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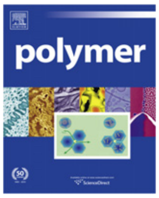

Free volume and crystallinity of poly(ethylene naphthalate) treated in pressurized carbon dioxide

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ABSTRACT

The free volume and crystallization behaviour of poly(ethylene naphthalate) (PEN) treated in pressurized carbon dioxide was studied, using Positron Annihilation Lifetime Spectroscopy (PALS) and Differential Scanning Calorimetry (DSC). PALS probes the values of free volume cavity sizes in materials, thus making it possible to investigate the effect of pressurized carbon dioxide treatment on free volume hole sizes in PEN. The crystallinity and melting behaviour of PEN was analyzed with temperature modulated DSC. We found that the carbon dioxide pressure during treatment of PEN was the prime parameter affecting the value of free volume after the treatment. The free volume sizes were observed to be insensitive to the other two parameters, temperature and time. Increasing the time of the treatment however, increased the crystallinity of PEN. Interestingly, this was not coupled to a decrease in ortho-Positronium intensity as was expected, indicating that positronium may form in the crystalline fraction of the polymer as well as in the amorphous fraction.

1. Introduction

Poly(ethylene naphthalate) PEN is a semi-crystalline engineering plastic with a range of properties that make it an attractive alternative to commonly used polymers. The enhanced physical properties such as tensile strength, barrier properties, heat stability, chemical and UV resistance of PEN compared to poly(ethylene terephthalate) PET, is largely attributed to the additional phenyl ring in the main chain (Fig. 1). The increased stiffness of the main chain, as compared to PET, is the feature behind such superior properties, which makes PEN a suitable polymer for certain film, packaging and fibre applications.

PEN which exhibits a glass transition temperature of around 120 °C and a melting temperature close to 270 °C, also shows very interesting melting behaviour which has resulted in several studies of its intricate thermal properties [1–5]. It is well documented that PEN can demonstrate two different triclinic crystal forms α and β [4]. The α-form dimensions are $a = 0.651$ nm, $b = 0.575$ nm, $c = 1.32$ nm and $\alpha = 81.33^\circ$, $\beta = 144^\circ$, $\gamma = 100^\circ$. The corresponding β-form values are $a = 0.926$ nm, $b = 1.559$ nm, $c = 1.273$ nm and $\alpha = 121.6^\circ$, $\beta = 95.57^\circ$, $\gamma = 122.52^\circ$. There is furthermore evidence of a third monoclinic γ-form found in single crystal PEN [6]. The α-form is generally obtained by isothermal crystallization at temperatures below 200 °C and the β-form is obtained by isothermal crystallization at temperatures above 240 °C [4]. While most of the literature on thermal investigation of PEN refers to the α-form crystal of the semi-crystalline polymer, a few also take up the β-form.

Several groups report of a multiple melting behaviour of PEN when analyzed with Differential Scanning Calorimetry, DSC. The multiple melting behaviour as evidenced by two or three endothermic peaks in the DSC curve, has been explained by melting of secondary crystals, melting of primary crystals and melting and reorganization of crystals [1–3]. The lowest temperature endotherm which appears approximately 10 °C above the annealing or treatment temperature has alternatively been explained by the fusion of small and/or disordered crystallites [7]. The difficulties of accounting for the processes involved in a DSC measurement are further complicated by the parallel melting and recrystallization taking place during the measurement.

Modulated Differential Scanning Calorimetry MDSC, has also been utilized for further elucidating the thermal properties of PEN [3,8]. Kampert et al. demonstrate in their MDSC study that parallel melting and recrystallization occur in the temperature range between the low temperature endotherm and the main melting

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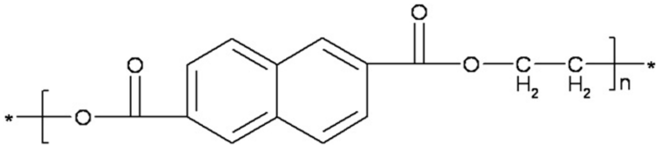

Fig. 1. Chemical structure of poly(ethylene naphthalate).

point of PEN [3]. There are still some unanswered questions regarding the thermal behaviour of PEN despite detailed DSC studies. The existence of an endothermic melting peak in the non-reversing curve of the MDSC study performed by Kampert et al. is still not satisfactorily accounted for. Furthermore it has not been explained why the low temperature endotherm, which has been attributed to melting of secondary crystals, appears in the non-reversing curve of MDSC measurements [3].

Free volume size of polymers is an important parameter influencing behaviour such as mobility, barrier properties and mechanical properties. Positron Annihilation Lifetime Spectroscopy (PALS) is a unique measurement technique in which an absolute value of the free volume hole sizes of polymers can be determined. Few free volume size data measured by PALS are available for poly(ethylene naphthalate). Two groups have studied the free volume by PALS of PEN in relation to gas transport and permeability [9–11]. McGonigle et al. studied the free volume hole sizes in biaxially oriented polyester films [9] and Liu et al. measured the free volume in cold-drawn polyesters [10]. There is, to our knowledge, no positron data on PEN treated in pressurized carbon dioxide.

Pressurized CO_2 treatment of polymers is known to alter the sizes of the free volume sites [13] and supercritical carbon dioxide $scCO_2$, has been utilized extensively for inducing crystallization in several semi-crystalline polymers such as syndiotactic polystyrene [12,13], poly(ether etherketone) [14] and poly(ethylene terephthalete) [15]. It easily swells and plasticizes polymers due to its liquid-like densities and gas-like viscosities above the critical point ($T_c = 31$ °C, $P_c = 7.4$ MPa). The solubility parameter δ reveals the compatibility of a solvent with a polymer. This parameter can be varied widely for $scCO_2$ by slightly tuning the parameters temperature and pressure in the $scCO_2$ treatment [16]. Asai et al. performed a detailed study of PEN treated in supercritical carbon dioxide [7]. They showed that the crystallization temperature can be significantly lowered by using $scCO_2$ as a crystallization aid. This was explained by the increased mobility of PEN in the $scCO_2$ as a consequence of the plasticization. They revealed that the glass transition temperature of PEN can be reduced as much as 60 °C during the $scCO_2$ treatment. Asai et al. hypothesize that the CO_2 molecules absorbed in the polymer during treatment increase the free volume of the polymer, which would be the explanation for the drop in T_g. In the present study, we aim to elaborate on some of the unanswered questions regarding the thermal properties of PEN and investigate the influence of pressurized CO_2 treatment on the free volume characteristics of PEN.

2. Experimental

2.1. Materials

Poly(ethylene 2,6-naphthalate) was obtained as a commercial material from ICI Americas Inc., with an intrinsic viscosity of 0.65 dl/g and a melting point of 265 °C. Amorphous films of 300 μm thickness were obtained by compression moulding at 290 °C and subsequent quenching in ice water. Carbon dioxide with a purity of 99.95% was supplied by the Beijing Analytical Gas Factory, China.

2.2. Treatment in pressurized CO_2

The treatment in pressurized CO_2 took place in a 25 ml high pressure vessel connected to a high pressure pump. The vessel was flushed with low-pressure CO_2 for 2 min before the desired temperature and pressure were set. The temperature was controlled with an oil bath, alternatively a water bath and the pressure, by a gauge mounted on the vessel. After the treatment the temperature was reduced to room temperature and the pressure was released to atmospheric pressure at a rate below 2 MPa/min. Tables 1 and 2 show the different treatment conditions used and which conditions resulted in amorphous samples and which ones resulted in semi-crystalline samples. All semi-crystalline samples have been identified as including the α-form crystal, under these conditions [16].

12.3. Temperature modulated differential scanning calorimetry – MDSC

MDSC was utilized because of its ability to separate the reversible thermal processes from the non-reversible in a DSC scan. The glass transition temperature can for example be clearly separated from a parallel enthalpy relaxation taking place. MDSC was performed on a TA Instrument Q1000 apparatus on samples of 5 mg. The modulation procedure was chosen so that a heating only method was obtained. The heating rate was 2 °C/min, the modulation amplitude 0.32 °C and the modulation period 60 s, if nothing else is indicated. For selected samples a standard DSC procedure with a heating rate of 10 °C/min from 40 °C to 300 °C was used.

2.4. Positron annihilation lifetime spectroscopy – PALS

PALS, has been shown to be a powerful technique to measure the free volume hole sizes in polymeric materials. Positrons are emitted from Na-22 and transferred into the polymer sample. One of the processes taking place is the formation of ortho-positronium o-Ps in the polymer. The o-Ps will undergo what is known as pick-off annihilation with an electron which coincides with two gamma-rays being emitted. The time between the emitting of the positron from Na-22 and the annihilation of the o-Ps is measured and related to the size of the free volume hole at which the o-Ps was trapped. The relation is generally described by the Tao-Eldrup equation [17,18]:

$$\tau_{\text{o-Ps}} = 0.5 \cdot \left(1 - \frac{R}{R_0} + \frac{1}{2\pi} \cdot \sin\left(\frac{2\pi \cdot R}{R_0}\right)\right)^{-1} \tag{1}$$

where R is the free volume hole size radius, $R_0 = R + \Delta R$ and ΔR is a fitted parameter with a value of 1.66 Å.

The PALS measurements were all performed 3–4 weeks after the treatment in pressurized CO_2. The apparatus used was a fast–fast coincidence system using detectors built-up with CsF crystals mounted on Hamamatsu photomultipliers. The source was a salt of Na-22 which gave an approximate count rate of 300 counts per second. A sandwich configuration was used for the sample set-up

Table 1
Treatment conditions for the time series samples. The result of the treatment, whether it remained amorphous or crystallized, is indicated.

Treatment temperature/ pressure	0.5 h	1 h	2 h	3 h	4 h	5 h	6 h	8 h	12 h
180 °C/Ambient air	Am.	Cryst.	Cryst.	Cryst.	Cryst.	Cryst.	Cryst.	Cryst.	Cryst.
160 °C/6 MPa CO_2	Am.	Am.	Cryst.	Cryst.	Cryst.	Cryst.	Cryst.	Cryst.	Cryst.

Table 2
Treatment conditions for the temperature series samples. The treatment time was 6 h for all samples. The result of the treatment, whether it remained amorphous or crystallized, is indicated.

Treatment time/pressure	60 °C	80 °C	100 °C	120 °C	140 °C	160 °C	180 °C	200 °C	220 °C
Ambient air	Am.	Am.	Am.	Am.	Am.	Am.	Cryst.	Cryst.	Cryst.
6 MPa CO_2	Am.	Am.	Am.	Am.	Am.	Cryst.	Cryst.	Cryst.	Cryst.
8 MPa CO_2			Am.						
12 MPa CO_2	Am.	Am.	Am.	Am.	Cryst.	Cryst.	Cryst.	Cryst.	Cryst.
20 MPa CO_2	Am.		Am.	Am.			Cryst.		

with stacked samples of a total thickness of 1 mm on either side of the source. The spectra, each containing 2.5×10^6 counts were collected in the MAESTRO software and subsequently analyzed with the PATfit program [19]. A resolution function containing two gaussians of 0.34 and 0.35 ns respectively was used in the analysis. All spectra were analyzed using three guessed lifetime components. A four-component analysis was performed as well, however it resulted in a split of the second lifetime to a third and a second lifetime. No longer lifetime than the ordinary third was obtained in any of the analyses.

PALS measurements at different temperatures were also performed for selected samples in a range between 30 °C and 140 °C. Three spectra, each containing 1 million counts, were collected at each temperature. The samples were thus held isothermally for 120 min at each temperature with increments of 20 °C from 30 °C to 110 °C and then with increments of 10 °C up to 140 °C. Spectra were collected similarly during cooling, i.e. the samples were held isothermally at the same temperatures during cooling.

3. Result and discussion

The effect of annealing temperature in pressurized CO_2 of 12 MPa on the thermal properties of PEN is shown in Fig. 2. The curves reflect the total heat flow of MDSC, corresponding to a standard DSC curve. Due to the semi-crystalline nature of the samples, the glass transition temperature is displayed as a weak step at around 121 °C. There is a clear melting at around 266 °C in all curves, which corresponds to the melting of primary α-crystals. The position of this peak does not appear to be affected by either the annealing temperature or the presence of pressurized CO_2 during the annealing procedure. The position of the low temperature endotherm on the other hand is clearly affected by the annealing temperature with a strong direct relation between annealing temperature and the position of the peak as demonstrated in Fig. 3. In this Figure, results are included for comparison from several different studies of the effect of annealing temperature on the position of the low endothermic peak of PEN. All studies show a linear correlation between annealing temperature and the position of the peak with a slope close to one. The exact position of the data points are somewhat affected by the heating rate of the DSC scan.

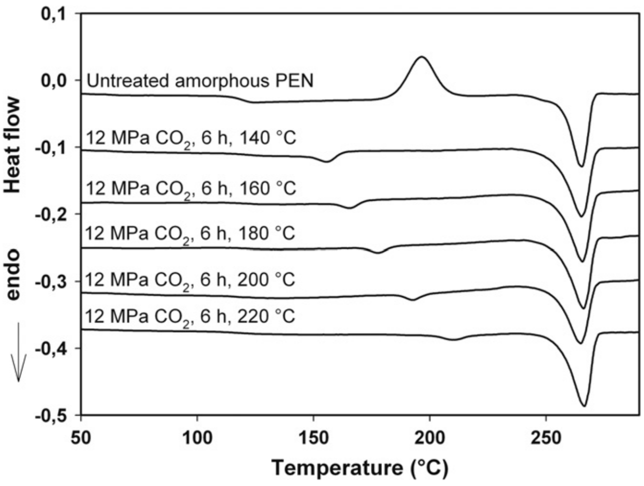

Fig. 2. Total heat flow curves from MDSC of PEN treated at the conditions indicated. The curves have been shifted vertically for clarity.

The surprisingly high level of the heat flow signal between the two endothermic peaks in each curve of Fig. 2 indicates that the signal originates from different thermal processes rather than being the level of the base-line. The separation of the curves into reversible and non-reversible signals (Fig. 4) reveals that parallel melting and recrystallization occurs, as described in literature [3]. It is interesting to note that the crystallization starts only above the low temperature endothermic peak, independently of its position. This indicates that restricted mobility of the polymeric chains is present prior to the crystallization, which points towards the low temperature endotherm being caused by either melting or enthalpy relaxation.

Although subject of some discussions in literature [2,3,5,20], several groups have concluded the low temperature endotherm to be an effect of melting of secondary crystals during the DSC scan. In the present study, the low temperature endothermic peak is clearly only displayed in the non-reversible signal of the MDSC curves, Fig. 4. However, melting is generally a reversible process and we would expect the peak to be separated into the reversible signal. If, however, the low temperature endotherm is a consequence of melting of secondary crystals, smaller in size and slower in their

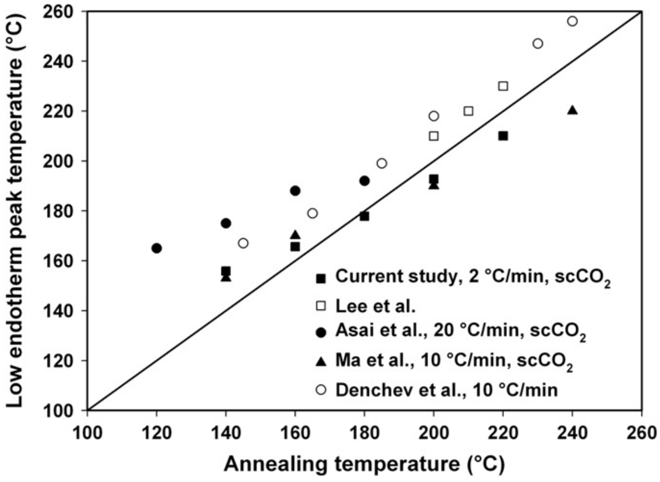

Fig. 3. The position of the low temperature endothermic peak as a function of annealing temperature for the PEN samples of the current study and PEN samples from literature where open symbols represent PEN treated at ambient conditions and filled symbols represent samples treated in pressurized CO_2. The heating rates of the DSC scans are indicated.

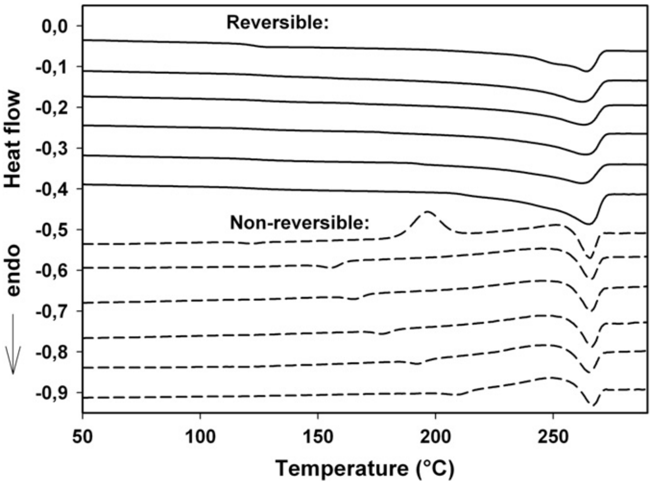

Fig. 4. Reversible and non-reversible heat flow curves from MDSC of PEN treated at 12 MPa, 6 h and 140, 160, 180, 200 and 220 °C. Increasing temperatures from the top and down. The curves have been shifted vertically for clarity.

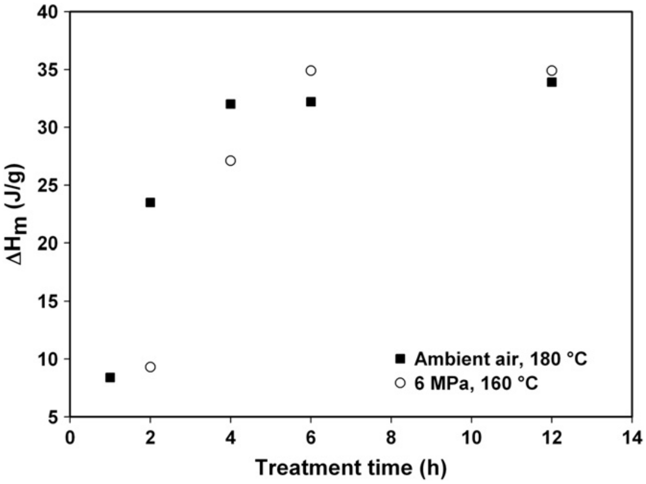

Fig. 5. The melting enthalpy ΔH_m for PEN samples treated at the conditions indicated.

crystallization kinetics, there might be arguments for the peak appearing in the non-reversible signal. If the crystallization rate is not sufficiently fast to allow crystallization in the short time available during the modulation period, the melting may appear as a non-reversible process. The endothermic melting peak at ~266 °C in the non-reversible curves is difficult to interpret as it is expected to appear fully in the reversible curve. We will come back to this subject in the further discussions.

None of the curves show any traces of a third endotherm, which has been reported previously, despite the fact that for several samples, the heating rate was varied between 2, 5, 10 and 40 °C/minute. None of the heating rates resulted in three endotherms. Since the multiple endotherms have been coupled to different sizes of crystals, a conclusion might be drawn that the crystal sizes are more uniform after treatment in pressurized CO_2, so that the main melting endotherm and the low temperature endotherm are the only two peaks present. This corresponds well to the results concluded by Asai et al. [7] of a higher order structure of semi-crystalline PEN samples treated in supercritical CO_2 compared to cold-crystallized PEN.

To investigate the influence of the CO_2 treatment on crystallinity of the PEN samples, the melt enthalpy ΔH_m was extracted from the total heat flow of the MDSC curves and plotted against treatment time, Fig. 5. The ΔH_m was calculated as the value of the main melting endotherm minus possible exothermic peaks. There is a clear trend of increasing crystallinity with treatment time. Although the absolute values of crystallinity were not used due to the difficulties in obtaining a consistent value of heat of fusion for 100% crystalline PEN, ΔH_f, by plotting ΔC_p against ΔH_m for the two time series of PEN, we were able to obtain a ΔH_f value for a two-phase model which could be used for approximate values of crystallinity. The results are shown in Fig. 6 together with values obtained by Schoukens et al. [8] in a previous study. All data points show a clear linear correlation between ΔH_m and ΔC_p and extrapolation of the fitted line crosses the x-axis at a value of slightly above 100 J/g. This value corresponds well to one of the ΔH_f literature values of 103 J/g by Cheng and Wunderlich [21]. Other values obtained in literature are 190 J/g [4] and 170 J/g [22]. Using our value of 100 J/g for ΔH_f the crystallinities fall in a range of 25%–35% for PEN samples treated at times of 4 h and longer. This corresponds well to the crystallinity values obtained by Asai et al. [7] from their WAXD measurement. It should be noted that the value of ΔC_p only accounts for the fraction of polymer available to take part in the glass transition relaxation; the rigid amorphous fraction can therefore not be extracted from such a plot (Fig. 6). If a substantial amount of material makes up the rigid amorphous fraction, the ΔH_f may differ from our estimates.

Because of the difficulties in satisfactorily explaining the endothermic melting peak in our non-reversible signals, we undertook a small study of the influence of modulation procedure (Table 3) on the obtained curves. The degree of separation of the signals into reversing and non-reversing could be controlled by tuning the modulation parameters amplitude, period and heating rate. Modulation period had the largest effect; with an increasing period the endothermic peak was diminished. It is interesting to note that none of the elaborated modulation procedures caused the low temperature endotherm to disappear from the non-reversible signal. Thus, certain peaks or processes seem to be sensitive to the modulation procedure whereas others remain unaffected.

To investigate the influence of pressurized CO_2 on the free volume size of semi-crystalline and amorphous PEN, PALS measurements were performed on samples which had been subjected to different times, temperatures and pressures during CO_2 treatment. Two important quantities are obtained from these measurements, τ_3, which is the mean o-Ps lifetime related to the free volume hole size and I_3, which is the probability of o-Ps formation. It is important to stress that all PALS measurements

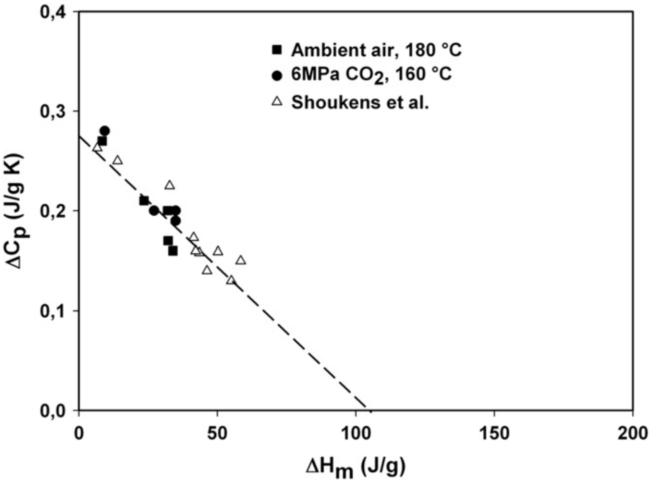

Fig. 6. ΔC_p versus ΔH_m for PEN samples treated at the conditions indicated and during different times.

Table 3
Modulation parameters for the temperature modulated DSC measurements.

	Mod 1	Mod 2	Mod 3	Mod 4	Mod 5	Mod 6	Mod 7
Amplitude (°C)	±0.16	±0.26	±0.16	±0.32	±0.32	±0.32	±0.32
Period (s)	30	40	60	60	65	80	90
Heating rate (°C/min)	2	2.5	2	2	2	2	2

were performed 3–4 weeks after the CO_2 treatment. Thus the samples were assumed to be completely free of CO_2, following the desorption study performed by Asai et al. [7], in which CO_2 was completely desorbed 36 h after treatment of PEN in supercritical CO_2 of 60 °C and 20 MPa. Considering the thickness of our samples were approximately 3 times that of the samples of Asai et al., 3 weeks was regarded as enough time for desorption.

Fig. 7 provides an overview of the influence of treatment parameters on the free volume hole sizes of PEN. In Fig. 7a the time has been varied and in Fig. 7b the pressure has been varied. There is a slight variation of τ_3 as function of time with a small trend of increased free volume size with treatment time for one of the time series. However the trend is weak compared to the clear trend seen with τ_3 as a function of pressure. With an increased treatment pressure τ_3 increases significantly. The τ_3 value for untreated PEN (pointed out in Fig. 7b) is 1.62 ns which correspond well to data obtained by McGonigle et al. [9]. The increase of τ_3 seems to follow a linear trend up to higher pressures then levelling off slightly. One should note that there is no remarkable step or other transition taking place when the treatment pressure is increased to the level of supercritical conditions. No such effect was seen in any of the MDSC curves either. The treatment pressure is observed to have an equal effect on free volume and thermal properties whether it is below or above the supercritical point. The effect of annealing temperature on free volume size is not significant, with no visible trend in any of the series.

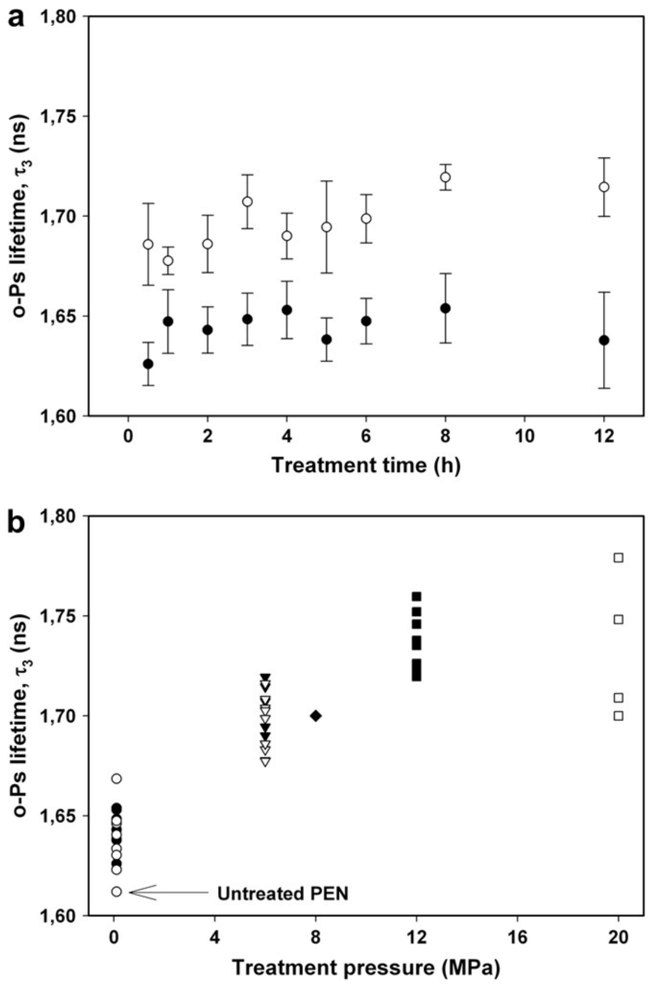

Fig. 7. (a): o-Ps lifetime as function of treatment time for PEN samples treated in ambient air, 180 °C (●) and 6 MPa, 160 °C (○) CO_2. (b): o-Ps lifetime as function of treatment pressure for PEN samples treated in ambient air, different temperatures (○) ambient air, different times (●), 6 MPa CO_2, different temperatures (▽), 6 MPa, different times (▼), 8 MPa, 100 °C (◆), 12 MPa, different temperatures (■) and 20 MPa, different temperatures (□).

Out of the three parameters investigated, treatment pressure was found to have the greatest effect on the free volume hole size, indicating that the amount of CO_2 in the sample during treatment has a direct effect on free volume of the sample. Interestingly the free volume size of PEN samples treated in pressurized CO_2 remained at a high level even though the CO_2 had desorbed completely and 3–4 weeks had past since the treatment. This indicates a long-time effect of expanded free volume in PEN treated in pressurized CO_2. However the free volume sizes are expected to relax slowly towards equilibrium during longer times, as has been observed for syndiotactic polystyrene [13]. An additional interesting point is that the treatment pressure is the parameter almost solely responsible for the free volume size expansion even though temperature showed to be the responsible parameter governing crystal dimensions, as described by Asai et al. [7].

The expanded free volume brought about by the treatment of PEN in pressurized CO_2 is present at least several weeks after the treatment. In order to investigate how a thermal treatment above the glass transition temperature (122 °C) would influence this expanded free volume and the crystallization behaviour, PALS measurement were conducted on three samples after their treatment in pressurized CO_2. The measurements were performed while thermally annealing at a number of temperatures in an interval between 30 °C and 170 °C both during heating and during cooling. The expanded free volume was observed to relax when the polymer was brought above its glass transition temperature. This is seen in Fig. 8, where the free volume size of amorphous untreated PEN (Fig. 8a) is identical during the heating sequence and the cooling sequence. For the PEN samples treated in 8 and 20 MPa CO_2 respectively (Fig. 8b and c) the initial higher level of free volume relaxes with increasing temperature towards the glass transition due to increased segmental mobility and the level of the free volume after cooling reaches the same low value as for untreated amorphous PEN.

Despite the fact that the CO_2 treatment of the samples showed in Fig. 8 (8 and 20 MPa CO_2, 100 °C, 6 h) did not bring about any crystallization in itself, the samples treated in pressurized CO_2 did crystallize during the subsequent PALS measurement which involved an extensive thermal procedure. The untreated PEN remained amorphous throughout the thermal procedure. This can be concluded by analyzing the DSC curves of the samples run before and after the PALS measurement, see Fig. 9. The only sample showing any cold crystallization during the DSC run after the PALS measurement is the untreated PEN. At the same time all post-PALS DSC spectra exhibited similar melt enthalpy values, indicating that the CO_2 treated samples had a significant degree of crystallization. The three samples thus exhibited different crystallization behaviour during thermal annealing despite having the same glass transition temperature after the CO_2 treatment (see Fig. 9). Also notable in Fig. 9 is the shift in the position of the cold crystallization peak for the DSC curves run before the PALS measurement. The position of the peak is clearly shifted to lower temperatures with increasing pressure. This supports the hypothesis of increased

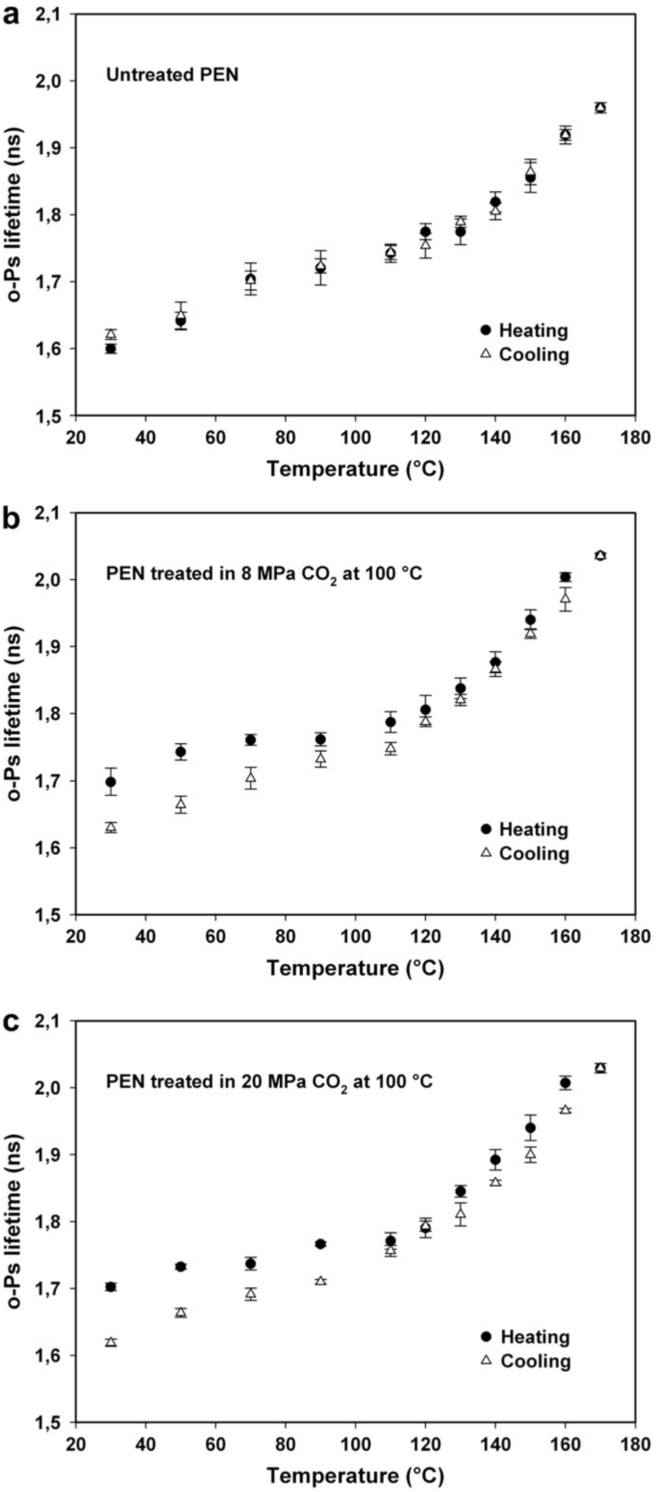

Fig. 8. (a): o-Ps lifetime measured as a function of temperature during a heating sequence and a cooling sequence of untreated amorphous PEN. (b): o-Ps lifetime measured as a function of temperature during a heating sequence and a cooling sequence of PEN previously treated in 8 MPa CO_2 at 100 °C for 6 h (c): o-Ps lifetime measured as a function of temperature during a heating sequence and a cooling sequence of PEN previously treated in 20 MPa CO_2 at 100 °C for 6 h.

mobility of PEN treated in pressurized CO_2 even several weeks after the actual treatment.

The o-Ps lifetime τ_3 is known to be directly related to the size of the cavity in which the o-Ps atom annihilates. The o-Ps formation and annihilation probability, represented by the relative intensity I_3, is however a more complex quantity which is strongly governed by radiation chemistry processes evolving during thermalisation of the high energetic positrons in the polymeric material [23–26]. Generally o-Ps is believed to form in the amorphous regions of polymers; therefore an increase in crystallinity, which reduces the amorphous fraction, is expected to reduce the o-Ps intensity. Similarly, addition of inorganic fillers also reduces the o-Ps intensity. We expect to observe a clear decreasing trend of I_3 plotted against ΔH_m, however the I_3 remained at a constant level independent of crystallinity in the two time series, see Fig. 10. A possible explanation for the constant level of I_3 is the small difference in density between the amorphous and the crystalline phases of PEN. The amorphous density of PEN is 1.33 g/cm^3 while the α-form crystalline phase has a density of 1.41 g/cm^3. This relatively small difference in density may cause the o-Ps to form in or at the surface of the crystalline regions of the PEN sample and subsequently diffuse into the amorphous fraction and annihilate there. Alternatively the o-Ps may form and annihilate in the crystalline region as well as in the amorphous regions of the PEN samples. Previously this mechanism has been suggested by Olson et al. [27] to explain their PALS data of syndiotactic polystyrene and by Winberg et al.

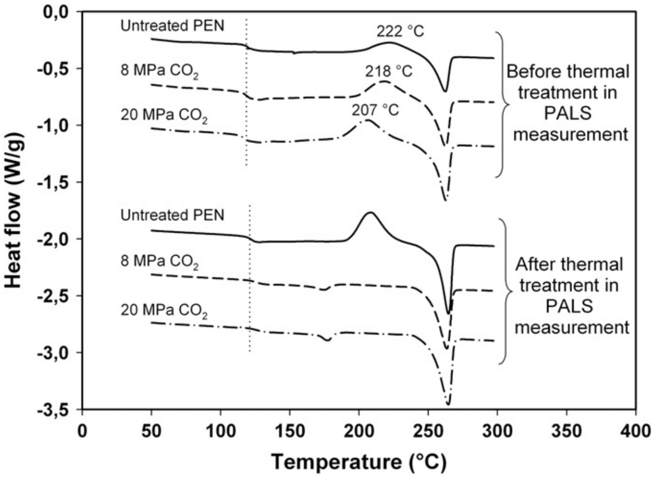

Fig. 9. DSC measurements of three PEN samples treated according to the procedures indicated on the left. The upper three curves are measured before the thermal procedure (during PALS measurement) and the lower three curves are measured after the thermal procedure.

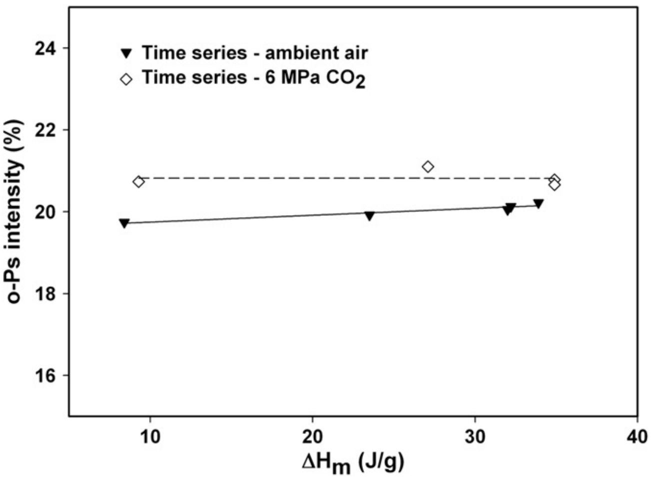

Fig. 10. o-Ps intensity as a function of the melt enthalpy ΔH_m of PEN samples treated at the conditions indicated.

[28] to explain the intensities of silica filled PDMS, where the o-Ps intensity behaved differently depending on the size of the filler particles. It has been mentioned in the literature that the size of the secondary crystals formed during thermal annealing of PEN are small in size compared to the primary crystals [5,20]. The unexpected effect seen in the I_3 could therefore partly be a consequence of the small size of the crystals leading to out-diffusion of o-Ps to the amorphous fraction.

4. Conclusions

The thermal properties and free volume hole sizes of PEN treated in pressurized CO_2 were measured with temperature modulated DSC and PALS. The modulated DSC revealed complicated melting behaviour of PEN, where it could be concluded that simultaneous melting and recrystallization of PEN occurs during the DSC heating scan above the temperature of the low melting endotherm. The position of the low temperature endotherm was directly coupled to the annealing temperature of the samples, as reported in the literature. Among the CO_2 treatment parameters, only pressure had a significant effect on the free volume hole sizes, indicating that the amount of dissolved gas governs the sizes. Thermal annealing – of samples previously treated in pressurized CO_2 – at several temperatures between 30 and 170 °C revealed a relaxation of the free volume when approaching the glass transition temperature. Interestingly such a thermal procedure resulted in crystallization for samples previously treated in pressurized CO_2 but left the untreated sample amorphous. The o-Ps intensity which is generally dependant on the degree of crystallinity showed unexpectedly an independence of ΔH_m, which indicates that o-Ps may form in the crystalline areas as well as in the amorphous fraction of the polymer. The o-Ps formed in the crystalline region can subsequently diffuse to the amorphous parts and annihilate there.

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