INFLUENCE OF FREE VOLUME ON PHYSICAL PROPERTIES AND MEMBRANE PERMEABILITY

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Introduction

The specific free volume (for unit mass) V_f can be defined as the difference between the specific

volume $\left(\dfrac{1}{\rho} = \tilde{V} \right)$ and the "occupied" volume V_0 which is the characteristic volume (or co-

volume) of the atoms or molecules, making up the materials, in the unit mass:

$$V_f = V\text{-}V_O. \tag{1}$$

V_o is the volume not entirely available for the molecular motion, which characterise the process under investigation. However the question of what to use for the magnitude of V_0 is quite a difficult one.

V_f rules therefore the rigidity and the mechanical properties of polymers and also the penetrant diffusion coefficients, which are fundamental for the study of transport properties.

The transition from rubberlike (liquid) to glassy state of amorphous polymers is paralleled by marked changes in viscosity, specific heat, thermal expansion coefficient elastic modulus, within a narrow temperature interval, centred about the so called glass transition temperature (T_g). This transition is not a thermodynamic phase change, but is due to the decrease of the free volume of the amorphous phase below some small characteristic value that does not allow the free movements of polymeric chains inside the material.

V_O is the specific volume of the polymer inaccessible to the particular molecular motion that is interested by the mass transport mechanism. With this definition it is possible to cover, for example, viscous motions above T_g [$f = f_g + \alpha_f \Delta T$) with $f_g = 0.025$], viscoelastic transitions below T_g , where mechanical dynamical transitions β, γ, δ can happen only if free volumes is higher than the

size of the vibrating groups. As to diffusivity the choose of V_O is not easy mainly in the glassy state. We found that holes can exist even much larger than the dimensions of the permeating gas: however in any case a certain selectivity exists. We think that the solution-diffusion mechanism can allow a flux partition so that the maximum resistance to flowing permeant is due to the membrane fraction, which is compact.

Free volume in polymers and diffusivity

Williams Landel and Ferry [7] extended the Doolittle equation valid for simple liquids to polymers, proposing:

$$\eta = \tau E = A \exp\left(+ \frac{B}{f} \right)$$

where $f = V_f/V_g$ is the free volume fraction; A and B are constants; τ is the polymer relaxation time, E is the elastic modulus. The dependence of viscosity η on entanglements can reasonably be considered a structural factor included in A.

They propose for the free volume the expression (at constant pressure):

$$V_f = V_g [\, f_g + \alpha_f(T - T_g)]$$

which satisfies the experimental behaviour of the amorphous polymers. V_g is the volume at the T_g ; $\alpha_f = \alpha_L - \alpha_g$ is the difference between the thermal expansion coefficients of the rubber (liquid) and the glass; f_g is the free volume fraction at T_g

W.L.F. formula relates the free volume to the relaxation time of the glass transition multiplied by the glass elastic modulus and therefore to the viscoelastic properties of the (amorphous) polymers. W.L.F. equation can be used with confidence above the T_g. The theoretical studies on diffusion , done using models of low molecular weight molecules assimilated to hard spheres, can be extended to systems made by macromolecules and by small amounts of small penetrant molecules mobile in the polymers, taking in consideration that their diffusion process is governed by the segmental motion of the polymer chains. Therefore it is justifiable to apply the results of studies concerning polymer segmental mobility (e.g. viscosity temperature relations) to the study of diffusion of small molecules in polymers.

This observation justifies the Fujita expression of the mobility m_α of the diffusant relative to the

polymer: $m_\alpha = A_d \exp\left(-\dfrac{B_d}{f}\right)$. A_d and B_d are assumed independent of concentration and

temperature. The thermodynamic diffusion coefficient is given by:

$$D_t = RT\, m_\alpha = RTA \exp(-B/f)$$

f is assumed as an additive function of the diffusant volume fraction Φ and of temperature.

f(T, Φ) = f (T, 0) + γ (T)*Φ where T is the temperature, Φ is the volume concentration Fujita equation is satisfactorily applicable to large organic molecules in amorphous polymers but not of small molecules as water in polar polymers. We found that it can be used satisfactorily with different polymers and for low MW gases rather insoluble in the polymers: in this case the equation can be used for free volume in the temperature range $T_g < T < T_c$. Several models have been proposed to explain the diffusion data: they can be divided in two main classes: molecular models and free volume models. The first ones stress the importance of the detailed microscopic specific interaction polymer – penetrant and the change in the matrix due to this interaction.

The free volume models on the contrary accept the existence of pre-existing holes. The diffusion activation energy is postulated to be the energy needed for causing a volume increment of the holes to reach the volume needed to allow the passage of the molecule.

State equations (eg that of Simha) allow to calculate the free volume of polymers both in the rubberlike region and in the glassy state, but are valid only at equilibrium, while glasses free volume changes with time. So relaxation volume study is needed to follow V_f; then diffusivity can be estimated (Duda's or dual sites equations could be used).

Models always have to be confirmed by experiments. Time life of positronium is a modern possible tecnique to find the mean radius and size distribution of the existing holes at level of Angstroms and nanometers. Absolute number of holes in the unit volume, can be estimated only in some cases, but relative cavity numbers in the different physical states can be achieved. Different crosslinked polyurethanes, synthetized ad hoc were tested. The free volume expansion coefficient through the Tg zone was found to be the sum of two coefficients due respectively to the variation of the number of holes and to the variation of the hole size [1].

A very interesting example of higt Tg glassy polymers is trimethylsilyl propyne (PTMSP) [2].

After of the spectrum investigation of all the PAL data, two long-lived components, may be assigned to o-Ps annihilation in two different-sized holes.We suggest a bimodal distribution of free volume holes: large cages (mean value of $R = 0.75$ nm) originated from the non- equilibrium state of the glassy polymer and channel- like, or structural, holes (mean values of R = 0.45 nm) due to chain-to-chain separation. About 5-6% of the free volume is due to smaller holes and 94-95% to larger holes. The o-Ps lifetimes τ_3 and τ_4 are related to the average hole size $vi(\tau_i)$; moreover the relative intensities may be assumed to be proportional to their density number Ni (mL^{-1}).

The percentage variation of the free volume in 60 days results in 21.2% for PAL measurements on samples in air and 24.3% on samples under vacuum. The two values are in good agreement and a mean value of free volume decrease of 22.7% may be assumed.

From density data, the specific volume variation results as $\Delta v_t = 1.185 \ 10^{-2}$ (mL/mL) and it is equal to the total variation of the free volume f, because from definition of the free volume the occupied volume cannot change. Therefore, for f one obtains: $f = 5.22 \ 10^{-2}$.

From the mean volume of the holes and the fraction of the free volume of small and large holes, it is possible to evaluate the density number N of holes

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References

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