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Effect of physical aging on the gas transport properties of PVC and PVC modified with pyridine groups

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Abstract

The gas transport coefficients of polyvinyl chloride (PVC) and PVC modified with pyridine groups have been studied. It has been observed that there is a strong time dependence of the permeability and diffusivity of oxygen, nitrogen, carbon dioxide and methane in membranes prepared by solvent casting of PVC and pyridine modified PVC. For PVC there is a two-fold reduction of the diffusion coefficients during the first two days, and about one order of magnitude, a month after the membranes are prepared, and no stabilisation of the trend is seen after a month. Membranes prepared from modified PVC show a short-term diffusion rate reduction which is similar to that found in PVC, while at longer times the diffusion rate decrease levels off quickly, attaining constant values after about ten days. The time dependence of the transport coefficients is attributed to the samples' physical aging and an attempt is made to fit the experimental data by considering a stretched exponential time dependence of the volume contraction on aging.

Keywords: Poplyvinyl chloride; Physical aging; Gas transport

1. Introduction

Physical aging is a phenomenon common to all amorphous materials in the glassy state, which in the case of polymers, has a great practical importance as it alters all the temperature dependent physical properties, which drastically change on cooling through the glass transition temperature, as for example, mechanical [1,2] and transport properties. Macroscopically, physical aging implies a greater fragility of the material caused by the volume decrease. According to some authors this process takes place in the temperature range between the glass transition and the β relaxation [1], while others [3] believe that it can also take place at temperatures below the β relaxation.

At temperatures below the glass transition, polymers are not in thermodynamic equilibrium, and the values of enthalpy, entropy and volume are above those corresponding to equilibrium. Hence, enthalpy, entropy and volume change with time towards their equilibrium values if molecular mobility allows it. In consequence, the glassy state cannot be described just by pressure and temperature; the simplest theories suppose that the addition of just one parameter, related to free volume, suffices to entirely describe the state. It is true that using the concept of free volume in a simple way, these free volume theories are able to qualitatively explain many aspects of the physical aging process but not all of them. The best-known example is the volume expansion in experiments such as those by Kovacs [4,5].

The various relaxation models proposed in the 1970s, introduce essentially two elements, a broad spectrum of relaxation times and a dependence of the relaxation times on temperature and structure. Kovacs et al.[6–8] proposed a multi-parametric model in which the relaxation time spectrum is composed of two parts, a wing of short relaxation times followed by a main region of longer relaxation times which are associated to most of the available free volume. This distribution manages to describe well the volume contraction, but not so the volume expansion. Robertson's model [9] is very similar to that of Kovacs, the main difference being the introduction of conformational reorganisation. Contrary to these models, the Adam–Gibbs theory [10] on structural relaxation has a thermodynamic basis. The existence of independent regions which reorganise cooperatively is proposed, being the relaxation times dependent on the potential barrier against reorganisation, on the configurational entropy of the smallest unit able to reorganise and on temperature. Nowadays, these three models are still the basis of many attempts to completely describe physical aging [2,11–14].

More recently, Ngai and co-workers [15] applied the coupling model to the physical aging process, as this

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model has been successful in explaining a number of problems related to the dynamics of relaxations in complex systems. This model supposes that the time dependent relaxation rate is the result of an original relaxation rate, which at long time periods is modified by a time dependent factor brought about by the coupling of the moving entity with a complex environment. The relaxation function which is obtained in this model obeys a Kohlrausch–Williams–Watts law

$$\varphi(t) = \mathrm{e}^{-[t/\tau^{\beta}]}. \tag{1}$$

In this equation, β is the coupling parameter, which varies from 1 (uncoupled systems) to 0. This model is able to predict [16] the experimental results by Kovacs and pictures the continuous variation of the interaction of local regions with their surroundings all along the relaxation. It is at this moment [17] considered as the most successful model in describing the dynamics of the glassy state.

A huge amount of literature on the effect of the structural changes on mechanical properties, occurring in a glass during aging, has appeared in the last thirty years. Surprisingly, very little on the effect of this same phenomenon on the gas transport properties has been published, though free volume and segmental relaxation are the main structural features involved in the diffusion mechanism. Only recently, attention is being paid to the effect of physical aging on the gas transport properties, mainly the effect on diffusion coefficients, permeability and permselectivity. Studies have been performed on polycarbonate [18–20], polyimide [21] and polyethersulphone [22] but most of all on extremely permeable polymers such as poly(1-trimethyl-silyl-1-propyne) (PTMSP) [23–25]. It is generally found that aging diminishes the permeation rates of many polymers, which is attributed to the decrease in free volume. However, to our knowledge, a definite quantitative relationship between the time evolution of the polymer structure and the time evolution of the transport coefficients seems to be lacking, apart from some recent attempts [26], probably due to the absence of an unquestionable mathematical description of the glass structural relaxation.

In this work we present results on the effect of physical aging on the gas transport properties of PVC and chemically modified PVC. Our initial aim was to study the effect of systematic chemical modification on the transport properties of PVC, as the controlled modification of PVC and of other glassy polymers, which pack efficiently, appears lately as a means of selectively improving transport properties of high barrier polymers through a controlled manipulation of free volume and free volume distribution [27]. However, the somewhat confusing data referring to diffusion in PVC has obliged us to first clarify the effect of aging on the transport coefficients in PVC and related polymers. We have therefore divided the work in two parts. In the first one we mostly deal with the effect of aging on transport properties of PVC and slightly modified PVC, while in the second one, the effect of the chemical modification of PVC on the long-term transport properties is studied.

2. Experimental

2.1. Gases

The transport properties of these PVC films have been tested using four gases supplied by Praxair. These were methane (purity 5.0), nitrogen and oxygen (purity 6.0) and carbon dioxide (purity 4.8).

2.2. Membranes

Commercial bulk polymerised PVC was obtained from Rio Rodano Industries, Spain. The average molecular weights determined by GPC were $M_{\mathrm{W}} = 112\,000$ g/mol and $M_{\mathrm{N}} = 48\,000$ g/mol. The tacticity measured by ^{13}C NMR was syndio = 30.6%, hetero = 49.8% and iso = 19.6%.

The polymer was purified three times using THF/methanol as a solvent–precipitant system.

PVC modified with pyridine groups was obtained by nucleophilic substitution reaction of PVC with 4-mercapto pyridine sodium salt as described elsewhere [28]. Degrees of substitution of PVC, expressed as mol% of ethyl thiopyridine/ethyl thiopyridine + ethyl chloride, were determined by ^{1}H NMR. Spectra were recorded at 25°C in 5% (w/v) DMSO-d solutions with a Varian Gemini 200 MHz under standard conditions.

In this work, three samples have been used, unmodified PVC, and PVC substituted up to 6.8% (PVC-pyr7 hereafter) and 11% (PVC-pyr11 hereafter) The glass transition temperatures of the three samples, as determined by DSC at 10°C/min in a Perkin–Elmer DSC7, are 85°C for PVC, 87°C for PVC-pyr7 and 88°C for PVC-pyr11.

The membranes were prepared by casting of THF solutions ($c = 100$ mg/ml) on a glass plate, and finally they were extracted with ether in a Soxhlet for 24 h. The end of extraction is considered as day 0 in our time scale. Before starting the diffusion experiments the films were dried for two hours at reduced pressure and ambient temperature.

In order to avoid unwanted dependence of physical aging upon thickness, only very thick films have been used. McCraig and co-workers [26] have shown that there is a strong dependence of the volume relaxation rate on the thickness of the film for films thinner than roughly 5 μm and that negligible dependence exists over about 25 μm. Thus, care has been taken to keep the thickness of our samples ranging from 35–65 μm.

2.3. Permeation measurements

A lab-made permeator described elsewhere has been used [29]. Briefly, it consists of a gas cell in the middle of which the polymer membrane is placed. This membrane separates the upstream and downstream chambers. In order that the simplified equations relating the gas flow through the membrane to the transport coefficients can be valid, the downstream pressure has to be kept very low, which is accomplished by means of an Edwards turbomolecular pump. At the low pressure side, a MKS Baratron type 627B absolute pressure transducer (pressure range 1–10^{-4} torr) measures the pressure increase, while upstream a Gometrics pressure detector is used to control the gas pressure at which the experiment is performed. The whole set-up is temperature controlled at 25°C by means of a water bath.

To perform the measurements, vacuuming is done overnight in order to remove any traces of solvent from the membrane and to attain a low downstream pressure. A measurement of the pressure increase due to imperfect vacuum isolation of the downstream chamber is first recorded. This blank experiment is then subtracted from the permeation experiment performed immediately afterwards in order to calculate the gas transport coefficients from the corrected pressure curves. In that way the pressure increase is related solely to the gas diffusing across the membrane. Pressure data are recorded every 5 s.

The measurement of the aged samples has been performed as follows: films of the three polymers studied, PVC, PVC-pyr7 and PVC-pyr11, were cast, extracted and dried as explained above. In each case, the sample used for the short time measurements was placed in the permeator immediately after its preparation, while the others were kept in an oven at 25°C until the corresponding measurement was carried out. Three different pure PVC samples have been used. One was introduced in the permeator and the transport coefficients were measured after 1, 2 and 10 days. Another one was used to perform measurements after 1 and 30 days and finally the third one was kept in the oven for 100 days and then measured. In the same way, two samples of PVC-pyr7 and three of PVC-pyr11 have been measured. The use of several samples has two aims. First, to check the reproducibility of the measurements and second to save time, as once extracted from the permeator, samples cannot be reused; thus long time measurements would be very time consuming if only one sample of each polymer was used.

3. Results

Though usually aging experiments are performed by quenching from above T_g, we have studied the physical aging of samples prepared by casting from a solution. The aging process that occurs when obtaining a glass by quenching from the melt or by casting from a solution is essentially the same. In both cases the material passes from an equilibrium state, either a rubbery liquid or a solution, to a non-equilibrium state, a glass. Once the glassy state is attained, physical aging begins, irrespective of the previous state of the material. Obviously the structure of the glass originated from a quench or from the evaporation of a solution is not the same, and thus free volume, conformational structure and other structural features of the glass are not the same, as they would not be the same in two different quenching experiments in which the cooling rates were different. As a matter of fact, an important part of membrane preparation technology is related to the conditions of film casting and their effect on the transport properties, and a large number of commercial membranes are prepared in this way. For this reason, we have chosen to study the effect of physical aging on the gas transport coefficients of our samples after casting and without previously quenching from above T_g.

3.1. Physical aging effect on the gas transport properties of PVC

A survey of the diffusion and permeation data regarding PVC available in the literature reveals strong disagreement between different authors [30–33] during the last 40 years. Though diffusion experiments may carry important errors, differences of over an order of magnitude are not often seen. In 1985 El-Hibri and co-workers [31] noted this inconsistency of the literature data and performed an experiment on PVC in which they obtained diffusion coefficients which were almost an order of magnitude lower than those published in 1968 by Tikhomirov and co-workers [32] which, in their turn, were much smaller than those previously published by other authors [33] in 1963. However, the exact reason for this disagreement was not given.

If transport measurements are performed on lab-made PVC films, it soon becomes apparent that there is a strong time dependence of the diffusion and permeation coefficients. In this work, data on the time evolution of the diffusion coefficients of O_2, N_2, CO_2 and CH_4 in PVC is presented. Fig. 1a and b show the time evolution of both permeability and diffusivity in a PVC sample. As shown in these figures, the diminishing of the diffusion coefficients during the first week is very quick: in all four gases there is a two-fold decrease in the first three days. Though more gently, this trend continues for over a month, and as a matter of fact no stabilisation of the diffusion data can be seen during this period. After a month, the diffusion coefficient of methane becomes so small that accurate measurement using our equipment becomes impossible. As appears in Fig. 1, after a month, a strong decrease of almost an order of magnitude has taken place for the diffusion coefficients of all four gases, and clearly there is still a trend to diminish, i.e. the real diffusion coefficients for these four gases are smaller than the values measured after a month. This effect can largely explain the inconsistency found in the literature data concerning PVC. Table I compares the values given by other authors for diffusion in PVC with those presented in this work. It is noteworthy that the data published by Tikhomirov would correspond for the four gases to a roughly four days time lag in our Fig. 1a. Furthermore, taking into

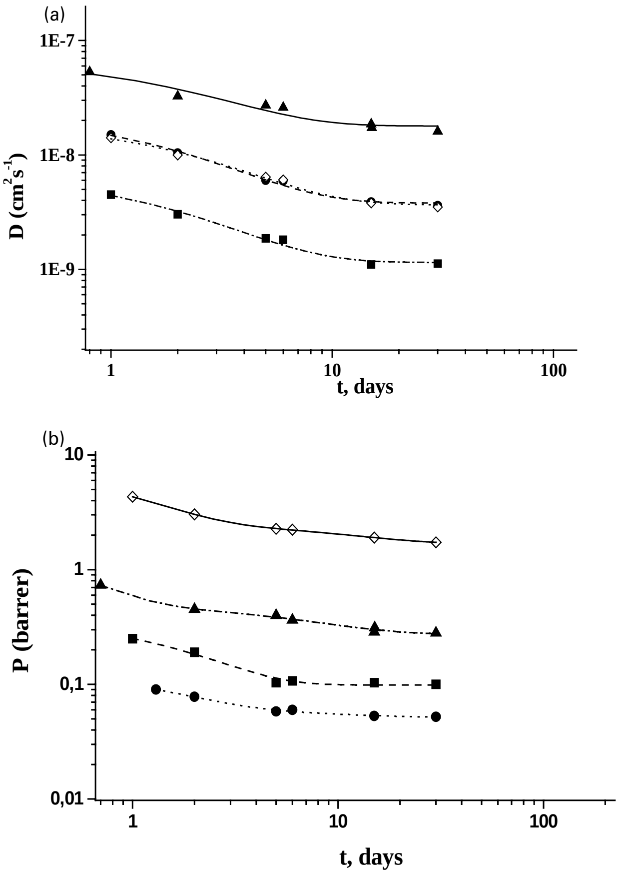

Fig. 1. Time dependence of the diffusion coefficients (a) and permeability (b) of O_2(▲), N_2(●), CO_2(◇) and CH_4(■) in PVC.

account the different measuring temperatures, the data by El-Hibri and co-workers are very similar to our results after more than 30 days. The experimental procedure followed by these authors in the measuring of the transport coefficients sufficiently explains these observations, as Tikhomirov's data were recorded only 12 h after annealing above the glass transition, while those by El-Hibri and co-workers have been obtained on a film devoid of additives (except for a 2% weight of a tin stabiliser) used as received from B.F. Goodrich.

This time dependence of the transport coefficients is to be attributed to the physical aging of the samples. It is well known that this phenomenon implies a diminishing of free volume in the bulk of glassy materials as chains reorganise to allow volume and entropy to decrease, approaching their thermodynamic equilibrium values. An estimation of the real values of the diffusion coefficients in PVC can be made by fitting the data to a simple mathematical function and obtaining the values for long times. A dependence of the diffusion coefficient on the fractional free volume is given by the well-known Doolittle equation

$$\frac{D}{D_e} = e^{-B[(1/f)-(1/f_e)]} \qquad (2)$$

where D is the diffusion coefficient and D_e is the coefficient at the equilibrium. To obtain the time dependence of the diffusion coefficients, an expression providing the time dependence of the fractional free volume is needed. As explained above this is not straightforward as there is no unique model describing the dynamics below the glass transition. According to McCraig and Paul [26] the fractional free volume f can be expressed as [26]

$$f = f_e + (f_0 - f_e)e^{-(t/\tau)} \qquad (3)$$

where f_e and f_0 stand for the fractional free volume at the equilibrium and at time zero, and τ is the relaxation time of the material. Instead of an exponential, we have modified Eq. (3) in the following way, i.e. introducing a stretched exponential:

$$f = f_e + (f_0 - f_e)e^{-(t/\tau)^{\beta}} \qquad (4)$$

The new parameter β adopts values lower than or equal to one, so when $\beta = 1$, Eq. (3) is obtained. When $\beta < 1$, instead of a unique decay time, an apparent distribution of relaxation times is obtained. Thus, combining Eqs. (2) and (4) we can write:

$$D = D_e \exp\left[\frac{f_0 - f_e}{f_e(f_e(e^{(t/\tau)^{\beta}} - 1) + f_0)}\right] \qquad (5)$$

where β has been assumed to be 1. This equation gives the time evolution of the diffusion coefficients in the glassy state in terms of the fractional free volume at time zero and at the equilibrium, and of the two parameters β and τ. This function has been used to fit all the experimental data regarding the time dependence of the diffusion coefficients, and the parameters which result appear in Table 2, together with those corresponding to the other two samples studied in this work. Though apparently five parameters are to be fitted, we have chosen to fix f_e. These parameters will be commented on in the next section.

3.2. Physical aging on modified PVC

A strong time dependence of the diffusion and permeation coefficients is also observed in modified PVC. Figs. 2 and 3 present the time evolution of diffusivity and permeability of O_2, N_2, CO_2 and CH_4 in two samples of PVC modified with pyridine groups up to 6.8% (PVC-pyr7) and 11% (PVC-pyr11).

Two important effects of the introduction of pyridine groups in the PVC structure are seen. First, there is a large increase of the actual values of the diffusion and permeation coefficients and a modification of the permselectivity, which will not be discussed in this work. Second, the diffusion coefficients of the four gases in the two modified PVC samples show, as in the case of PVC, a strong decrease during the first days but contrary to what happens in the former, the decreasing trend levels off after a week. This tendency is the more pronounced the higher the degree of

Table 1
Diffusion coefficients for PVC given in 10^8 cm^2 s^{-1}

Gas	Thikomirov	Paul[a]	This work after			
			1 day	10 days	30 days	D_e
O_2	1.2	–	2.9	1.0	0.49	0.41
N_2	0.38	0.14–0.19	0.58	0.27	0.09	0.094
CO_2	0.25	0.145	0.49	0.26	0.10	0.104
CH_4	0.13	0.033	0.33	0.08	0.027	0.0011

[a] Measured at 35°C.

modification. As a matter of fact, while the decreasing trend in sample PVC-Pyr7 is seen for over a month, the diffusion coefficients reach an apparently constant value after only five days in sample PVC-Pyr11.

When compared to other authors' data on polyarylate [30], polyether sulphone [26] or polyimide and polysulphone [19], it seems that the effect of aging on the transport coefficients of PVC and modified PVC resembles strongly that found by other authors. As very often the published data provide information on permeability or even permeance and not on diffusivity, both sets of data are given in this work. Comparison of the diffusivity and permeability time dependence in Figs. 1–3, shows that these two properties evolve similarly in the systems studied in this work. As $P = DS$, this implies that solubility is either constant or varies linearly with aging time. However, as diffusion data appear to be more directly connected to structural relaxation in the sample, we have preferred to refer mainly to the time dependence of the diffusion coefficients.

Good fitting of all the diffusion decay curves is possible by using Eq. (5). The parameters for each of the twelve curves appear in Table 2. As the number of parameters is high, there is no unique combination which fits each of the curves. Thus, no deep interpretation of the values of each parameter for each polymer/gas system can be made. Only general features deserve comment.

First, f_e is a constant and not a parameter, as it has the same value for the experiments performed on the same material at a given temperature. We have arbitrarily fixed it, though if a physical sense is to be given to the parameters in Eq. (5), it should be measured.

For $t = \infty$, D_e gives an estimate of the long-term values of the diffusion coefficients in each of the samples. In the case of PVC where no stabilisation of the decay curve is noted, it is this D_e which has been used to give an estimate of long-term values of D. The $D_e$values calculated for each of the gases in PVC are collected in Table 1. It is seen when comparing these D_e values to those measured after a month that the larger the volume of the gas is, the greater the difference found between D_e and D measured after a period of 30 days.

Parameter β is, according to the coupling model, an estimation of the coupling degree of the system. Thus, strongly coupled systems show low β and, accordingly, apparently broad distribution of relaxation times. In all twelve curves, the best fits lead to values of $\beta < 1$. It is well-known that PVC shows a peculiar behaviour regarding the β values

Table 2
Fitting of the experimental data with Eq. (5)

	O_2	N_2	CO_2	CH_4
PVC				
D_e 10^8 (cm^{2}s^{-1})	0.41	0.094	0.104	0.0011
τ (days)	8.94	12.2	9.3	8.36
f_0	0.02641	0.0262	0.02604	0.02854
β	1	1	1	0.41
PVC-pyr7				
D_e 10^8 (cm^{2}s^{-1})	1.78	0.379	0.366	0.115
τ (days)	3.4	3.65	4.34	3.63
f_0	0.02585	0.02616	0.02608	0.02615
β	1	1	1	1
PVC-pyr11				
D_e 10^8 (cm^{2}s^{-1})	2.28	0.591	0.503	0.170
τ (days)	1.446	1.96	2.64	2.06
f_0	0.02551	0.0254	0.02544	0.02541
β	1	1	1	1

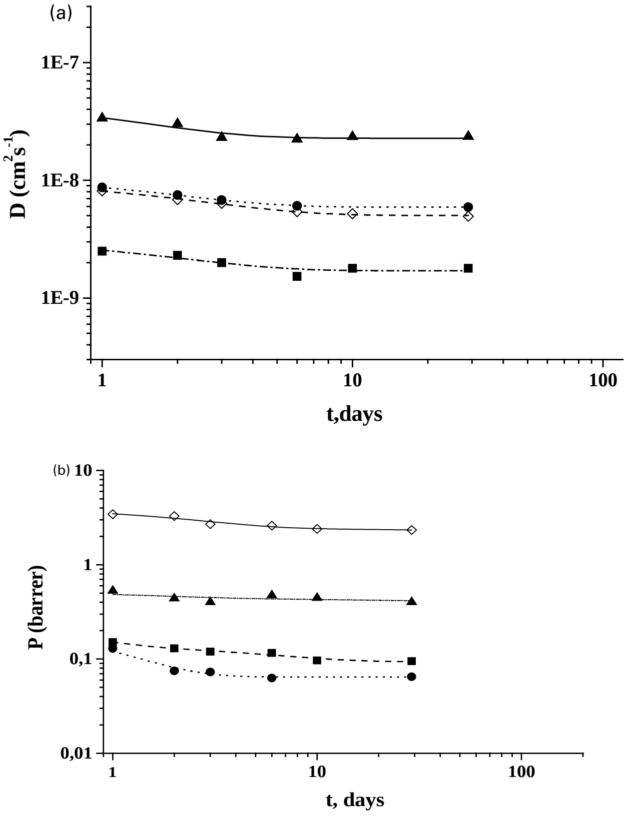

Fig. 2. Time dependence of the diffusion coefficients (a) and permeability (b) of O_2(▲), N_2(●), CO_2(◇) and CH_4(■) in PVC-pyr7.

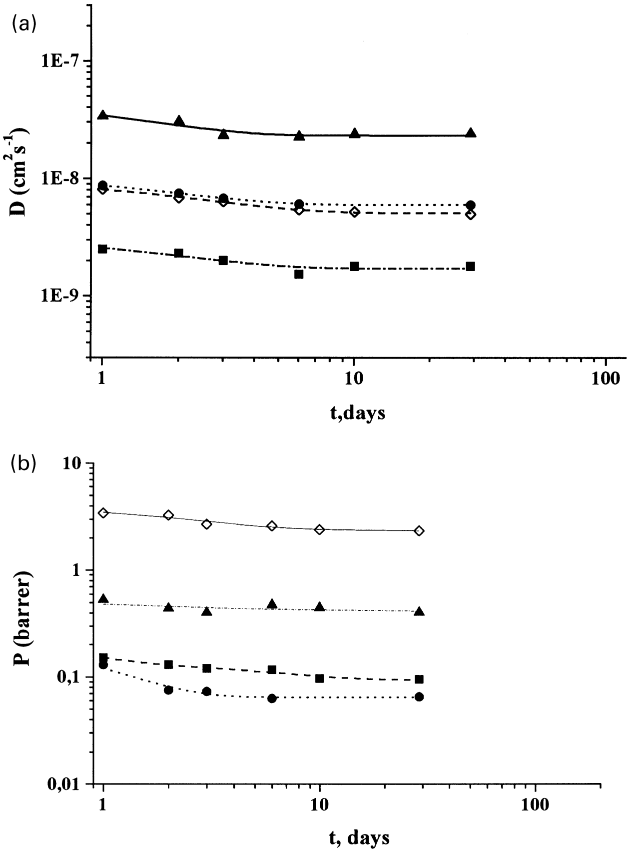

Fig. 3. Time dependence of the diffusion coefficients (a) and permeability (b) of O_2(▲), N_2(●), CO_2(◇) and CH_4(■) in PVC-pyr11.

obtained for this polymer, for example in dielectric relaxation experiments below T_g. Together with some mixtures of elastomers, PVC renders one of the lowest β values known for polymers, about 0.2. This implies that the relaxation times associated to movements taking place below T_g show a very broad apparent distribution of relaxation times, even when compared to other polymeric substances. Some years ago, we showed that when studying the dielectric relaxations in the vicinity of T_g, very slight chemical modification of this polymer in cyclohexanone brings about an increase of the β values from 0.2 for PVC up to about 0.4 for 13% nucleophilic substitution and about 0.33 for 7% nucleophilic substitution [34]. It is to be expected then, that the best β values to fit the diffusion curves using Eq. (5) would be about 0.2 for PVC, approximately 0.3 for PVC-pyr7 and about 0.4 for PVC-pyr11 if the β parameter is defined as in the coupling model.

However, at this point, and given that the number of parameters to be fitted is high and the number of data points small, any attempt to obtain a meaningful set of parameters would be very risky. Rather, the scope of the work is to show that, while the simple exponential decay behaviour of Eq. (3) would lead to fair fits of most of our results, it does not fit the diffusion of methane at all, the largest gas measured, in PVC. In this case, it is necessary to introduce a stretched exponential behaviour as that proposed in Eq. (4) to fit the experimental data points. Again, it must be stressed that in all cases better fits were obtained when β takes values lower than one, than when the parameter was fixed as $\beta = 1$.

An analysis in greater detail of the effect of physical aging on the diffusion coefficients will require an exhaustive investigation, specially obtaining more complete aging curves which will allow a fitting with Eq. (5) which leads to unequivocal and meaningful sets of parameters, and which permits further analysis on the adequacy of Eq. (5) and of its physical meaning.

The effect of physical aging on the diffusion coefficients is more evident in PVC than in the rest of the samples. It is also more evident the greater the diffusing gas molecules. The effect of volume contraction on the diffusion coefficients should logically be dependent to a certain extent on the ratio between the size of the gas and the available free volume in the polymer. This is in fact apparent, for example in Fig. 1a, where it is seen that the effect of time on the diffusion coefficient of O_2 levels off quickly, while the time evolution of the CH_4 diffusion coefficients lasts longer and leads to a very strong reduction of the transport coefficient.

These considerations justify the use of Eq. (4). The stretched exponential in Eq. (4) would give account of the effect of the volume time evolution on the diffusion coefficients. On the other hand, it is to be expected that the free volume reduction effect on the diffusion coefficients will have a limit. This limit is related to the value of the diffusion coefficient of each gas near the glassy “equilibrium” state. Thus, if different gases are considered, the smaller the gas, the sooner this limit will be attained. On the other hand, if different structures are considered, the D variation limit will be attained quickly, the larger the “equilibrium” free volume of the structure is.

At this moment, experiments are underway to further test the adequacy of Eq. (5) to describe the time dependence of diffusion coefficients on the volume contraction brought about by physical aging. Interesting conclusions could be derived from the interpretation of the values of β, τ and f_0 in different polymer/gas systems.

4. Conclusions

A strong time dependence of the transport coefficients of permanent gases in solution cast PVC membranes has been observed. The diffusion coefficients of oxygen, nitrogen, methane and carbon dioxide decrease by almost an order of magnitude during the first month after preparation of the membranes. This effect is also observed in PVC modified with pyridine groups up to 6.8 and 11%, though the decreasing trend in these polymers tends to level off much more rapidly than in PVC. The reduction of the diffusion and permeation coefficients has been already observed in some other polymers and has been attributed to the volume relaxation, which characterises physical aging of the glassy materials. It has been observed that the effect of physical aging is more conspicuous in PVC than in the modified samples and the larger the volume of the diffusing gas is. The time dependence of the diffusion and permeation coefficients has been successfully fitted using stretched exponentials to describe the volume contraction caused by physical aging.

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