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SUPERMOLECULAR STRUCTURE VARIETY OF PMP MEMBRANES
Thermogravimetric evidences

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Thermogravimetry was applied in order to study the variety of the phase structure of poly(4-methyl-1-pentene) (PMP) membranes. The results gave indirect information about the morphology of the polymeric systems. DTG curves, recorded for the membranes including residual amount of solvent, exhibited three processes. The processes were interpreted as a removal of the solvent molecules occluded in different local structures: 'real' amorphous; 'semi-ordered' amorphous, crystalline. The location of the molecules in those structures was correlated with chain behaviours studied using dynamic mechanical analysis. The relaxation processes (α_g, α_c) were analysed with a special attention to the amount of occluded solvent molecules.

Keywords: *polymeric membranes, α-relaxation, supermolecular structure, thermogravimetry*

Introduction

Thermogravimetry (TG) is a well-known thermoanalytical technique in polymer research. By means of microbalance, the mass of a material is continuously registered as a function of time or temperature. This provides information about mass changes, that may be related to the thermal degradation of the sample. Also, for the system composed of low-mass molecular substances, or included them in some matrix, this method provides information about the temperatures of their removal from the mixture. Usually, TG is used in combination with differential thermal analysis (DTA) for more complete material description. In such a case TG makes easier the DTA curves interpretation. Quantity analysis of TG curves is very easy. The mass loss is revealed by the step curve. One can point out precisely a mass change from the height of the step. The more complex system, the more multistep curve is registered. Multicomponent mixture may exhibit several steps adequately to the number of the components. Not only the component variety but also the structure heterogeneity can be detected by means of TG [1, 2]. Although the material was homogenous from the chemical point of view, 'different' kind of molecules was found [3–5]. It was a result of physical heterogeneity, it means, the variety of supermolecular structure of the studied system. The structure of the matrix, which the solvent molecules are occluded in, influenced the diffusion process of the molecules in such a manner that the boiling temperature of solvent might be shifted towards higher temperature. It is also well known that the molecules of solvent strictly affect the crystallisation from solution. That was discussed based on experimental evidences for poly(4-methyl-1-pentene) (PMP) membranes [6, 7]. The influence of the solvent on the crystallisation kinetics in biological systems was theoretical considered, too [8, 9].

The structure variety may affect a physical process, e.g. diffusion through membrane [10]. It was found that the miscellaneous amorphous phase influenced strictly the membrane properties. Two fractions of this phase were detected by means of different techniques: DSC, DETA, DMTA [10, 11]. The properties of the fractions were studied for different polymers, e.g. PMP or PE (polyethylene), and were determined by the thermodynamic and structural parameters [12, 13]. In this paper, we studied the phase structure of PMP membranes using thermogravimetry. And we show that this simple technique may indirectly reveal the supermolecular structure complexity as well as the more advanced one, which very often requires special sample treatment. We correlate the behaviour of the solvent molecules, occluded in different areas of the membrane, with the chain relaxations occurred in these areas.

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Experimental

Sample preparation

Granulated poly(4-methyl-1-pentene) (PMP) was dissolved in carbon tetrachloride. The concentration of PMP in solution was: 2, 4 or 8 mass%. The solutions were prepared at 55 or 65°C by stirring over 15 h and then cooled down to 40°C. All solutions were cast on glass substrates, which were heated up to 40°C. Membrane formation process was performed at room temperature (ca. 20°C) under ambient pressure. The membranes (except 2g(55)1w – after one week, 2g(55)4m – after four months) were tested for the solvent amounts after two weeks from the solutions casting. One membrane after one week formation, 2g(55)v, was hold at pressure of $3\cdot10^{-4}$ bar over 1 h. The membranes of different thickness were obtained: thin <0.15 mm (c), mid 0.2–1.0 mm (s) and thick >1.5 mm (g).

Methods

Thermogravimetric analysis were performed using a Pyris 1 TGA microbalance with the heating rate of 40°C min^{-1}. The ranges of the mass change were precisely determined from the first derivative of TG signals (DTG). Simple fitting procedure (three Gaussian peaks) was applied to the DTG curves in order to find the mass loss occurred in each of the range. The measurements were performed in nitrogen atmosphere (flow rate 20 mL min^{-1}).

Thermal characterisation of the samples by DSC was performed using a Perkin Elmer DSC 7 type. The first heating run of all samples was always analysed. The glass transition temperatures $T_g(1)$ and $T_g(2)$ were found as the maxima of the first derivative of the raw DSC signals (endo up). The melting temperature (T_m) was defined as the maximum of the melting endotherm. The analysis was performed under the following conditions: heating rate – 20°C min^{-1}; environment–nitrogen atmosphere; flow rate – 20 mL min^{-1}; reference–empty aluminium pan. The enthalpy of melting was evaluated from the area of the endothermic peak after a baseline subtraction.

Dynamic mechanical thermal analysis (DMTA) was carried out with a TA DMA Q800 system. Real and imaginary parts of Young's modulus were obtained in tensile mode. A frequency range was 0.01–200 Hz. The isothermal step procedure of the measurements in the temperature range of both α relaxations (α_g, α_c) was applied for the activation enthalpy estimation. The temperature ranges of those relaxations were determined based on temperature scan (heating rate – 1°C min^{-1}), performed for four chosen frequencies (0.5, 1, 5, 10 Hz).

Results and discussion

It had been shown that the supermolecular structure of a PMP membrane strictly depends on the formation conditions of the membrane [6, 7, 14–16]. The temperature and time of stirring of the solution, as well as the temperature of its casting, determined the kind of the crystal and amorphous phases of the membrane. The influence of the solvent sort on the crystal phase of the PMP membranes had been also described. The existence of two miscellaneous amorphous fractions in one system was postulated as a consequence of the crystal domain presence in the polymeric material. No residual amount of the solvent had been detected in TG measurements then. However, it must be emphasised, the rather thin (<0.2 mm) membranes had been taken for the investigations previously [10, 14, 17, 18]. The same was found in the present work for the thin membranes (thickness <0.15 mm) prepared from the 2% solutions: 2c(55) and 2c(65). (The number in the parenthesis gives the temperature at which the solution was obtained.) The glass transition temperatures and the enthalpies and temperatures of melting for these membranes are collected in Table 1. The values are presented together with our earlier results, for comparison [17, 18]. Taking into account all results, one can find that the amount of crystal phase in the formed membrane depends both on the solution stirring temperature and on the stirring time. The higher temperature and the shorter time, the higher melting enthalpy is. It was previously shown using WAXS (wide angle X-ray scattering) that the same unit cell of the crystal phase was form when the same solvent was used for the preparation of different solutions, even if the other conditions were different [6, 7, 15]. In order to clarify the ponderability of other factors of the preparation process, only carbon tetrachloride was used as a solvent for the membrane preparation.

Table 1 Parameters for PMP membranes cast from 2 mass% solutions prepared at different temperatures. The temperatures are given in parenthesis. The letter 'c' means that the membranes were thin. The numbers 6, 15, 2, 1 and 0.5 give the hours during which the solutions were stirred

Sample	$T_g(1)$/°C	$T_g(2)$/°C	T_m/°C	ΔH_m/J g^{-1}
2c(25)6	35.1	103.8	226.1	32.5
2c(55)15	35.5	160.9	239.0	37.4
2c(65)15	80.2	168.4	231.4	34.0
2c(77)2	31.4	115.0	228.4	33.5
2c(77)1	33.1	118.0	227.8	34.3
2c(77)0.5	–	109.0	228.6	40.9

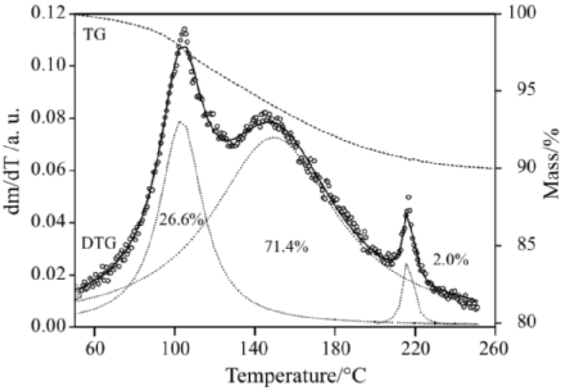

Fig. 1 A chosen example of the - - - – TG and ○ – DTG curves obtained for the studied membranes. The dotted lines (Gaussian curves obtained from the fitting procedure of the DTG signal) represent the amounts of the solvent occluded in different areas of the membranes, the solid line is a fitting curve

Analysis of the residual solvent

As we know, even small amount of low-mass molecular substance acts as a plasticizer shifting towards low temperature the glass temperature (T_g) and the maximum of the temperature of the relaxation process (α relaxation, e.g. studied by DETA or DMTA [19]). In the case of the thick membranes (>1.5 mm), rather big amount of solvent was found. The typical TG and DTG curves are presented in Fig. 1. Although all TG signals reflected one step mass loss between 50–250°C, the DTG curves exhibited three processes distinctly. Owing to the fact that two fractions of the amorphous phase of different morphologies and one crystalline phase coexist in one polymeric system, we can attribute the processes to the removal of the solvent occluded in each of the morphologically different areas. The first one, with the maximum slightly above the boiling temperature of the solvent and much above $T_g(1)$, would reveal the amount of the solvent molecules occluded in the 'real' amorphous phase (RAP). The second one, the widest temperature range including $T_g(2)$, would reveal the 'escape' of the molecules from the 'semi-ordered' amorphous phase (SAP). The third one, the narrowest range beginning above the PMP melting temperature, would confirm a confinement of the solvent in the crystalline domains (CD) [6, 7, 20]. However, this hypothesis require further investigation, that is in a progress. We used different kind of solvents in order to study the phenomenon of molecule location in the crystallites.

Using a simple mathematic fitting procedure (a convolution of three Gaussian functions, Fig. 1), the quantity relationship between the solvent amounts occluded in the different areas was determined for each sample (Table 2). The total amount of residual solvent, Δm_t, is given in grams, calculated for 100 g of the sample. Owing to the fact that the relative amounts of solvent (calculated in percent) in each area do not exhibit any tendency for studied membranes, and the relative value is less informative as compared with the absolute unit, the same unit was chosen for Δm_r (mass loss in RAP), Δm_s (mass loss in SAP) and Δm_c (mass loss in CD), as for Δm_t. One can easy find that the biggest residual amount of solvent was detected for the 'semi-ordered' amorphous phase. The highest contribution of this area to the total amount of the mass loss affected by the solvent removal was found in almost all cases. One can easy explain this phenomenon. The easiest diffusion of the solvent molecules occurs through the 'real' amorphous phase as compared with other areas, although the chains building RAP are tightly arranged. However, it must be emphasised, the membranes are formed at room temperature, that is in the first glass transition region, $T_g(1)$, but much below the second glass transition, $T_g(2)$. The α_g relaxation is highly activated at the membrane formation temperature that makes the diffusion from RAP much easier than from SAP or CD. The amount of solvent in the crystalline phase is the lowest because of the spherical restriction.

Another examples of DTG curves are presented in Figs 2a and b for 2 and 4% membranes, respectively. One can find that the residual amount of sol-

Table 2 Parameters found for membranes, which were cast from the solutions of different PMP concentrations (first number in the name of the sample). The temperature of the solution stirring is given in parenthesis. The thickness of the membranes is signed with the letters: c – thin; s – mid; g – thick. All membranes were transparent except $4g(65)^+$, which was opaque

Sample	$T_g(1)$/°C	$T_g(2)$/°C	T_m/°C	ΔH_m/J g^{-1}	Δm_t/g	Δm_r/g	Δm_s/g	Δm_c/g
2s(55)	40.1	140.9	229.3	41.7	6.8	2.1	3.7	1.0
2s(65)	52.6	167.8	231.2	36.6	19.1	1.6	14.2	3.3
2g(55)	41.4	144.3	232.5	46.5	15.2	2.4	11.2	1.6
2g(65)	61.2	148.5	241.4	38.2	18.8	2.0	13.2	3.6
4c(65)	–	141.5	235.2	31.1	9.3	1.6	7.3	0.4
4g(65)	57.2	141.5	233.1	32.8	11.3	1.5	8.8	1.0
$4g(65)^+$	30.7	141.7	231.3	38.7	0.0	0.0	0.0	0.0
8g(65)	51.2	148.7	232.5	23.6	14.5	5.2	8.3	1.0

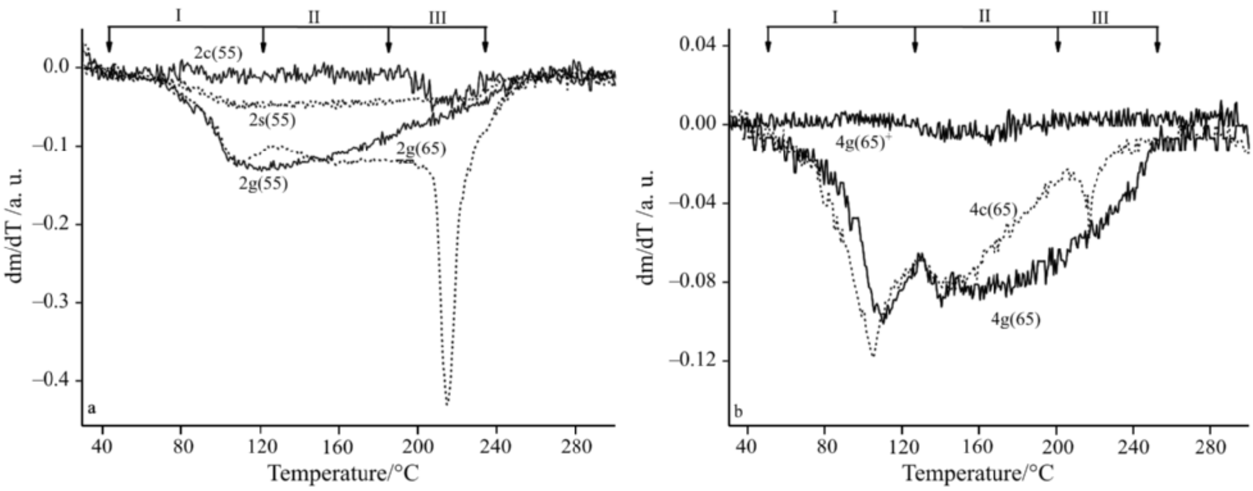

Fig. 2 a – the DTG signals obtained for the 2% membranes of different thickness (c – thin, s – mid, g – thick) and different temperatures of the solution stirring (values in parenthesis). b – the DTG signals obtained for the 4% membranes of different thickness (c – thin, s – mid, g – thick)

vent in the membrane depends on the membrane thickness and the PMP concentration in the prepared solution. The 2% thin membranes did not include the solvent after one week. The thick once have included the solvent after two weeks yet (2g(55)–15.2 g, Table 2), and even after four months (2g(55)4m–8.2 g) or when the membrane was hold under pressure of $3\cdot10^{-4}$ bar (2g(55)v–13.7 g). The total amount of solvent, measured after one week from the solution casting, in the thick 2% membrane was 16.4 g (2g(55)1w). One can find, Fig. 3, that the 'escape' of the solvent molecules took place from RAP mostly. Therefore, increase of the contribution of the solvent amount with the membrane thickness is the highest for the solvent occluded in CD whereas the contribution of the solvent in RAP is almost constant with the membrane thickness (Table 2). The contribution of the solvent from SAP decreased with the amount of CD decreasing. One can also find that the total amount of the occluded solvent decreased with the PMP concentration in the solutions. It was found that opaque membranes did not include residual amount of solvent although the membrane was thick and was formed from the 4% solution, $4g(65)^+$. The morphological variety of the opaque and transparent membranes was explain in details previously [14–16, 21].

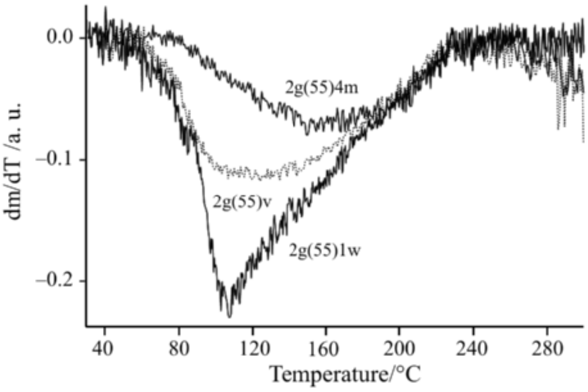

Fig. 3 Comparison of the DTG signals obtained for the membranes treated in a different way just after casting. Evaporation of the solvent was performed in the air atmosphere at room temperature and the signal was recorded for the membranes stored one week, 2g(55)1w, or four months, 2g(55)4m. Additionally, evaporation of the membrane stored one week was performed in vacuum, 2g(55)v

Effect of solvent molecules on relaxation

The distribution of the total amount of the occluded solvent is shown in the last columns of Table 2. For instance, if the total amount of solvent for 2s(55) is 6.8 g, 2.1 g is located in RAP, 3.7 g is occluded in SAP and the rest of solvent (1.0 g) is trapped in CD. In order to study the influence of the solvent molecules on the relaxations, the DMTA measurements were performed for the prepared membranes. Two groups of membranes were selected and the solvent contents were determined for them, Table 2. The *E*' and tgδ curves for the 2% membranes and the 4% membranes are presented in Figs 4a and b, respectively. Our interest was focused on both α relaxations, i.e. α_g and α_c [17, 18], which determine the diffusion properties of the membranes, especially, their selectivity.

One can easy find that the α_g relaxation is narrow as compared with the α_c one. Both relaxations are influenced by the solvent molecules. However, the effects observed for them exhibit opposite tendencies with rising amount of the molecules. The solvent located in RAP acts on the chains, building up this fraction, as a plasticizer (α_g relaxation), that is typical ef-

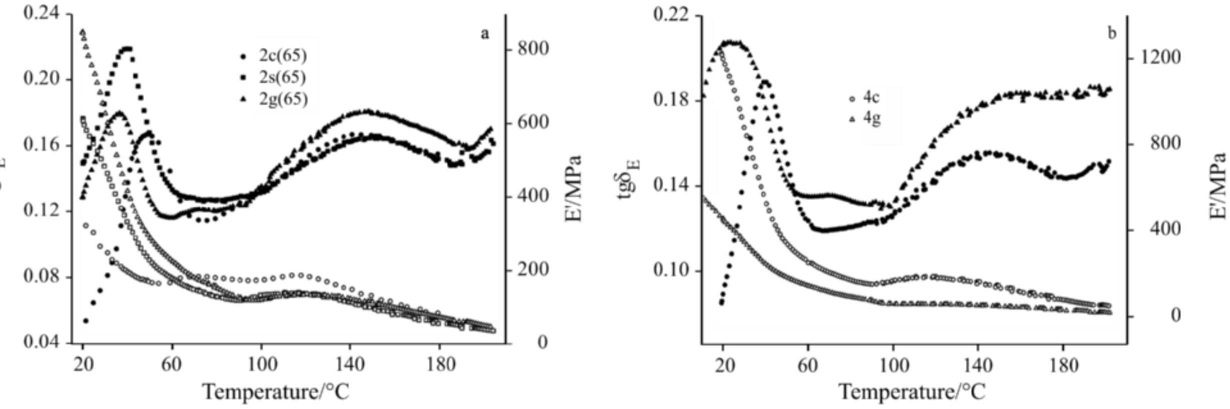

Fig. 4 DMTA curves recorded for a – the 2% membranes and b – the 4% membranes: solid symbols – tgδ, open symbols – *E*'. The presented curves were obtained for 10 Hz

fect, well known from literature, for the interaction between polymer and a low-mass molecular substance [19]. The maximum of tgδ values (tgδ_{max}) shifts towards low temperature with increase of the solvent amount, Δm_r. The following activation enthalpies were calculated: 2c(65) – 413±43 kJ mol^{-1}; 2s(65) – 304±10 kJ mol^{-1}; 2g(65) – 135±13 kJ mol^{-1}. This tendency would confirm the effect of polymer plasticization. However, the molecules occluded in SAP caused the opposite effect, it means, they restricted the motion of the polymer chains and the temperature of tgδ_{max} was higher with the solvent amount rising. The activation enthalpies were estimated to be: 2c(65) – 86±3 kJ mol^{-1}; 2s(65) – 93±6 kJ mol^{-1}; 2g(65) – 114±3 kJ mol^{-1}. It must be emphasised that the temperature shift was not so big as for the effect observed in RAP. One could conclude that the relaxation occurred in RAP is more sensitive to additives (the solvent molecules) than the relaxation taken place in SAP. Such a behaviour of the solvent molecules would be a consequence of different free volume in both fractions of the amorphous phase. It was supposed that the radius of the free cavity in SAP should be larger as compared with the radius of the cavities in RAP [10]. This would be another reason of biggest solvent amount in SAP, Δm_s. Unfortunately, it was impossible to find the relation between the solvent contents and the intensities of the tgδ (or *E*”) curves. The relation found for SAP occurred in the 2% membranes was confirmed for the 4% membranes. The larger amount of solvent, the higher temperature of tgδ_{max} maximum was recorded. However, the tendency found for RAP of the 4% membranes was opposite to the tendency observed for the 2% membranes. Owing to the fact that the intensity and the position of the *E*” curves are the question of the quantity and quality of the supermolecular structure, the relations discussed in the paper still require further investigations, most likely with using WAXS.

Conclusions

Thermogravimetry is a good tool for the study of the phase structure in some cases. DTG gave the proofs of the amorphous phase variety. The curves exhibited three well separated processes of solvent removal from the heterogenic supermolecular structure of the PMP membranes. Each of the process would reveal the diffusion properties of each of the local systems, i.e. ‘real’ amorphous (RAP), ‘semi-ordered’ amorphous (SAP) and crystalline (CD) structures. As the molecules of solvent acted on chains located in RAP like a plasticizer, the motion of the chains built SAP was restricted, that was confirmed by the increase of the activation enthalpies with increase of the amount of solvent molecules. The opposite tendencies concerning the behaviour of the chains built SAP or RAP would result from the different sizes of the free cavities existed in both local supermolecular structures of the amorphous phase. The calculated values of the activation enthalpies and the manner of the temperature of tgδ_{max} could confirm the conclusions concerning the interpretation of the process of the solvent removal and the location of the solvent molecules.

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