of distilled water (about 40 g of material per litre of water) at 70 °C in a Grant W38 thermostatic bath.

The aging was followed up to 24 weeks for condition (i) and 37 weeks for condition (ii). At each follow-up time, part of the samples were removed from the degradation medium, quickly wiped and weighed on a Mettler balance with an accuracy of 0.1 mg in order to assess their mass variation. The water content M_t at any time t was calculated as:

$$M_t(\%) = \frac{W_t - W_0}{W_0}$$

where W_0 and W_t denote specimen weights prior and after aging exposure, respectively.

After hydrothermal exposure, samples returned to their original weight when dried, thus showing no mass losses (dissolution or migration) during aging.

2.3. Sample characterization

Molar mass was determined by means of viscometric measurements performed at 25.0 °C in an Ubbelohde viscometer (type 1C) on diluted dichloroacetic acid/polymer solutions. All solutions were stirred for 45 min at 100 °C in order to obtain a complete dissolution of rPET specimens in the selected solvent. The relationship between intrinsic viscosity (IV in dl/g) and the number-average molar mass (M_n in g/mol) under this condition is given by the following Mark–Houwink equation [42]:

$$IV = 6.7 \times 10^{-3} M_n^{0.47} \quad (1)$$

Differential scanning calorimetry (DSC) measurements were conducted with a Mettler DSC 30 calorimeter. A first heating ramp from 0 °C up to 300 °C was followed by a cooling stage from 300 to 0 °C and by a second heating ramp up to 300 °C. Both heating and cooling rates were fixed at 10 °C/min and all tests were

conducted in nitrogen flushing at 150 ml/min. The crystallinity content was assessed by integrating the normalized area of the melting endothermic peak and ratioing the heat involved to the reference value of a 100% crystalline PET (140.2 J/g) [43]. All tests were conducted on humid specimens.

3. Results and discussion

3.1. Water uptake

As reported in Table 1, the initial equilibrium water content of samples before hygrothermal aging decreases as the fibre content increases, as expected. However, if these values are referred to the matrix content of samples (see Table 1), the water percentage is found to increase slightly with the fibre content, thus indicating that the presence of fibres influences the equilibrium water content under laboratory conditions. Jabarin and Logfren [23] reported equilibrium values for the water uptake of a thin (about 25 microns) amorphous PET film at 23 °C in the range 0.3–0.7%, depending on the relative humidity. The lower values obtained in this study can be explained by taking into account the fact that rPET sample has an initial crystallinity content of about 30% (see Section 3.3) and that water diffuses preferentially into the amorphous regions of the polymer [27–29]. Fig. 1 shows the moisture absorption for rPET and its composites at 70 °C, during exposure at 80% RH and 100% RH, as a function of the

square root of time. Each data point represents the average of three experimental results. First of all, it is worthwhile to note that while specimens exposed to a relative humidity of 80% reach their equilibrium water content, samples immersed in water do not. During the initial period of exposure, water uptake increases linearly with the square root of time: as expected, the apparent diffusivity decreases as fibre content increases and as relative humidity decreases. A diffusion coefficient, D , can be obtained by supposing a Fickian behaviour according to the following formula [44]:

$$M_t = M_\infty \left\{ 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp \left[- \left(\frac{D(2m+1)^2 \pi^2 t}{h^2} \right) \right] \right\} \quad (2)$$

where h is the thickness of the sample and M_∞ is the equilibrium sorption attained theoretically after infinite time.

At short times, and for $(Dt/h^2) > 0.05$, Eq. (2) reduces to [16]:

$$\frac{M_t}{M_\infty} = \frac{4}{\sqrt{\pi}} \sqrt{\frac{Dt}{h^2}} \quad (3)$$

Since samples immersed in water do not reach an equilibrium water content within the exposure period, values of D and M_∞ can be evaluated only for samples exposed to 80% RH (see Table 2). The value of

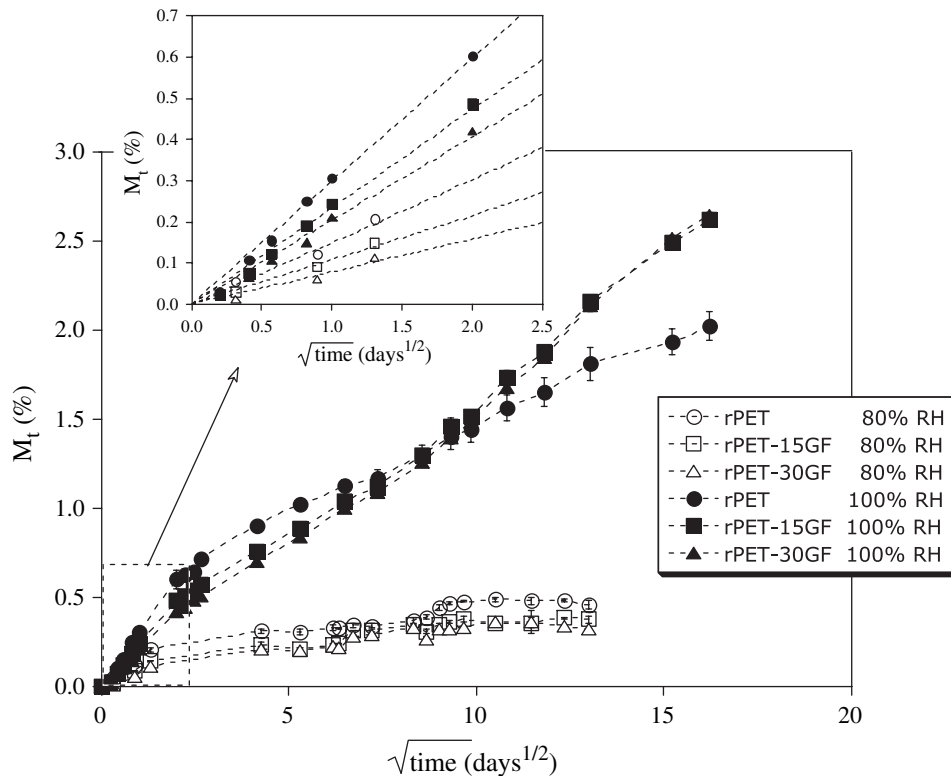


Fig. 1. Water uptake as a function of the square root of aging time for rPET and its composites.

Table 2
Diffusivity, D , and equilibrium moisture content, M_∞ , of rPET and its composites at 70 °C and 80% RH

Material	D ($\times 10^{-12}$ m ² /s)	M_∞ (wt%)
rPET	2.5	0.476
rPET–15GF	2.1	0.373
rPET–30GF	1.4	0.341

1.4×10^{-12} m²/s obtained for rPET–30GF is in good agreement with the value of 2.2×10^{-12} m²/s reported by Bastioli et al. [32] for long glass fibre reinforced virgin PET immersed in water at 67 °C. Moreover, the trend observed in this study for the effect of fibre content on the water sorption kinetics is consistent with the results reported by Ishak et al. [16,20,22], who investigated the behaviour of PBT and its short glass fibre composites. The water sorption curves reported in Fig. 1 for the samples immersed in water indicate that during initial exposure (up to 70 days) the absorbed water is lower as fibre content increases. From this period onwards an inversion of this trend can be observed with a higher absorption for composites with respect to rPET matrix. It is quite interesting to evaluate the amount of absorbed water normalized to the matrix content of the composites. In fact, by assuming that the glass fibres do not absorb moisture, and that diffusion in polymer matrix is the only mechanism of moisture penetration, sorption data of various samples should lie on the same curve for a given humidity condition. As reported in Fig. 2 this trend is reasonably well followed by the samples hydrothermally aged at 80% RH but not for the samples exposed to 100% RH. Consequently we may assume that other mechanisms, like capillarity and/or

transport in microcracks [16,20–22], are active when composites are immersed in water.

3.2. Molar mass

Number-average molar mass values as a function of time are reported in Fig. 3a for rPET hydrothermally aged at 70 °C and 80% or 100% RH. As expected, rPET shows a molar mass decrease during aging with a rate depending on the relative humidity conditions, in agreement with literature results obtained on amorphous PET [24,25]. In a steric exclusion chromatography study of the hydrolysis process of PET in boiling water, Launay et al. [29] concluded that the number-average molar mass tends towards an asymptotic value of about 2000 g/mol. The authors explained this result by considering the fact that water diffuses only in the amorphous regions and, consequently, the crystalline fraction is insensitive to hydrolysis. Therefore one expects that the residual polymer, after complete degradation of the amorphous phase, is composed of chains of length equal to the crystalline lamellae thickness [45]. In the present study M_n reached a minimum value of about 4200 g/mol and therefore we may assume that the hydrolysis does not reach its maximum possible conversion within the observed aging time. In Fig. 3b the molar mass is reported as a function of water uptake. It can be observed that the molar mass is not unequivocally related to the water content, since the same molar mass can be reached for different amounts of absorbed water. This suggests that the polymer chain degradation is related to both variables, i.e. the water content and the time of exposure. In fact, it

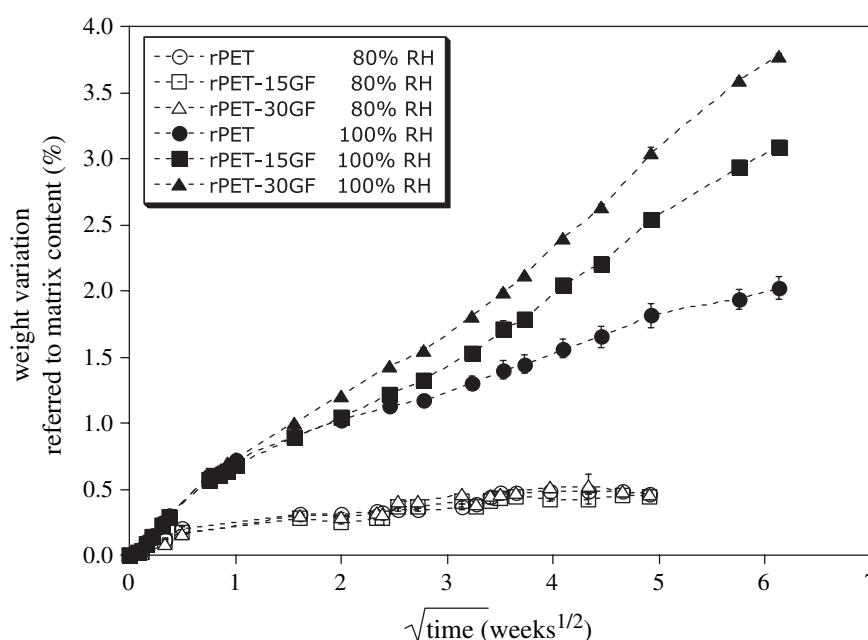


Fig. 2. Water uptake referred to matrix weight fraction as a function of the square root of aging time for rPET and its composites.

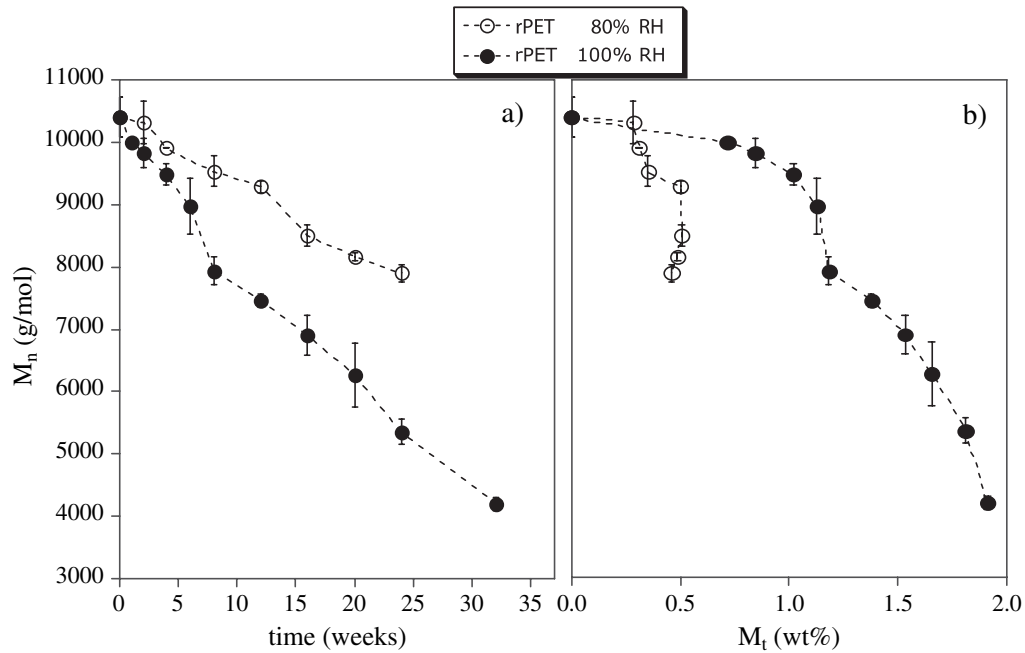


Fig. 3. Number-average molar mass as a function of (a) aging time, (b) water uptake.

is interesting to observe that the degradation curves overlap if plotted as a function of the product of exposure time and the corresponding water uptake (see Fig. 4).

The average number of random chain scissions per unit mass, n_t , is given by [27,28]:

$$n_t = \frac{1}{M_n} - \frac{1}{M_{n0}} \quad (4)$$

M_{n0} and M_n being the number-average molar masses of the polymer at zero and time t during degradation. As reported in Fig. 5, the number of chain scissions increases almost linearly in time for both humidity conditions up to 20 weeks of exposure, and then accelerates for sample immersed in water. This acceleration could be related to an increase of hydrophilicity or autocatalysis during the hydrolysis, as reported by other authors [24–28]. Ravens and Ward [46] suggested that the bulk hydrolytic chain scission of PET is autocatalysed by the

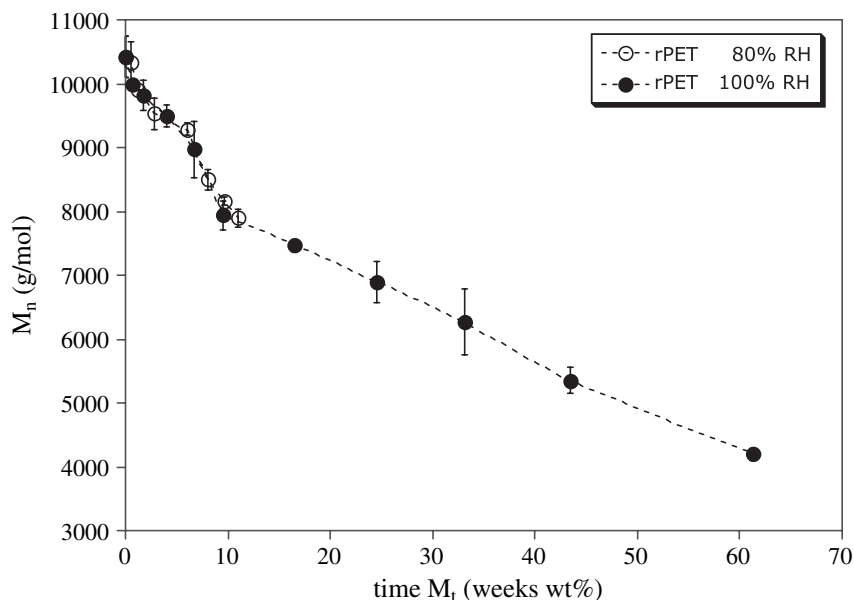


Fig. 4. Number-average molar mass as a function of the product of aging time and the water uptake.

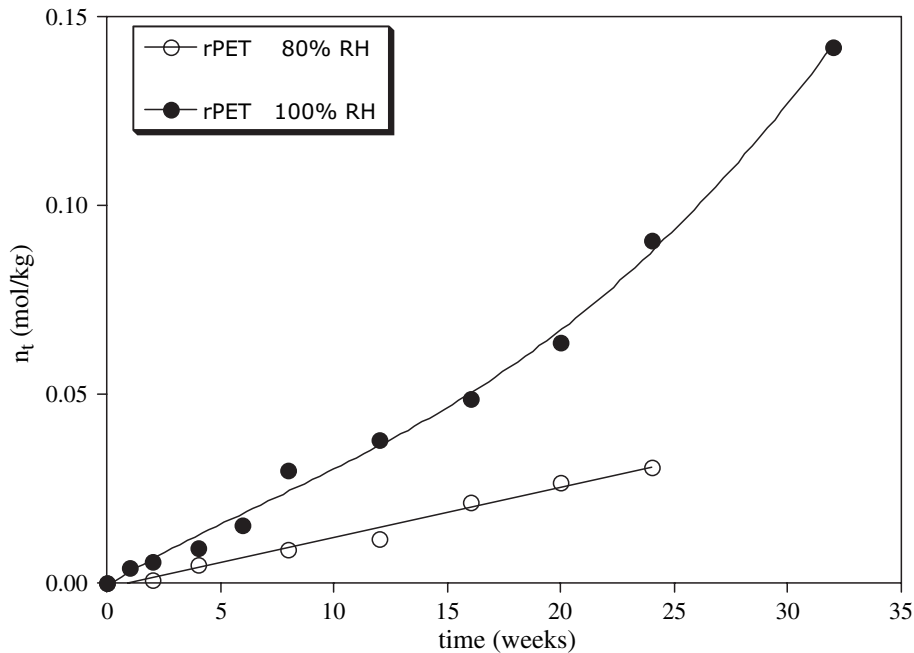


Fig. 5. Average number of random chain scissions per unit mass for rPET exposed to 80% or 100% relative humidity.

carboxylic acid end groups. The process of hydrolytic degradation of poly(lactic acid) (PLA) and related aliphatic polyesters have been successfully modelled by Pitt and co-workers [47,48] as an autocatalytic process, whose overall rate equation can be written as:

$$\frac{d[\text{COOH}]}{dt} = k[\text{COOH}][\text{H}_2\text{O}][\text{E}] \quad (5)$$

where $[\text{COOH}]$, $[\text{H}_2\text{O}]$ and $[\text{E}]$ are the concentrations in mol/kg of carboxylic end groups, water and ester groups in the polymer, respectively. As long as the extent of chain cleavage remains small, both $[\text{H}_2\text{O}]$ and $[\text{E}]$ can be assumed constants and Eq. (5) simplifies to the following pseudo first-order relationship:

$$\frac{d[\text{COOH}]}{dt} = k_{\text{H}}[\text{COOH}] \quad (6)$$

where $k_{\text{H}} = [\text{H}_2\text{O}][\text{E}]$. The integrated form then describes the change in the carboxylic end group concentration with time:

$$[\text{COOH}] = [\text{COOH}]_0 \exp(k_{\text{H}}t) \quad (7)$$

that can be also written as:

$$\ln \frac{[\text{COOH}]}{[\text{COOH}]_0} = k_{\text{H}}t \quad (8)$$

In the case of poly(ϵ -caprolactone) [47] and various poly-DL-lactic acid copolymers [48] the kinetic expression given by Eq. (8) was found to hold surprisingly well for an extended degradation period, during which M_n decreased to less than 10% of its initial value.

Considering that the average concentration, $[b]$, of the chain ends can be estimated as [27]:

$$[b] = \frac{2}{M_n} \quad (9)$$

and that the chain ends consist of the same amount of COOH and OH groups, we can estimate the carboxylic end groups concentration $[\text{COOH}]$ as:

$$[\text{COOH}] = \frac{1}{M_n} \quad (10)$$

Eq. (8) can be now rewritten in the following form:

$$\ln \frac{M_n}{M_{n0}} = -k_{\text{H}}t \quad (11)$$

As represented in Fig. 6, such a kinetic relationship appears to be followed reasonably well by rPET for both humidity conditions considered in the present study. It is quite interesting to observe that the slope k_{H} of the fitting lines increases as the aging humidity level increases, as expected from its dependence on the water concentration.

The presence of fibres does not change the degradation rate of the rPET matrix. In fact, as reported in Table 3, intrinsic viscosity (and, consequently, the number-average molar mass), measured on filtered solutions of samples hygrothermally aged in water for 20 weeks, is found to be practically independent of the fibre presence.

3.3. Thermal behaviour

Typical DSC thermograms representing first heating, cooling, and second heating of unaged rPET are

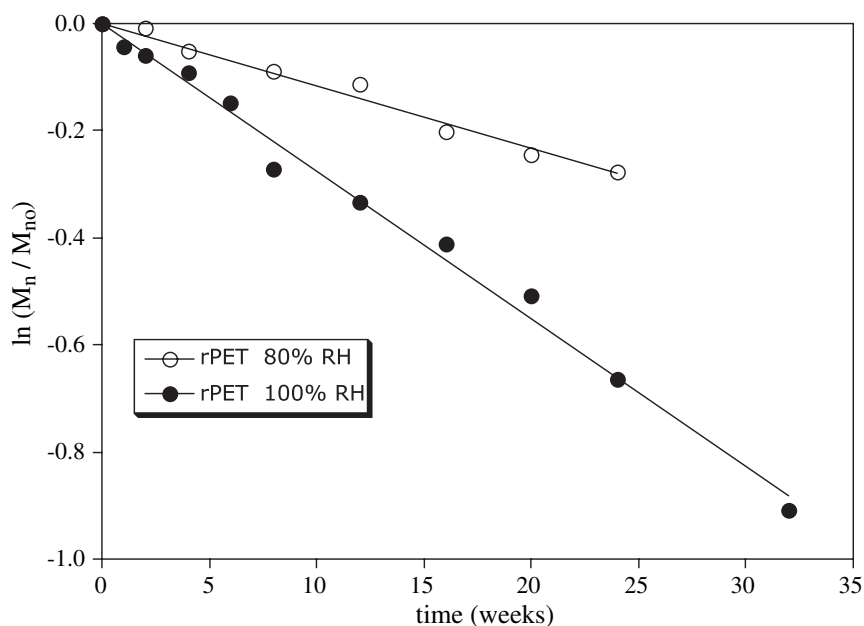


Fig. 6. Semi-logarithmic plot of the number-average molar mass for rPET as a function of time of exposure at 80% or 100% relative humidity.

reported in Fig. 7. Thermograms of the composites are quite similar and not reported. During the first heating, a glass transition (T_g) and two endothermic melting peaks are detectable. The first small endothermic peak is related to the presence of a commercial nucleating agent dispersed in polypropylene, while the second endothermic peak is associated with the melting of the crystalline phase of rPET. No exothermic crystallization peak is observed, thus confirming that the material is fully crystallized after moulding. As clearly shown in Fig. 8, the temperature of the melting peak of rPET and its composites is not affected by the investigated hygrothermal treatments. However, the area under the endothermic peak increases steadily during aging for all samples, thus indicating the presence of a crystallization process favoured by temperature, by the plasticising effect of water, and by the reduction of molar mass (see Fig. 9). Such a phenomenon, known as chemicrystallisation, has been previously reported on virgin PET [25,27,28] and widely observed even on biodegradable semicrystalline aliphatic polyesters [49–55]. This process can be explained by considering that chain scission in the amorphous phase may release previously entangled

chain segments that become sufficiently free to find a spatial rearrangement into the crystalline phase. It is worth noting that, when hygrothermal history is erased by first DSC scan and subsequent cooling at controlled rate, the crystallinity content increases on aged samples. This is evidenced by the cross symbols in Fig. 9 that refer to the crystallinity content as determined during the second DSC heating on rPET specimens hygrothermally aged in water. A possible explanation of this behaviour could be based on the consideration that a molar mass decrease generally favours the chain mobility and their possibility to arrange in an ordered habit (i.e. to crystallize).

Table 3
Effect of filtration on the intrinsic viscosity and number-average molecular weight for materials aged in water at 70 °C for 20 weeks

Material	IV (dl/g)	M_n (g/mol)
rPET	0.408	6270
Filtered rPET	0.406	6200
Filtered rPET–15GF	0.407	6230
Filtered rPET–30GF	0.409	6300

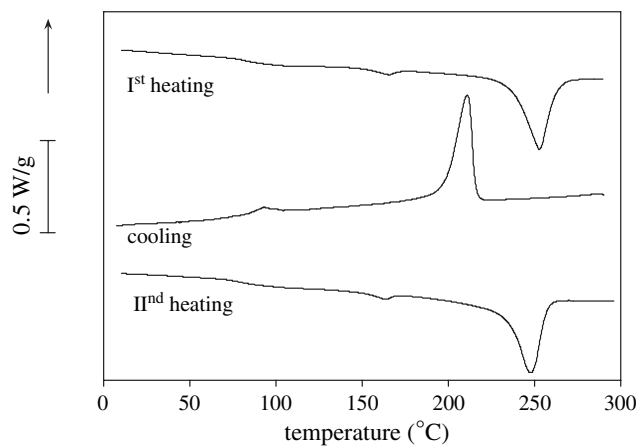


Fig. 7. DSC thermograms obtained during the first heating, cooling, and second heating of unaged rPET sample.

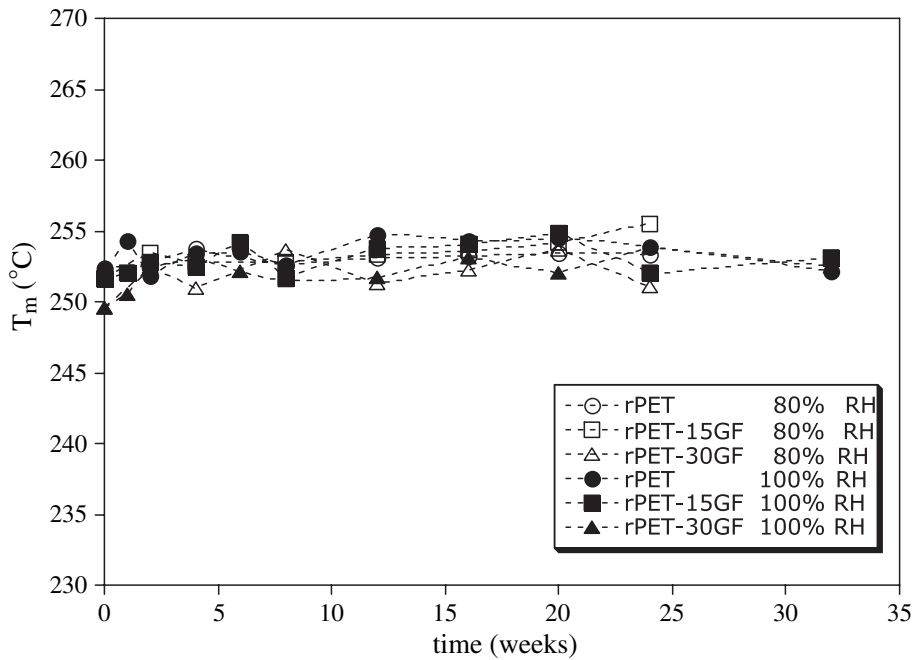


Fig. 8. Melting temperature of rPET and its composites during aging at 80% or 100% RH.

As the hygrothermal exposure proceeds, an endothermic peak related to the evaporation of the absorbed water, overlaps the glass transition signal, which is no longer detectable (see Fig. 10). On the other hand, glass transition is always detectable during the second heating run, since the material is completely dry during the first DSC scan. As shown in Fig. 11a, the glass transition

values detected during the second heating in the DSC chamber are clearly decreasing during the time of exposure at 80% or 100% RH. Since both thermal history and humidity content are erased during first DSC scans and subsequent cooling, the observed trend can be related to the molar mass dependence of T_g . The dependence of T_g on the number-average molar mass

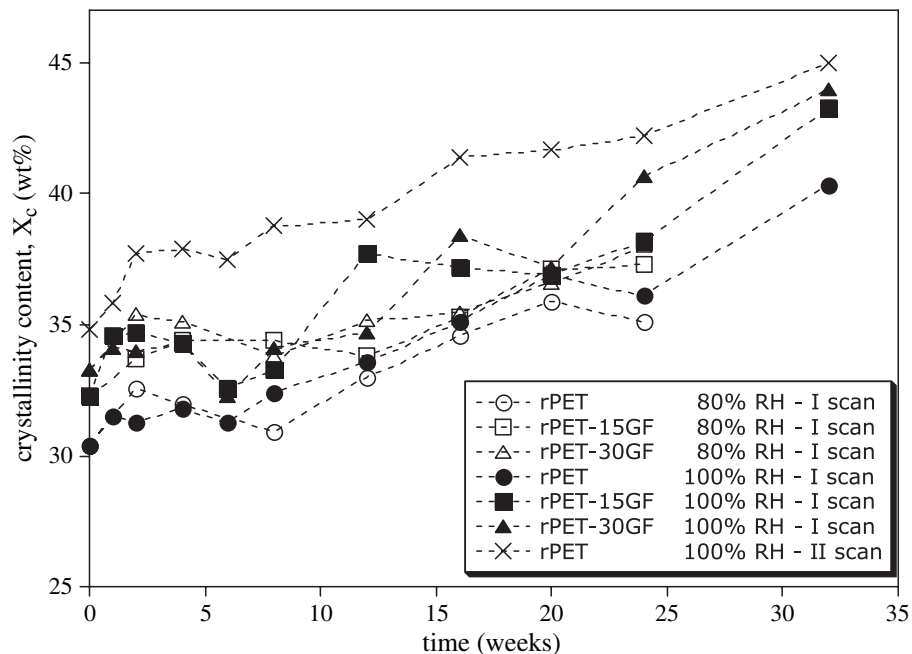


Fig. 9. Crystallinity content of rPET and its composites during aging at 80% or 100% RH.

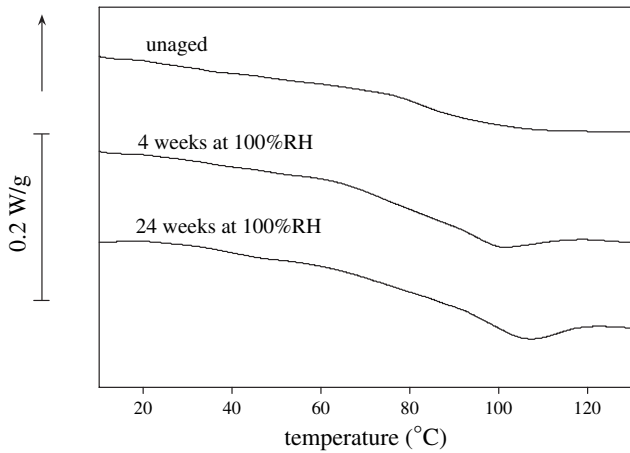


Fig. 10. Effect of water sorption during aging on the DSC thermograms in the glass transition region for rPET sample.

can be expressed according to the equation proposed by Fox and Flory [56]:

$$T_g = T_g^\infty - \frac{K}{M_n} \tag{12}$$

where K is a constant depending on the polymer and T_g^∞ is the limiting value of T_g at infinite molar mass. In practice this limit is usually reached for values of M_n of the order of 10^5 g/mol [57]. This equation can be deduced from the free volume theory, taking into account that terminal groups are associated with more free volume than the intermediate ones. The relationship between the T_g measured in the second DSC scan and the inverse of number-average molar mass for rPET and its composites is represented in Fig. 11b. Even if quite scattered, the data points agree reasonably well with the trend predicted by Eq. (12). In fact, data obtained under

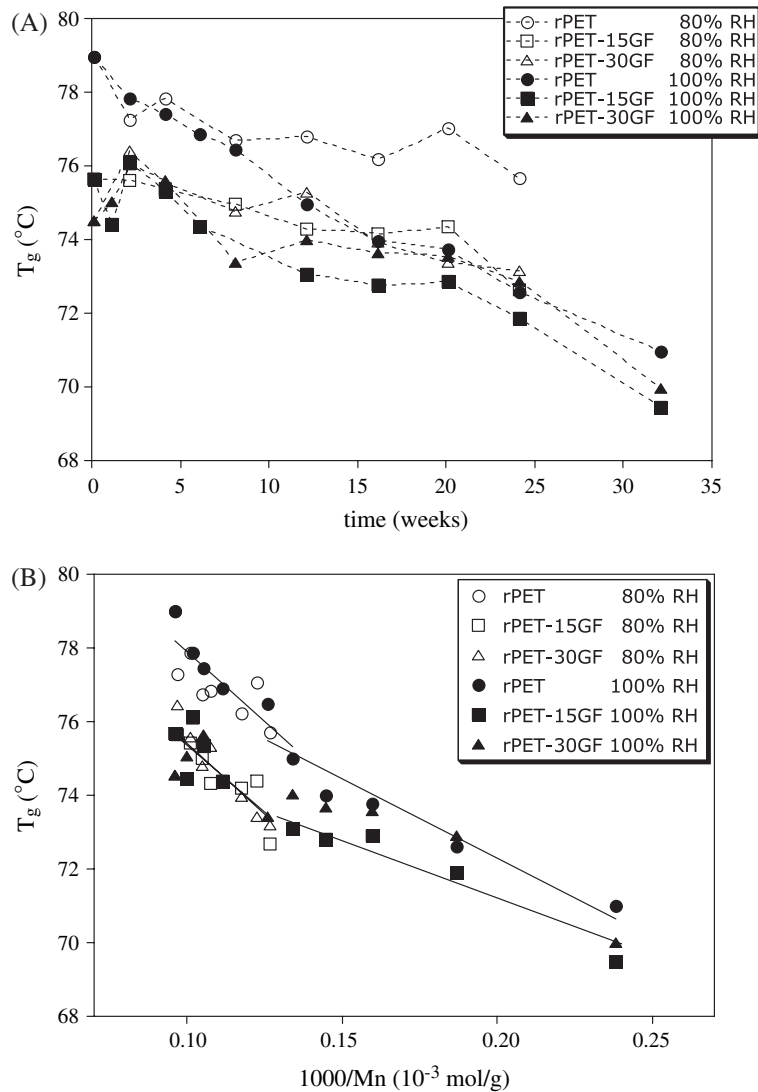


Fig. 11. (a) Glass transition temperature measured during second DSC scan of rPET and its composites during aging at 80% or 100% RH. (b) Glass transition temperature measured during second DSC scan as a function of the inverse of number-average molar mass for rPET and its composites.

different humidity conditions tend to follow a common line thus indicating that glass transition depends on the molar mass and not on the way this is reached. A slope change is evident for molar masses lower than about 7500 g/mol. This effect could be tentatively explained by considering that crystallinity increases during aging, thus influencing the glass transition temperature. In effect, it is well known that T_g is often increased in temperature by the molecular-motion restricting crystallites [58]. Therefore, molar mass decrease and crystallinity increase have two opposite effects on T_g that could account for the observed trend.

4. Conclusions

From this investigation on the hygrothermal aging of rPET and its short glass fibre composites at 70 °C, and 80% or 100% RH, the following conclusions can be drawn:

- (i) During the initial period of exposure water uptake increases linearly with the square root of time and apparent diffusivity decreases as fibre content increases and as relative humidity decreases. Samples exposed to 80% RH reach an equilibrium water content while samples immersed in water do not. Composites absorb more water than is expected by considering only diffusion into polymer matrix, thus suggesting that other mechanisms, like capillarity and/or transport by microcracks, are active.
- (ii) The observed molar mass decrease has been successfully modelled as a pseudo first-order reaction whose rate constant depends on the humidity conditions.
- (iii) The crystallinity content of rPET and its composites increases during aging due to chemocrystallisation. The glass transition temperature measured on the second DSC scan decreases during hygrothermal aging and is found to depend on the number-average molar mass.

Acknowledgements

This work was carried out with the financial support of the “Ministero dell’Istruzione dell’Università e della Ricerca” (MIUR—Italy), COFIN 2000 (Grant No. MM09012922_005). The authors sincerely wish to thank Mr. Stefano Bonafini for conducting most of the experimental work and Dr. Gianluca Gottardi of Eco Selekt Europa Srl (Salorno—Italy) for the help in materials preparation.

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