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DYNAMIC MECHANICAL RELAXATION IN THE OPAQUE AND TRANSPARENT POLY(4-METHYL-1-PENTENE) FILMS

The glass transition zone

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Abstract

The thermomechanical properties of opaque and transparent polymer films of a solution of poly(4-methyl-1-pentene) (PMP) in cyclohexane and carbon tetrachloride obtained by casting on teflon and glass plates were investigated. The dynamic mechanical thermal analysis was applied in a frequency range from 0.01 to 100 Hz. The curves of loss tangent *vs.* temperature varied depending on the sample thermal history. The first part of these curves could relate to the backbone α relaxation into the unperturbed amorphous phase while the next relaxation could result from the backbone α relaxation into amorphous phase perturbed by the presence of the crystal domains. The Arrhenius plots of the first relaxation show a stronger curvature found in each of the transparent samples indicating strong dependency on specific volume. The second one in the case of transparent films and the first one for opaque samples might be approximate to straight lines.

Keywords: α relaxations, glass transition, PMP

Introduction

Five different crystalline forms of isotactic poly(4-methyl-1-pentene) (PMP) were obtained from crystallisation in semidilute solutions depending on the solvent and thermal history of the solution [1]. Under certain growth conditions the crystal lamellae formed of different perfection are square and nearly flat. Thermal treatments at different temperatures showed that for more perfect crystals the greater number of defects (holes) are found at or near the crystal edge, whereas for the smaller crystals, defects can be found in the interior as well. Moreover, it was confirmed that annealing led to the creation of lines and ridges on the morphology of PMP crystals. Generally, as the annealing temperature is increased (the melting temperature region), the greater number of holes exists and the density of holes depends on the crystal preparation with some crystals being most stable [2–3]. Therefore, PMP exhibits a morphology that can be described as consisting of lamellar crystals and amorphous material. In this type of semicrystalline polymers including semiflexible chains a crystal-amorphous in-

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terphase is well known to exist [4–5]. The interphase allows for the dissipation of rearrangement existing at the crystal surface (a steric packing problem) and the segmental mobility in the amorphous phase is reduced, the more so the closer to this surface [6]. The main consequence of this is that the amorphous phase has not a single T_g but two T_g when both of amorphous regions (constrained and unconstrained) are distinctly different or a T_g-distribution in the case of weak separated regions. The lower glass temperature is equal to the T_g of the bulk amorphous material and the higher one depends on the interaction between the phases [7].

Our previous study of PMP films gave the information about the temperature-dependent relaxation of interphase chains which are constrained and exhibit decreased molecular mobility [8]. In this paper the dynamic mechanical thermal analysis (DMTA) results and their comparison with dielectric relaxation are discussed to clarify the origin of two α relaxation.

Experimental

Sample preparations

PMP is the same as used in previous work [8, 9]. The solvents were used without further purification. Opaque and transparent films were prepared from the cyclohexane and carbon tetrachloride solutions by casting on different type of plates. Polymer concentration in solution was 2, 3, 4 and 5 wt%. Dissolution was achieved at room temperature or by heating at the boiling temperature of the solvent.

Methods

DMTA carried out with a Polymer Laboratories DMTA Mk III system. Loss tangent and E' curves were obtained in the tensile mode. The frequency range used was 0.03–100 Hz and the same heating regime (2°C min^{-1}) within a temperature range from 15 to 210°C for all samples was applied. Thermal characterisation of the films by DSC was performed with the using of a Polymer Laboratories STA 625 type and the first heating run (20°C min^{-1}) was recorded. The glass transition temperature (T_g) was defined from the midpoint of the change in a heat flow *vs.* temperature curve. The melting temperature of PMP crystals (T_m) was defined as the maximum of the melting endotherm.

Results and discussion

Thermal analysis was performed for the PMP opaque and transparent films cast from the two solutions. In wide range of conditions applied for the samples preparation the opaque films were obtained from cyclohexane (C_6H_{12}) (that was described earlier [9]) and carbon tetrachloride (CCl_4) solutions of PMP. The results are summarised in Table 1a and 1b. The data are collected into four groups showing distinctly an influence of solvent, dissolution and casting temperatures, the type of casting plates and PMP concentration in solution. In the case of the films cast from cyclohexane solution it was easy to obtain the opaque (B^*) or transparent (B) forms when the temperature which was established for the forming process was –10 or above 0°C, respectively. The higher PMP concentration is in a solution the lower temperature is required to obtain the opaque type of films. These films show low T_g giving an evidence that the amorphous phase is less stress. Additionally, the lower T_m and ΔH_m values indicate the worse crystalline phase existing and/or its less amount. Because X-ray measurements did not show distinct differences in the crystal unit-cell of the opaque and transparent films, most likely square lamellae of the opaque film formed during crystallisation (which are responsible to supermolecular structure creation) are more defected as compared to the transparent film [2].

Table 1a Transition temperatures (T_g, $T(1)$, $T(2)$, T_m), enthalpies (ΔH_m, $\Delta H_m(1)$) and the change of specific heat ($\Delta C_p(T_g)$) of the opaque (B^*) and transparent (B) films cast from cyclohexane solution. The value in parenthesis gives the temperature of film annealing

Sample	T_g/ °C	$\Delta C_p(T_g)$/ J (g °C)$^{-1}$	$T(1)$/ °C	$\Delta H_m(1)$/ J g^{-1}	$T(2)$/ °C	T_m/ °C	ΔH_m/ J g^{-1}
B^*	19.8	0.09	n	n	123.5	225.7	25.9
B^*(85)	25.2	0.03	n	n	s	224.2	36.4
B^*(120)	28.6	0.03	n	n	s	224.2	24.9
B	26.9	0.12	67.5	1.0	116.4	226.5	38.8
B(85)	x	x	n	n	n	226.8	39.5
B(120)	27.8	x	n	n	n	225.4	29.7

n – no peak; s – one peak splitted into two peaks (Fig. 1); x – no data

Table 1b Transition temperatures (T_g, $T(1)$, $T(2)$, T_m), enthalpies (ΔH_m, $\Delta H_m(1)$) and the change of specific heat ($\Delta C_p(T_g)$) of the opaque (A^*) and transparent (A) films cast from carbon tetrachloride solution. The number in parenthesis gives the PMP concentration in solution and the letter describes the type of casting plate: T-teflon, M-metal, G-glass

Sample	T_g/ °C	$\Delta C_p(T_g)$/ J (g °C)$^{-1}$	$T(1)$/ °C	$\Delta H_m(1)$/ J g^{-1}	$T(2)$/ °C	T_m/ °C	ΔH_m/ J g^{-1}
A(T/2)	29.2	0.04	55.8	2.2	103.2	225.1	31.8
A(M/2)	39.4	0.08	56.8	1.6	103.1	225.6	32.3
A(G/2)	35.1	0.12	57.8	1.9	103.8	226.1	32.5
A(G/3)	37.1	0.08	61.0	1.93	121.3	226.9	29.0
A(G/5)	45.0	0.07	66.0	1.51	114.0	227.9	17.5
A^*(G/2)	x	x	58.3	3.7	120.0	228.6	40.9

An opposite effect can be observed for the opaque films cast from carbon tetrachloride (A*). The rather high melting temperature and big enthalpy indicate well formed crystalline structure being without defects within the lamella. Annealing performs at 85 and 120°C for the opaque films cast from cyclohexane resulted in the T_g value rising and the $\Delta C_p(T_g)$ value changing which is understandable [10]. When the annealing temperature is too high, the destruction of the crystalline phase occurs which results in T_m and ΔH_m decreasing. It is worthy noticing that the opaque film obtained from CCl_4 solution was cast at room temperature whereas the opaque film caste from C_6H_{12} had to be formed in the temperature range below 0°C. However, for both of them PMP was dissolved at the boiling temperature of the solvents mentioned above. The forming temperature in the case of the B* samples is as important as the temperature of PMP dissolution in the case of the A* samples is. Most likely, the concentration of PMP in CCl_4 solution and time of stirring at the boiling temperature are important factors too. This problem is under investigation and will be presented later.

The influence of a surface on the PMP films properties was studied earlier [9]. However, the investigations were performed for very thin films only cast on one type of plate. In this paper, the relation between metal, glass and teflon used as plates for the films casting and the structure of the amorphous phase reflected in the T_g value is discussed. Because the A(M/2), A(T/2) and A(G/2) films were prepared from the same solution (2 wt% of PMP in CCl_4 solvent dissolved at room temperature, casting plate: M-metal; T-teflon; G-glass), one can conclude that the differences in the values of some thermodynamic parameters are the consequence of using different casting plates. Especially, different T_g could prove that each amorphous phase of the PMP films is constrained with different rearrangement due to adhesion phenomenon. Similar ΔH_m (32.1±0.4 kJ mol^{-1}) and T_m (225.6±0.5°C) for these films give the evidence that the crystallisation already occurs in the solution during the first step of the film formation.

Single crystals of isotactic PMP grown from dilute solution were studied by Morrow *et al.* and Nakajima *et al.* DSC traces revealed four endotherms (for details [2, 11]). Thermal analysis of the films presented in this paper showed only three endotherms (Fig. 1) although for other solutions four peaks were found [9]. Most likely, the high-temperature peaks signed in the literature as 3 and 4 due to overlapping gave one broad endotherms (the measurements were performed with 20°C min^{-1} heating rate). The peak 2 pointed out in earlier papers appears at much higher temperature in the case of the studied films (Table 1a, 1b and Fig. 1) but for the B* films similar to the literature value (125°C [11]), about 123.5°C, was found. However, in all studied films a second step transition followed by this peak (revealed on DSC trace as a rather small or splitted into two peaks endotherm) was found.

Frequency dependent DMTA and DETA studies are very important because of complexity of the relaxations in semicrystalline polymer systems. Also, one must be careful in interpretation because some relaxations are stronger dielectri-

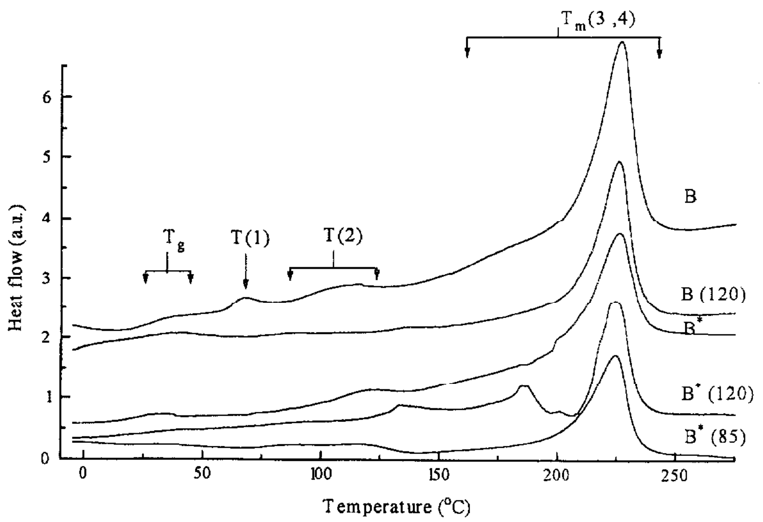

Fig. 1 DSC traces for the opaque (B^*) and transparent (B) films cast from cyclohexane solution. For sample description see Table 1

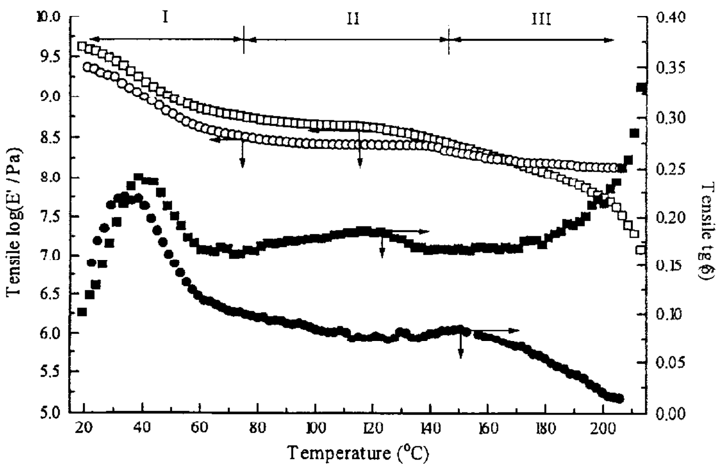

Fig. 2 DMTA data at 3Hz for the opaque and transparent films: I – temperature range of α_g relaxation, II – temperature range of α_c relaxation, III – temperature range of δ relaxations

cally than mechanically. DMTA spectra at 3 Hz for the opaque and transparent films cast from C_6H_{12} are shown in Fig. 2. However, the same tendencies were observed for the films cast from CCl_4. Mechanical loss data of both samples show that the temperature range can be divided into three subranges I, II and III being consistent with the DSC data discussed above. In the first one occurs clearly the α relaxation, corresponding to the large drop in *E′*. The modulus retains a larger value for the transparent films in the first and second subranges because of samples higher crystallinity. The third one reveals relaxations (δ) occurred in the crystal phase, which are activated when the melting process begin.

The differences on the E' curves observed into the third region for the transparent and opaque films lead to conclusion that the crystalline phase which is built of the same crystalline unit-cells must include different crystalline aggregates (dendrites) with their different distribution and rearrangement. Bigger and more rigid aggregates would be responsible for the creation of the opaque and more porous films. However, low T_m and ΔH_m give the evidence that the aggregates must be defected. It is clear that the size and number of aggregates induce

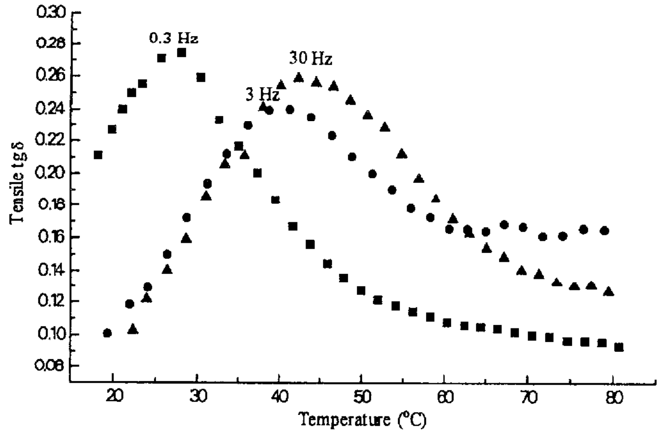

Fig. 3a Loss tangent curves at different frequencies for the opaque film cast from cyclohexane solution

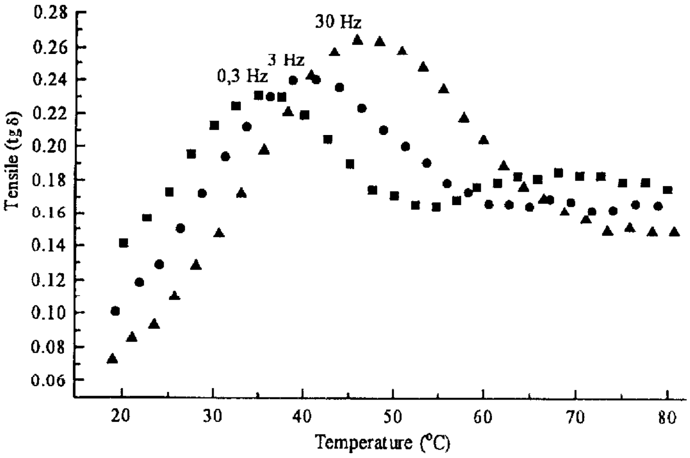

Fig. 3b Loss tangent curves at different frequencies for the transparent film cast from cyclohexane solution

differences in the amorphous phase rearrangement resulting in different DMTA curves in the second temperature range for the opaque and transparent samples [7]. It is understandable that the bigger aggregate, which is more defected, includes inside and/or on its edge more amorphous regions perturbed by the crystalline phase. The lower tgδ in the second temperature subrange for the opaque samples implicate weaker movement inside this amorphous regions which is consistent with the *T*(2) value being always higher for the opaque samples cast from C_6H_{12} and CCl_4. The E' values in the case of B* sample is much lower but this fact could be connected to lower crystallinity. However, most important seems to be the boundary surface of two phases which is likely bigger in the opaque samples including the aggregates created by more defected square lamellae (the case of the B* samples) which decrease the amount of unperturbed amorphous phase. As a result two amorphous regions within the system are formed. One region contains the chains oriented by the crystalline aggregates and the second one is composed of completely disordered chains unless one takes into account the effect of interaction with a plate [9]. This means that two glass transitions and two α relaxations should be observed. It is interesting to note that the tgδ of the opaque samples is higher for the low frequencies (0.01–1 Hz) than for the high frequencies (1–100 Hz) (Fig. 3a). A quite different tendency can be observed for the transparent samples (Fig. 3b).

Mechanical and dielectrical [8] loss data for the opaque and transparent samples give proofs that several relaxations occur in the temperature range. Those are referred to δ, α_c, α_g and β relaxations in order of decreasing temperature. Activation enthalpies for them were calculated using an Arrhenius equation. It can

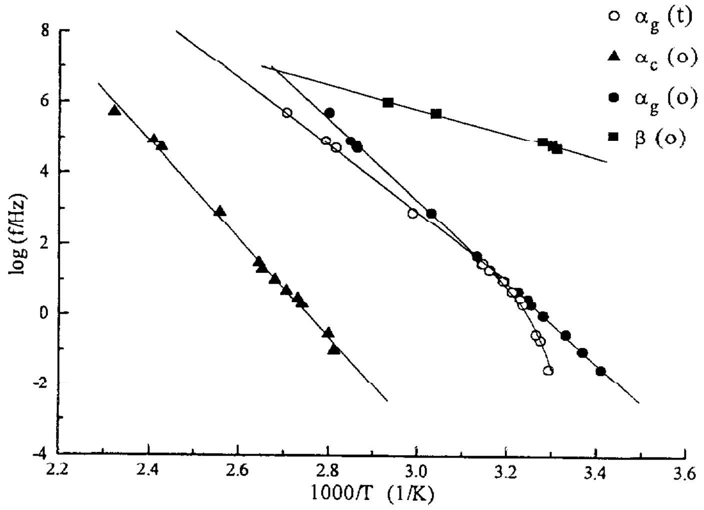

Fig. 4 Arrhenius plot for the opaque and transparent films cast from cyclohexane solution: solid symbols – B* sample, open symbols – B sample. High frequency data obtained in DETA experiments are taken from [8]

be seen that for the transparent and opaque films cast from cyclohexane the β (65.50 kJ mol^{-1}) and α_c (267.44 kJ mol^{-1}) relaxations occur with the same enthalpy and the adequate straight lines overlap (Fig. 4). The activation enthalpies of α_g relaxation found for the opaque and transparent films are 220.28 and 186.30 kJ mol^{-1}, respectively. Low frequency DMTA studies show a new group of relaxations, δ, which were not observed earlier [8]. The lines plotted based on the Arrhenius relation for all local relaxations converge at one point on the plot ($\log f \rightarrow f(1/T)$) for each type of samples. It is worthy noticing that the temperature about 218°C is the same in the opaque and transparent samples but the frequencies are 40 kHz and 30 Ghz, respectively. A likely source of this behaviour is backbone co-operative motions within the crystalline aggregates when their melting occurs. Because their size in the opaque and transparent films is different, it seems to be clear that the bigger aggregate the lower frequency should be found.

Conclusions

The idea of an extended glass transition in semicrystalline polymers appears to be applicable for the opaque and transparent PMP films. The existing of two α relaxations consisted with adequate T_g values proves that the amorphous phase is two-component system. The first one, α_g, (lower T_g) concerns undisturbed amorphous regions which properties and thermodynamic parameters (e.g. T_g) are identically to those of the bulky amorphous polymer. The second one, α_c, concerns regions disturbed by the presence of crystal phase and exhibits high T_g value.

When the percent of crystallinity is similar and the crystal phase is created by the same in size and perfection crystalline forms the second glass transition temperatures for the PMP samples ($T(2)$) are equal. Using different plates for films casting it was shown that the region with lower T_g (undisturbed) due to an adhesive phenomenon is also modified, and the glass transition temperatures of the films cast on the metal, glass and teflon plates slightly differ. However, interaction with surface does not disturb amorphous phase as much as the presence of crystal forms and its T_g is still low.

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