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THERMAL ANALYSIS AND FREE VOLUME STUDY OF POLYMERIC SUPERMOLECULAR STRUCTURES

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Abstract

Positron annihilation lifetime measurements were performed on samples cut down from commercially available polyethylene (PE) and poly(4-methyl-1-pentene) (PMP). The effect of a free volume on the segmental relaxation behaviour was examined. The samples were isothermally annealed at different temperatures. In order to study the effect of annealing on supermolecular structures of the polymers, the annealing temperatures were chosen between the transition temperatures of the polymers. All thermodynamic parameters varied as compared to the parameters of the samples which were not annealed. A slight change of the free volume was observed. The idea of two miscellaneous amorphous fractions in polymer was under consideration. Differential scanning calorimetry, dynamic mechanical thermal analysis were used to study the effect of specimen heat treatment on both glass transitions, too. The degree of crystallinity of the PE and PMP samples was determined. An attempt to estimate this parameter from positron annihilation data was undertaken.

Keywords: free volume, glass transition, polyolefines, α-relaxation

Introduction

Over the last several years, poly(4-methyl-1-pentene) (PMP) has been studied in this laboratory. During the course of selecting the appropriate way of composite membrane formation, some distinct differences in supermolecular structures of the PMP membranes were noticed. PMP films cast from certain solvents were opaque whereas other solvents formed transparent films [1, 2]. PMP is a semicrystalline polyolefine for which five crystal modifications (designed I, II, III, IV,V) of the isotactic chain were found. Influence of the crystal modifications on an arrangement of the chains building the amorphous phase was studied, too [3–6]. The idea of coexistence in one polymeric system of two amorphous fractions was proposed [6]. A large body of experimental data indicated that the properties of both fractions, i.e. 'real' and 'semi-ordered' amorphous structures, depended on external and internal factors. Former factors stronger affected the 'real' amorphous fraction, while the 'semi-ordered' fraction was more sensitive to the latter ones. As the crystal structure changes required rather strong stimulus, the amorphous fraction was sensitive to weak disturbing factors. The

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study on PMP membranes properties showed that the crystal unit cell was strongly influenced by solvents, temperature and time of solutions steering. A degree of crystallinity depended on PMP concentration in solution. The properties of the ‘real’ amorphous fraction mostly depended on a used substratum, which the film was cast on [6–8]. The supermolecular structure of the ‘semi-ordered’ fractions was distinctly forced by the presence of the crystalline domains in the amorphous matrix and by the fact that some space for energy dissipation of the crystals was required from thermodynamic point of view. Therefore, this fraction is also named the crystal-amorphous interphase. The role of the interphase was already postulated (defined) by Flory in 1962 [9]. Due to lack of proper equipments this was confirmed first time experimentally for many polymers in the late 1980’s [10]. More detailed studies on the influence of different disturbing factors on the crystalline phase, performed on the PMP films, showed that the interphase could have been interpreted as a fingerprint of the adequate crystalline phase [8]. Although the number of crystallites and their size were different for each studied PMP films, the thermodynamic parameters of the interphase did not change too much. Recently, similar results were obtained for polyethylene (PE) [11, 12]. The existence of the interphase in PE was also proposed for clearing our knowledge on the structural relaxation of polymeric systems in general. Both polyolefines, PMP and PE, exhibited two glass transitions ($T_g(1)$, $T_g(2)$) and two α-relaxations (α_g, α_c). $T_g(2)$ and α_c, as parameters of the interphase, were affected by the crystalline phases of the adequate systems.

Altering thermal history of a sample changes physical properties of polymer. It is known that thermal treatment might drastically influence the supermolecular structure and hence a free volume of the system. The free volume (V_f) is defined as a space which is not occupied by the macromolecules and its value is equal a difference between the specific and the occupied volumes of the polymeric system [13]. The specific volume is measured in dilatometric experiments whereas the free volume is estimated from the positron lifetime data. Positron annihilation spectroscopy is widely used for investigations of different aspects of polymer properties [14]. When a positron with a kinetic energy of several keV, for instance from a radioactive source, enters an absorber it quickly reaches thermal energies. The thermalized positron can annihilate with an electron from the absorber (annihilation of free positrons) or it may form, with the electron, a bound system – positronium (Ps) and then annihilation from the bound state takes place. The ground state of Ps atom consists of two substrates: *para*-Ps (total spin of the particles is zero) and *ortho*-Ps (total spin of the particle is one). Conservation of charge parity allows to decay *para*-Ps into an even number of photons and to decay *ortho*-Ps into an odd number of photons. In vacuum a *para*-Ps lifetime is equal 125 ps and *ortho*-Ps lifetime is equal 140 ns. In condensed matter this long *ortho*-Ps lifetime maybe considerably reduced. In amorphous regions of a polymer substance free volumes exist where *ortho*-Ps may live for several nanoseconds. Positron lifetimes in polymer matter may be perturb by different factors, for instance: changes in degree of crystallinity, blending of polymers, plasticisation of polymers, aging of polymers and so on [15–17].

The purpose here is to report the differences of the supermolecular structures caused by thermal treatment. In order to study the effect of annealing on supermolecular structures of the polymers, the annealing temperatures were chosen between the polymers transition temperatures. In the case of PE, it was the temperature between the temperatures of the second glass transition and the melting process ($T_g(2)<T<T_m$). Three annealing temperatures were applied for PMP because the first glass transition of PMP occurred at temperature higher than ambient temperature. The effect of the influence of a free volume on the segmental relaxation behaviour was examined for PMP and PE samples. New approach to calculation of the degree of crystallinity is proposed. This paper leads to a broader understanding of the relationship between thermal history and morphology of the interphase in PE and PMP products. A wide range of thermal conditions applied for the samples preparation made it possible to obtain specimens of different morphologies resulting from various arrangements of the macromolecules.

Experimental

Sample preparation

Commercial PMP (trade name TPX, Goodfellow Cambridge Ltd.) and PE (Zakłady Chemiczne 'Blachownia', Poland) plates were under investigation. The same materials were used previously [1–8, 11–12]. The samples used in a positron annihilation lifetime spectroscopy (PALS), DSC and DMTA were cast from melt as a sheet of 0.5 mm thickness and further thermal treatment was applied before the measurements. The samples were cut down from the plates or tapes. The sample shape was adequate for the measurement technique used. It must be emphasised that the sample used in different experiments passed the same thermal history. Also, for comparison, the granulated PE and PMP materials were investigated.

Because the temperature of the lower glass transition for PE was about 180 K, the annealing temperature for this system was chosen as a temperature above the second glass transition, i.e. 373 K, PE_{100}. Both glass transition temperatures for PMP are higher than ambient temperature, therefore three temperatures of annealing were applied: $T_g(1)<353\text{ K}<T_g(2)$, PMP_{80}; $T_g(2)<393\text{ K}$, PMP_{120}, and $473\text{ K}<T_m$, PMP_{200}. The temperatures of annealing are pointed out as subscripts. In all cases, time of annealing was 1 h.

Methods

Thermal characterisation of the samples by DSC was performed by using a Perkin Elmer DSC7 instrument and the first heating run was analysed. The melting temperature (T_m) was defined as the minimum of the DSC endotherm. The enthalpy of melting (ΔH_m) was calculated from the area of the DSC peaks after a base line subtraction. It is obvious that the value of ΔH_m strongly depends on the base line shape used. Therefore, the same type of sigmoidal base line was applied for all area calculations.

The glass transition temperature (T_g) was defined from the inflection point of the change in a heat flow *vs*. temperature curve. Also, the first derivative of the DSC trace was analysed when the glass transition was very broad in a temperature scale. The analyses were performed under following conditions: environment – nitrogen atmosphere; flow rate – 20 ml min^{-1}; sample pan–aluminium, reference – empty aluminium pan; sample size – about 2 mg; heating rate – 20°C min^{-1}; calibration procedure – done with indium standard.

Dynamic mechanical thermal analysis was carried out with a Rheometric Scientific ARES system and G" and G' curves were recorded within a temperature range from 135 to 375 K and from 135 to 470 K for PE and PMP samples, respectively. The samples were cut down from the polymeric plates as bars nearly the same size. A frequency range of 0.01–15 Hz was applied after temperature stabilisation.

For the positron lifetime measurements a conventional slow–fast coincidence spectrometer with plastic scintillators was used. Four exponential components were fitted to the measured spectra. The shortest component, τ_1, is related to the annihilation of parapositronium (*p*-Ps), τ_2 is attributed to the annihilation of the free positrons and τ_3 describes the annihilation of orthopositronium (*o*-Ps) in crystallites. The component with the longest lifetime, τ_4, is attributed to the pick-off annihilation of *o*-Ps. According to the model proposed by Tao and Eldrup *et al*. [18, 19], the component with the longest lifetime of the positron lifetime spectrum may be related to the mean radius of the free volume cavity, *R*, in the polymer matrix. The relative intensity of the *o*-Ps lifetime component, I_4, is assumed to be proportional to the number of the free volume holes because it gives the information on the probability of *o*-Ps formation.

Results and discussion

T_g and ΔC_p determination

T_g and $\Delta C_p(T_g)$ are important parameters giving information about the structure changes in a glass transition range. Very often, the change of the specific heat is small and the base line of the DSC trace before and after the transition is not a smooth straight line. The traditional evaluation of $\Delta C_p(T_g)$, as a midpoint, is complicated and burdened by relatively large error. Therefore, this value and T_g are pointed out from the first derivative of the C_p curve. Then, T_g is defined as an extremum and ΔC_p equals the peak area. The calorimetric and structural results for PE and PMP, for various thermal treatment, are summarised in Table 1. The first heating run was analysed. However, the parameter of the first glass transition for the PE samples were pointed out from the first cooling run following the first heating run. The parameters of the transition were as follows: $T_g(1)$=182.9 K; $\Delta C_p(T_g(1))$=0.189 J g^{-1} K^{-1}. Most likely, various engineering conditions applied for polymer production as a granulate or band caused that the supermolecular structures of both polymeric systems underwent changes, which did not create large amount of the 'real' amorphous fraction. The other possibility is that the structural variety between the 'real' and the 'semi-ordered' fractions of both PE systems were not significant. However, latter explanation seems to be less probably from thermodynamic point of view. The drastic different values of T_g, $\Delta C_p(T_g)$ and ΔH_m for PE_g (PE produced as a granulate) and PE (PE produced as a band) would confirm such conclusion. The endotherms of melting for PE_g and PE_{100} were split into two or three peaks, respectively. Annealing at the temperature above $T_g(2)$ changed a little the amount of crystallites. The drastic change of the glass transition parameters was observed. Free volume evaluated for PE_{100} increased significantly as compared to PE. This value is calculated from the R_4 value with the assumption that the volume is a sphere [18–19]. That might suggest more freely fluidity of chains in the 'semi-ordered' amorphous fraction. However, this system is still under thermo-mechanical investigation and the results of DMTA will be discussed in a next paper.

Better situation for the study of the both glass transitions took place in the case of PMP samples. DSC curves exhibited two glass transitions, well pronounced for PMP films [6–8]. However, the commercial products, prepared as a granulate or tape (plate), little exhibited in raw DSC curves the step transitions. Therefore, the first derivative of the DSC traces was analysed in the case of all PMP samples (Fig. 1). For comparison, the data of the PMP membranes cast from carbon tetrachloride (PMP(C)) and cyclohexane (PMP(Ch)) are also presented in Table 1. It was found that the PMP samples obtained from melt or solution exhibit various crystalline phases (five modifications) [20, 21]. However, there is only one value of ΔH_m=61.9 J g^{-1} for 100% crystalline polymer in literature, which is used for the evaluation of the degree of crystallinity. It was shown earlier that the $T_g(2)$ values were the same when the same number of crystallites of the same unit cell was obtained for the PMP membranes [4–6]. Furthermore, it was concluded that the kind of crystalline unit and the number of crystallites affect strongly the crystal-amorphous interphase, it means, the parameters of the second glass transition and the parameters of the structural relaxation of the 'semi-ordered' amorphous fraction (α_c). The first glass transition was sensitive to the kind of substratum used for the membrane production.

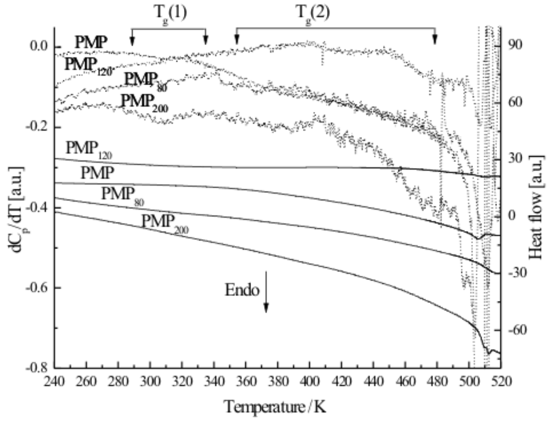

Fig. 1 DSC traces (right scale, solid lines), calculated in the specific heat dimension, and their first derivatives (left scale, dotted lines). The temperature ranges of the first, $T_g(1)$, and the second, $T_g(2)$, glass transitions are signed in the picture

Table 1 Data of the first and the second glass transition for the PE and PMP samples, obtained under different thermal conditions, are presented. The question mark means that the peak (the first derivative of the DSC trace was taken into account) was too small and it was impossible to perform the calculation due to larger calculation errors. The melting process is represented by the melting temperature, T_m, and the enthalpy of melting, ΔH_m. The intensities of the fourth, I_4, and the third, I_3, components of PALS and the radii, R_4 (this value is calculated according to the model proposed by Tao *et al*. [18–19], of the free cavity are given, too)

Sample	$T_g(1)$=K	$\Delta C_p(T_g(1))$/J g^{-1} K^{-1}	$T_g(2)$/K	$\Delta C_p(T_g(2))$/J g^{-1} K^{-1}	T_m/K	ΔH_m/J g^{-1}	R_4/Å	I_4/%	I_3/%
PEg	–	–	353.3	0.089	#	60.3	–	–	–
PE	+	+	321.6	0.362	388.3	103.5	3.27	22.9	8.8
PE_{100}	–	–	317.2	0.141	*	90.8	3.37	20.7	8.6
PMP_g	315.6	0.018	377.1	0.096	501.7	14.6	–	–	–
PMP	307.1	0.041	383.2	0.290	499.0	26.9	3.35	15.9	10.0
PMP_{80}	?	?	353.0	?	517.3	22.1	3.28	19.8	9.0
PMP_{120}	305.3	?	(367.9) 423.0 (476.7)	? 0.283 ?	506.2	22.5	3.28	20.3	9.4
PMP_{200}	307.8	0.105	383.7	0.327	510.3	25.2	3.27	18.1	9.7
PMP(C)	308.2	0.121	374.0	0.180	498.2	31.8	–	–	–
PMP(Ch)	300.1	0.121	389.5	0.089	499.7	38.8	–	–	–

* – 3 minima; + PE: $T_g(1)$=182.9 K; $\Delta C_p(T_g(1))$=0.189 J/(g·K); # PE_g: T_m=386.0 K (408.2 K)

The stronger influence of the annealing process and the wider temperature range of the glass transition were observed for the second glass transition (Fig. 1). The annealing at 473 K seems to influence only the amount of amorphous phase of both fractions. The position of the glass transition is changed barely. Such results would mean that the supermolecular structure of the 'real' fraction was affected only in the quantity sense. The transitions temperature for PMP and PMP_{200} were nearly the same. Most likely 473 K is a temperature at which the melting process begins. Hence, some crystallisation after the crystalline domains premelting would be possible. $\Delta C_p(T_g(2))$ increased slightly as compared to the increase of the $\Delta C_p(T_g(1))$ value for the annealed sample (PMP_{200}). Quality and quantity effects of annealing for the 'semi-ordered' fraction were found. The $T_g(2)$ values varied much more than $T_g(1)$ in the case of all PMP samples. One can easily find that the first glass transition in the case of PMP_{80} and PMP_{120} almost disappeared from the DSC traces. However, a double glass transition was observed at the annealing temperatures for each samples. The annealing process drastically decreases the free volume of cavities of the amorphous phase but no difference was observed among three samples annealed at 353, 393 and 473 K, see the R_4 values presented in Table 1 and [18–19].

Degree of crystallinity

One of the basic method for the calculation of the degree of crystallinity is to compare the melting enthalpy of the studied polymeric system with the melting enthalpy of the same polymer of 100% crystallinity. We know that there is no 100% crystalline polymers and the value for such a polymer is taken from extrapolation, very often perform for a low mass molecular compound, which the chemical constitution is similar to the repeating unit of the polymer. Such a procedure do not take into account the crystals polymorphism and the change of the system volume. Moreover, if we consider the problem with the base line for DSC measurement, it would seem that the procedure should not give correct values. However, it is generally known that some correlation with the X-ray procedure existed, although the calculations, based on the X-ray data, were performed with some procedure error. In this paper, we give another example, how the amount of crystals in the polymeric system could be evaluated.

Looking through Table 1 one can find the value of I_4 and I_3, the intensity of the fourth and the third component of the lifetime spectrum. The relative intensities of the σ-Ps lifetime components I_4 and I_3 are assumed to be proportional to the number of the free volume holes in the amorphous regions and in the crystallites, respectively. Taking I_3+I_4 as 100%, one can easy calculate the relative part of each component in the sum. The comparison of the calculation perform based on the DSC and PALS data are presented in Table 2. Although the results differ the tendency is preserved. It must be emphasised that both methods include the measurement errors. The method of calculation of the crystallinity degree from PALS data will be tested for its utility.

Table 2 Degree of crystallinity calculated from DSC (PE100%–146.8 J g^{-1}; PMP100%–61.9 J g^{-1}) and PALS results. The activation enthalpy of the second α relaxation, α_c, is given in the last column

Sample	d(DSC)/%	d(PALS)/%	$\Delta H_\alpha(2)$/kJ mol^{-1}
PE_g	20.6	–	–
PE	35.3 (70.5)	27.8	298
PE_{100}	31.0 (62.0)	29.3	+
PMP_g	23.6	–	–
PMP	43.4	38.6	114
PMP_{80}	35.7	31.2	121
PMP_{120}	36.3	31.6	114
PMP_{200}	40.7	34.9	98
PMP(C)	51.4	–	53
PMP(Ch)	62.7	–	231

Mechanical study

The modulus of shear was measured for the PMP plates. G' and tgδ are presented for all PMP samples in Figs 2a and b, respectively. Both relaxations are pronounced (α_g and α_c). One can find that the α_g relaxation occurs in a narrow temperature range while the α_c relaxation occurs in a wide temperature range. This typical behaviours were discussed in detailes for different PMP membranes earlier [6]. Different

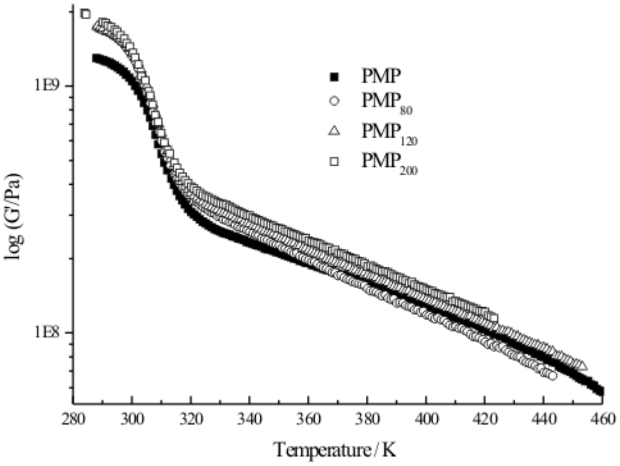

Fig. 2a The real part of shear modulus for PMP samples in the temperature ranges of both glass transitions data for 1 Hz

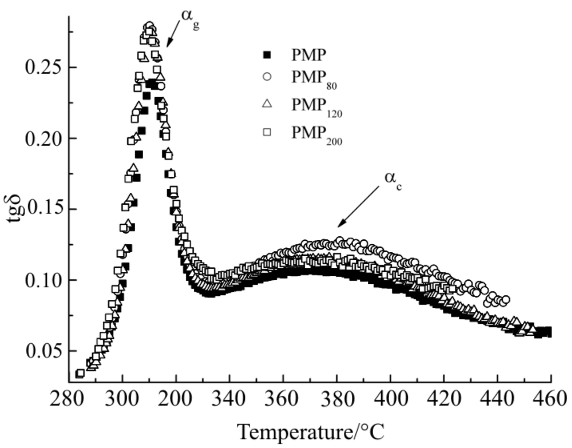

Fig. 2b tgδ curves of α_g and α_c relaxations for PMP samples, data for 1 Hz

supermolecular structures, obtained for PMP membranes cast from solutions, influenced strongly on the transport phenomenon of different substances through the membranes [3, 22]. It was shown, that not only the structure of the interphase but also the motion of the segments chain affect the transport properties. It is easy to find that all of the PMP samples exhibit different mechanical and relaxation parameters. The activation enthalpies of the α_c relaxation, calculated from Arrhenius relationship, are presented in Table 2. We found that annealing increased the amount of amorphous phase (Table 1 (ΔH_m)), but the fluidity of the chains building the amorphous areas was almost similar for PMP samples, except the PMP membranes (Table 2 ($\Delta H_\alpha(2)$)). Therefore, the increase of tgδ in the temperature range of the α_g and α_c relaxations means that some changes of the supermolecular structure of both amorphous fractions took place. The maximum of tgδ for the α_g relaxation is at the same temperature for all PMP samples. It would confirm the suggestion that supermolecular structure of the 'real' fraction was changed quantitatively due to annealing. However, the position of the maximum for the α_c relaxation depended on the annealing temperature. The highest temperature of the tgδ maximum was found for the PMP_{80} samples. Also the largest $\Delta H_\alpha(2)$ value was calculated for PMP_{80}. It might mean that the most stiff structure for this sample was created due to annealing.

Conclusions

The observed variety of properties for the annealed PE and PMP samples resulted from different arrangement of the macromolecules, it means, from different supermolecular structure, that was reflected in the values of the structure (V_f, I_4, I_3) and the thermodynamic (T_g, ΔH_m, ΔC_p, ΔH_α) parameters. The 'semi-ordered' amorphous fraction (the interphase region) was disturbed stronger than the 'real' amorphous one. In some cases, the ‘semi-ordered’ fraction was predominant for this kind of polymers, PMP and PE. It is important for the properties of products made of semi-crystalline polymer particularly.

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