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INFLUENCE OF THE FREE VOLUME AND CHAIN FLEXIBILITY ON TRANSPORT PROPERTIES OF MEMBRANES

Summary. The results of positron annihilation lifetime spectroscopy, calorimetric measurements and mechanical spectroscopy are presented for the chosen membranes. The concept of the two amorphous fractions in the semicrystalline system is applied, as the first attempt, in order to better explain the transport phenomenon. New formula, for the relaxation time evaluation (τ), is proposed. Some correlation between the transport parameters and the τ values was found.

WPŁYW OBJĘTOŚCI SWOBODNYCH I GIĘTKOŚCI ŁAŃCUCHA NA WŁASNOŚCI TRANSPORTOWE MEMBRAN

Streszczenie. Przedstawiono wyniki badań objętości swobodnych metodą anihilacji pozytonów oraz ruchliwości segmentów łańcucha polimerowego w wybranych membranach. W celu wyjaśnienia transportu, dla procesu dyfuzji przez membranę substancji lotnych, poddaje się pod dyskusję możliwość zastosowania koncepcji zakładającej istnienie dwóch obszarów amorficznych. Zaproponowanie nowego równania dla czasu relaksacji (τ) pozwoliło określić korelację pomiędzy parametrami transportowymi, a strukturą nadcząsteczkową membrany.

1. Introduction

A membrane, in this paper, is understood as a thin molecular phase that acts as a barrier between two bulk phases, which may be gaseous or liquid. . Such treatment of the membrane material can be found in literature [1-2]. The membrane is permeable to some species in the bulk phases and impermeable to others. It can be prepared by dissolving polymer in some solvent. Then, the detailed characteristic of the final membrane depend on the polymer, but it

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also depends on the nature of the solution and the mode of preparation of the final product. Thus, a wide range of supermolecular structures may be produced by a single molecular moiety. Since the proposed attempt to correlate polymer features with transport phenomenon is just limited, in the paper, to the membranes kind mentioned above, the other polymer processing might be applied, too. However, this would require further investigations. Some theoretical consideration had led to the conclusion that a crystal-amorphous interphase may exist in semicrystalline polymers. The role of this interphase as a transition region, where chains assumed their isotropic orientation differ from those of a truly amorphous phase unperturbated by a presence of crystal domains, was already discussed in 1962 [3]. The consequence of the interphase existence is some restriction in macromolecular fluidity [4-6] that additionally may influence on the transport properties and the selectivity of membranes. The fluidity results from a steric packing of the macromolecule in a polymer chain and a free volume existed between them. It is a consequence of the interaction, which takes place among segments of different chains, and chemical bonds. Various correlations between the temperature and time dependencies of segmental relaxation time (α relaxation) have been demonstrated [7-9]. However, attempts to relate the transport properties to temperature dependence of the relaxation time (τ) and the free volume (V_F) , measured in an positron annihilation experiment, remains unaddressed.

In this paper, some correlation between the transport properties of a polymeric membrane (diffusion, selectivity, permeability) and the supermolecular structure of polymer is demonstrated. Two types of the amorphous phase are postulated in order to better describe the behaviour of the transport parameters. A summary and analysis of the experimental data pertinent to the free volume approach are presented.

2. Experimental

The polymeric samples are the same as used in the previous works [5-6,10-13]. The wide world experimental methods, described in handbooks, i.e. differential scanning calorimetry (DSC) [14], dynamic thermal analysis (DMTA) [15] and positron annihilation lifetime spectroscopy (PALS) [16] were applied for the description of the membrane morphology and the segmental mobility of the polymer chains. The standard procedures (calibration, calculation) during all measurements were adapted that was described in details previously [4-6,17-19]. Some additional comments required for the better understanding of the results will be done in the results and discussion section.

3. Results and discussion

One of the most important factor influencing a mechanism of molecules transport through a membrane is a structure of the membrane, i.e. an arrangement of macromolecules. As for every polymeric material, the morphology of the membrane structure is complicated. It usually shows heterogeneity in a physical sense. The structure is built of domains of different morphology. It seems to be acceptable, that in semicrystalline polymers, one chain must emanate from an ordered area, e.g. lamella, and goes into an ordered area [3]. Such a supermolecular structure consisted of lamellae located in an amorphous matrix includes another one, very important, a structural element. It is an interphase, which allows the dissipation of rearrangement at the crystal surface. The segmental mobility into such an crystal-amorphous interphase is reduced, as compared with the bulk amorphous phase, the more so the closer to this surface [4-5]. The main result of this is that the amorphous phase has not a single glass temperature (T_g) but two T_gs since fractions of amorphous phase are distinctly different [6,20]. The lower glass temperature is equal to T_g of the bulk amorphous fraction whereas the higher one is strictly related to the amorphous interphase. The structure, which is built by chains being immersed in crystalline and/or amorphous domains of two types, play important role in the transport phenomenon through the membrane.

Free spaces existed into the amorphous and the crystals domains are different [16-19]. The transport of the molecules, occurred in such regions, should be reflected in the experimental parameters. Some thermodynamic, transport and structural parameters for chosen polymers are presented in **Table 1**. Unfortunately, a simple correlation between the free volume and the permeability, for the presented polymers, can not be found. However, if we divide the polymers into two groups, as it is proposed in Table 1, the correlation seems to be clear.

Table 1

Thermodynamic, transport and structural parameters for selected polymers (data for the P parameter are taken from ref. [2]). The date in parentheses represent the temperature of the second glass transition

Polymer	T_g [K]	P [Barrer]	V_F [Å^3]
PS	375	11[a]	99
PVC	370	0.16[a]	82
PMP	318(377)	37.2[b]	137
PP	263	1.6[b]	151
PE LD	183(309)	2.9[b]	155

a) P for CO_2, b) P for O_2

The first group includes the polymers which the first glass temperature ($T_g(1)$) is much higher then the temperature of the measurement (T_{mt}). The second one includes the polymers for which the measurement of the diffusion coefficient (D) and the permeability (P) were performed at the temperature higher then $T_g(1)$ but lower then the second glass transition temperature ($T_g(2)$). It is easy to find that the correlation between the free volume and the permeability, for the first group, seems to be clear. It should be noticed that the higher V_F the higher P is obtained. In order to clarify the lack of the correlation, for the second group of the polymers, another one factor must be taken into account. It is widespread experience that the transport mechanism does not depend on the chemical constitution of the membrane and on the mutual arrangement of chains only, but also on the dynamics of the polymer chains, which build the membranes [2]. Therefore, the mechanical spectroscopy was applied to study the segmental mobility and some description of the α relaxation with using a new mathematical formalism is proposed. To understand the formalism some assumptions, resulted from the experimental observation, must be done. For the better clarity of the text, the formalism and the formulae describing the relaxation time (τ) will be discussed in a separate section (in Appendix).

The relaxation times (τ(1),τ(2)) of the α relaxations related to the $T_g(1)$ and $T_g(2)$, together with the diffusion coefficients for the PMP membranes, are collected in **Table 2**. In this paper, the membranes are the same as used previously [5-6,10-13].

Table 2

Data for the PMP membranes were obtained under different conditions (see ref.[11]). Diffusion coefficient data are taken from ref. [11]. The number in parentheses means that the first (1) or the second (2) relaxation was taken into account

PMP membrane	τ(1)[s]	τ(2)[s]	D[cm^2/s]	$\Delta H_\alpha(T_{mt})$[kJ/mol]
No.1	6.1	$1.5*10^8$	1.86^a	201.0(1)
No.2	$1.9*10^9$	$3.9*10^9$	5.06^b	158.9(1)
No.3	10^{857}	7.5	1.11^b	95.8(2)
No.4	10^{181467}	6.4	0.69^b	95.8(2)

a) [10^{-8}], b) [10^{-12}]

Their different supermolecular structures were obtained by casting the PMP different solutions on the various substrates that influenced on the membrane surface. It was shown that the morphology of the crystal phase was nearly the same in the presented samples [12], therefore, the idea concerning the molecules transport through the crystal domains should be rejected. If we only take into account the mobility of the segments located into the bulk fraction of the amorphous phase, the correlation between the diffusion coefficient, D, for the acetone vapour and the relaxation time, τ(1), is observed. If the D parameter decrease the τ(1) values

increase for the adequate membranes. It means, that the following sequence can be written: $D_1 >> D_2 > D_3 > D_4$ and $\tau_1(1) << \tau_2(1) < \tau_3(1) < \tau_4(1)$. However, the difference between the D and $\tau(1)$ parameters for the first membrane and the rest of membranes is rather significant. It was observed previously [11], that this membrane showed big porosity due to the specific arrangement of the crystalline domains. Such a supermolecular structure was quite similar to the fractal picture and, as it was proposed, the transport phenomenon would have been described applying the fractal dimension parameter for the diffusion coefficient evaluation [11]. The same tendencies for the diffusion coefficient of water and methanol vapours were observed, although, the distinct differences between the D values for the different vapours were found.

The correlation between D and $\tau(2)$ is not so clear: $D_1 >> D_2 > D_3 > D_4$ and $\tau_4(2) << \tau_3(2) < \tau_1(2) < \tau_2(2)$. However, we can find an other relation between τ and P (permeability) if we take into account that at room temperature, the transport parameters were pointed out at this temperature, the mobility of the segments located into the various amorphous fractions of the same membrane is different. Hence, the higher mobility, it means shorter τ, should be considered for the transport phenomenon. In such a case the matrix, the channels for the molecules diffusion, is more flexible that makes the transport easier. The following tendencies can be found: $\tau_1(1) << \tau_4(2) < \tau_3(2) < \tau_2(1)$ and $P_1 >> P_4 > P_3 > P_2$ (data for the P parameters are taken from ref. [11]). The relation for the D parameter looks a bit different, however, $P = D \cdot S$: where S is a solubility of the permeate molecules in the polymeric matrix. Most likely, the supermolecular structure also affect the solubility and the relations do not show the same tendency as in the case of P. The values of the adequate relaxation times, e.g. either the first $\tau(1)$ or the second $\tau(2)$ relaxation, were calculated from the following equation :

$$\tau = \tau_1 \cdot \exp\left(\frac{\Delta H_a}{\Delta C_p(T_g)} \cdot \frac{1}{T}\right) \tag{1}$$

The explanation of the symbols is done in Appendix.

For visualisation of the segments mobility effect in the PMP membranes, the data are presented in **Figure 1**. It is easy to see that the $\tau(2)$ values in the case of the membranes no. 4 and no. 3 are shorter then the adequate $\tau(1)$ at room temperature: $\tau = (2\pi f)^{-1}$. Therefore, the relaxation time of that process and the mobility of the segments located into the interphase should be taken into consideration for the transport phenomenon. It means that at some measurement temperature the permeate molecules diffuse through the pure amorphous fraction ($T_{mt} << T_g$) and the transport parameters depend mainly on the free volumes. The other case takes place when the diffusion occurs at the temperature range of the glass transition ($T_{mt} \geq T_g$). Then, the segments flexibility exhibits strong influence on the transport parameters,

too. The selectivity of the transport process would reflect the changes of the supermolecular structure. Unfortunately, it is impossible to distinguish the both amorphous fraction in the positron annihilation measurements. Furthermore, the proportion between the both fraction cannot be pointed out. The both disadvantages of the applied measurement techniques should be removed in further studies on a supermolecular structure of polymer. This require some improvements of the model used for the calculation of the V_F and application of other experimental techniques, e.g. infrared spectroscopy (polarised light), small angle x-ray scattering or nuclear magnetic resonance (in solid).

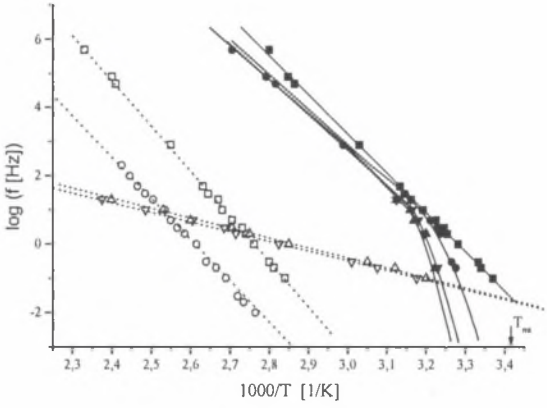

Fig. 1. Arrhenius plot of two α relaxations. The solid and open symbols reflect the relaxations occur in the first and the second amorphous fractions, respectively: ● - membrane no.1; ■ - membrane no.2; ▲ - membrane no.3; ▼-membrane no.4

Rys. 1. Diagram Arrheniusa dwóch relaksacji α. Symbole pełne i puste są użyte odpowiednio dla pierwszego i drugiego procesu relaksacyjnego: ● - membrana nr 1; ■ - membrana nr 2; ▲ - membrana nr 3; ▼ - membrana nr 4

4. Conclusions

The transport phenomena depend on both the free volume and the mobility of the segments creating the supermolecular structure of the membrane. However, at temperatures much lower then T_g of the polymer (at temperature being out of the range of the glass transition temperature region) the former factor seems to play a dominant role. The later is very important when the transport through the membrane takes place at temperatures much above T_g. Moreover, we should distinguish the both fraction of the amorphous phase that gives bet-

ter description of relaxation and transport phenomenon. It is tempting to believe that the new formula and the new approach to the transport process of molecules through the membrane will advance the theoretical understanding of such a process. Also, it will allow the better modelling of the membranes for utility purpose. As the presented attempt to correlate the polymer features, as the free volume and the segment relaxation, with transport phenomenon is quite preliminary. The idea requires some further improvements. However, the measurements, i.e. transport and structural parameters, must be performed exactly on the same membrane.

5. Appendix

In order to find out one mathematical formula describing the α relaxations, the following assumptions are taken: a) it is thermally activated process (Arrhenius type of relation, $\tau \rightarrow f(1/T)$); b) a number of mers taking part in the molecular motion increases with temperature due to the free volume increase ($n_\alpha \rightarrow f(T)$); c) the activation enthalpy of the motion decreases with temperature ($\Delta H_\alpha \rightarrow f(1/T)$); d) the activation enthalpy, ΔH_α, is a function of the number of mers and of the enthalpy of the macromolecules interaction (($\Delta H_\alpha \rightarrow f(n_\alpha, H_i)$); e) the relaxation time is strictely related to the free volume of the polymeric system; f) the H_i value decreases with temperature due to the free volume increase.

The empirical relation referred to the above assumptions combines the Arrhenius and the Vogel-Fulcher relations. According to the model of relaxation, the formula is given by

$$\tau = \tau_l \cdot \exp\left(\frac{\Delta H_\alpha}{\Delta C_p(T_g)} \cdot \frac{1}{T}\right) \tag{1}$$

where: τ_l- the relaxation time at high temperature ($T \rightarrow \infty$, a mathematical approximation, in practice, it is the τ value in a liquid state at temperature below the temperature of polymer decomposition); ΔH_α- the enthalpy of activation of the α relaxation; $\Delta C_p(T_g)$- the change of the specific heat taken at the glass transition temperature (all values, taken from DSC measurements, are always obtained for the zero heating rate extrapolation).

$$\Delta H_\alpha = n_\alpha \cdot H_i \tag{2}$$

Both n_α and H_i are the functions of the temperature given by the following formulae:

$$n_\alpha = n_i \cdot \left(1 - \frac{1}{1 + \left(\frac{T}{T_c}\right)^\beta}\right) \tag{3}$$

$$H_i = H_l \cdot \exp((\frac{\Delta T^*}{T - T_0})^2) \quad (4)$$

where: $\Delta T^* = T_m - T_t$, T_m- the melting temperature of the crystalline (liquid-crystalline) phase, T_t- the temperature of the transition involving the α relaxation, T_0- the temperature at which the relaxation starts.

The β parameter is calculated using the experimental thermodynamic parameters taken from DSC measurements after their zero heating rate extrapolation. The following definition of the β parameter is postulated:

$$\beta = 2 \cdot (\frac{T_g}{T_m - T_t})^2 \quad (5)$$

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Streszczenie

Zjawisko transportu przez membrany polimerowe jest wyjaśniane w oparciu o tezę dotyczącą istnienia dwóch obszarów amorficznych w materiałach częściowo krystalicznych. Obszary te, jak stwierdzono we wcześniejszych pracach [4-6,20], wykazują różne własności fizyczne. Czynnikiem decydującym o ich wystąpieniu w membranie polimerowej jest pewien stopień krystaliczności materiału. Zjawisko dyfuzji wykazuje głównie zależność od objętości swobodnych w temperaturach znacznie niższych od temperatury zeszklenia (T_g), co zostało zademonstrowane w **Tabeli 1**. Jeżeli proces dyfuzji cząsteczek zachodzi w temperaturze wyższej od T_g lub w temperaturach przejścia szklistego, gdzie występuje silna zależność relaksacji α od objętości swobodnej [7-9], wówczas parametry transportowe wykazują silną zależność od ruchliwości segmentów łańcucha budującego fazę amorficzną. Zależność współczynnika dyfuzji od czasu relaksacji α została przedstawiona w **Tabeli 2**.

Omówiono została również zależność współczynnika przenikalności od ruchliwości segmentów łańcucha, jednak tym razem z uwzględnieniem istnienia dwóch obszarów amorficznych w membranie. Konieczność takiego podejścia spowodowana jest nakładaniem się w temperaturze pomiarowej dwóch procesów relaksacyjnych dla odpowiednich łańcuchów budujących obydwa obszary amorficzne. Zjawisko to może być zobrazowane poprzez analizę zależności czasu relaksacji od temperatury. Taka analiza została przeprowadzona w oparciu o nowo zaproponowane równanie (1), którego sens fizyczny wyjaśniono w osobnym rozdziale (Appendix). Zależność czasów relaksacji od odwrotności temperatury dla wybranych membran otrzymanych z poli(4-metylopentenu-1) została przedstawiona na **Rysunku 1**. Struktura nadcząsteczkowa tych membran, jak wykazano wcześniej [10-13], wykazuje silną zależność od sposobu ich otrzymywania. Oznacza to, iż dobierając odpowiednie warunki wytwarzania membrany, można odpowiednio regulować procesy transportu. Kontrolując ilość oraz jakość (strukturę nadcząsteczkową) obydwu obszarów amorficznych, można uzyskać odpowiedni stopień selektywności dla mieszaniny.