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SMR/206- 3

"SCHOOL ON POLYMER PHYSICS"

27 April - 15 May 1987

"TRANSPORT PROPERTIES AND MEMBRANES"

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TRANSPORT PROPERTIES AND MEMBRANES

The solution and transport behaviour of low molecular weight substances in polymeric materials is a topic of interest for many fields of science and technology.The relevance of such behaviour has became more evident in the last 10 years with the big development of separation membrane systems,highly impermeable or selectively impermeable packaging films and the overall increase in the use of polymeric materials for many different applications with consequent exposure to various environmental agents.

The possibility to select or develop a polymeric material with a particular transport behaviour requires knowledge of the many factors which affect the transport properties.An aim of reaserch in this field is to establish mechanism and laws relating solubility and transport in multicomponent systems with the molecular properties of the components.On the other hand the nature of the movement of a penetrant molecule in a solid can give information about structural characteristics of the solid,as flexibility and configuration of the molecular chains and the overall morphology.In this sense,transport properties can be considered as a molecular probe in the same way as are X rays,electron microscopy and light scattering.But,whereas these techniques are suitable to study the crystalline component of polymeric materials,Transport properties are particularly able to give information about the amorphous component. This is very important since in the last years there has been an increasing interest in the study of the amorphous component in semycrystalline polymers.As a matter of the fact scientists have recognized the importance of knowing the overall morphology of a polymer in order to relate the structure with the properties of a solid.Furthermore many properties of a solid are directly related to the amorphous component.

Definitions and Basic equations

In a homogeneous ,uniform and isotropic solid we can describe the transport of gases and vapors by two independent coefficients: Sorption S and Diffusion D.Their product is the Permeability P.

Solubility coefficient

Sorption is a general term to describe the penetration and dispersal of penetrant molecules in a polymeric solid to form a mixture. The manner in which sorbed molecules are held and distributed within a polymer is termed "mode of sorption".Any given system may involve a number of concurrent modes of sorption each of which may predominate as conditions are changed.

The equilibrium amount of penetrant sorbed and its sorption mode distribution in a polymer,under given conditions,are governed by the thermodynamic of the system.

Four general types of sorption isotherms found for sorption in polymers,are illustrated in Fig.1.

The simplest case is that of ideal solution behaviour with sorbed penetrant randomly dispersed within the solid such that Henry's law is obeyed.

The solubility coefficient is then constant independent of sorbed concentration at a given temperature and the sorption isotherm is a linear relation of concentration versus pressure(or vapour activity)

$$c_1 = S\, p_1$$

This solution behaviour is observed when permanent gases are sorbed by polymers at pressures not higher than 1 atm.(Fig 1 a).

The isotherm shown in (b) represents a preference for the formation of polymer penetrant pairs at relatively small pressure, with a smaller amount of sorption of more nearly ideal solution behaviour at higher pressures. This type of isotherm results when gases are sorbed by glassy polymers containing voids.Two modes of sorption are considered to be involved: true solution and sorption into pre-existing voids which act in a manner equivalent to that of specific sites.

The isotherm shown in (c) represents a preference for the formation of penetrant-penetrant pairs, such that the solubility coefficient increases continously with pressure. The physical interpretation of this behaviour is that the first molecules sorbed tend to loosen the polymer structure locally and make it easier for subsequent molecules to enter in the neighborhood of the first than to go elsewhere. This interpretation implies that the sorbed penetrant plasticizes the polymer and we observe this isotherm when a liquid or vapour penetrant is a strong solvent or swelling agent for the polymer.

The isotherm (d) is a combination of type (b) at low pressures and (c) at higher pressures. Initially there is a preferential sorption on specific sites,whereas at higher vapour pressure,solution or clustering processes predominate.

In all the isotherms examined,but the (a) type,in which the Henry's law is obeyed,the solubility coefficient varies appreciably with sorbed concentration c of penetrant. Mathematical expressions which represent the variation of pressure,activity or solubility coefficient with the penetrant concentration or volume fraction are thermed "Isotherm equations". They describe the different dependence of sorption on pressure as reported in Fig. 1.

Dependence of S on temperature

The temperature dependence of solubility in small ranges of temperature can be represented by an Arrhenius type relation

$$S = S_0 \exp\left(-\Delta H_S / RT\right)$$

where ΔH_S is the heat of solution and can be expressed as

$$\Delta H_S = \overline{\Delta H}_{COND} + \overline{\Delta H}_1$$

the molar heat of condensation and the partial molar heat of mixing.

A value of $\overline{\Delta H}_1$ can be obtained from the cohesive energy densities of the penetrant and the polymer by the Hyldebrand equation

$$\overline{\Delta H}_1 = \overline{V}_1 \left(\delta_1 - \delta_2\right)^2 \phi_2^2$$

The solubility parameters δ_1 and δ_2 are the square roots of the cohesive energy densities of the penetrant and polymer, $\overline{V}_1$ the partial molar volume of the penetrant and ϕ_2 the volume fraction of polymer in the mixture.

Diffusion

Diffusion is the process in which components are transported from one part of a mixture to another as a result of random molecular motion.

The diffusion flow or flux J of a substance is the amount passing during unit time through a surface of unit area normal to the direction of flow, that is

$$J = Q/At$$

Q is the total amount of substance which has passed through area A during time t. The first law of Fick

$$J = -D \frac{\partial c}{\partial x}$$

and the second

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

allow the determination of the Diffusion coefficient. Of course the appropriate solution of the diffusion equation is dependent on the sample geometry and the initial and boundary conditions for the particular system investigated. Generally D is not independent of concentration and then the second law must be written as

$$\frac{\partial c}{\partial t} = D(c) \frac{\partial^2 c}{\partial x^2} + \left[\frac{\partial D(c)}{\partial c}\right] \left(\frac{\partial c}{\partial x}\right)^2$$

A general method for obtaining variable diffusion coefficients D(c) is to perform experiments over sufficiently small intervals of concentration so that the term $\partial D(c)/\partial c$ is small and can be omitted. We obtain therefore a mean value of diffusion coefficient $\bar{D}$.
The dependence of the diffusion coefficient on sorbed penetrant concentration has usually been empirically represented by equations of the form

$$\bar{D} = D_0 \exp(\gamma c)$$

where D_0 is $\bar{D}$ in the limit of zero penetrant concentration and γ a characteristic parameter of the system at a given temperature. The parameter γ characterizes the effectivness with which equal amounts of various penetrants plasticize a polymer to facilitate segmental mobility and, hence, to increase the rate of diffusion of penetrant.

Methods of measurements

One of the central problems in the study of transport properties is to evaluate S and D for a given system as a function of such parameters as penetrant concentration and temperature.
Two experimental methods are available for this purpose: they are the sorption method and the permeation method.
In a permeation experiment, the amount of penetrant vapour flowed through a film of a given polymer is measured as a function of time under the condition that one surface of the film is allowed to get in contact with penetrant vapour at a constant pressure and the other surface is exposed to the vacuum.

In a sorption experiment a film of a given polymer is exposed to vapour of a given penetrant substance at a given activity or vapour pressure, and the gain or loss in weight of the film is measured as a function of time. Experimental data are plotted as the relative weight gain M_t/M_∞ versus $\sqrt{t}$ where M_t and M_∞ are the mass sorbed from a sample of thickness d at t=t and t=∞ respectively, as illustrated in Fig.2.
From the initial stage of sorption

$$\frac{M_t}{M_\infty} = \frac{4}{d} \left[\frac{\bar{D}t}{\pi}\right]^{1/2}$$

and it is possible to calculate $\bar{D}$.

The role of Fractional Free Volume (FFV)

It has long been a mystery why diffusion coefficients of polymer-diluent systems exhibit so pronounced a concentration dependence, especially when the diluent is a good solvent or swelling agent for a given polymer.
A very rough but quite satisfactory description of the dependence of transport parameters on polymer phase, size of permeant molecule and temperature, can be obtained on the basis of FFV concept.
The penetrant molecules are absorbed in the membrane only if there is space for their accomodation or it can be created. The probability for such an operation increases with the FFV of the polymer-penetrant system and decreases with the size of the penetrant molecule. The same applies to the mobility that is to the diffusion coefficient D. We can consider the value FFV as an entropic quantity measuring the probability for the creation of a sorption site, that is a hole for the accomodation of a molecule of penetrant. Such a statistical concept of FFV includes not only the specific volume of the sample in excess of the actual volume of the macromolecules and the sorbed penetrant molecules, but also the rigidity of the macromolecules and the intermolecular forces.
In the validity range of the linear additivity of FFV of sorbate f_1 and polymer f_2, we can write

$$f = f_1 v_1 + f_2 v_2$$

According to Hildebrand and Flory-Huggins theories

$$S = f_2 / f_1 p_T \exp(1+\chi_1) = f_2 / A_S$$

Therefore the Sorption is proportional to the FFV of polymer and inversely proportional to that of the penetrant.
For what concerns the dependence of diffusion on FFV, the usual definition of the molar mobility m_D of a penetrant is

$$\bar{D}_T = RT m_D$$

$\bar{D}_T$ is the thermodynamic diffusion coefficient of penetrant.
According to Cohen and Turnbull theory and Doolittle viscosity equation, the mobility of a penetrant molecule can be related to the FFV

$$m_D = A_0 \exp(-B_d/f)$$

therefore

$$\bar{D} = \bar{D}_0 \exp(-A_D/f)$$

As a consequence of the exponential dependence of D on FFV, the diffusion coefficient varies much more rapidly with FFV than the sorption coefficient. The concentration coefficient which relates diffusion and concentration also depends very strongly on FFV

$$\gamma = A_D f_1 / v_2^2 f_2^2$$

It is inversely proportional to the square of FFV. Therefore also γ depends much more than Sorption on FFV.

Two component system

The dependence of sorption,diffusion and concentration coefficient on FFV describes very well the enormous difference of transport properties between amorphous and crystalline phase in a semicrystalline system.
As a consequence of the so much smaller FFV of the crystals, the Sorption and Diffusion coefficients are negligibly small compared with those of the amorphous phase.Therefore in amixture of crystalline and amorphous phases the diffusive transport through the former can be completely neglected and we can cosider the crystals just as an impermeable obstacle hampering the diffusive transport through the material.
Under the assumption of completely uniform and relaxed amorphous component, the amount of sorbed penetrant, w , per unit volume of dry sample is proportional to the volume fraction ($1-\alpha$) of amorphous component

$$w = (1-\alpha)\, w_a$$

Since the amorphous phase exist as a complex network of tortuous and flat broad channels and the amorphous chains are restrained in mobility by their ends fixed in the crystals, the effective diffusion coefficient D of the sample will be smaller than D of the purely amorphous phase

$$D = \psi\, D_a / \beta$$

where ψ is the detour ratio and B the blocking factor.
The dependence of the transport properties on FFV and on the overall morphology of the system, makes the transport phenemena an extremely sensitive tool for the investigation of the packing of macromolecules in the amorphous phase,and its change under the influence of mechanical and/or thermal treatments.

Membranes

It is very important the fact that successful industrial and medical developments of membranes have been made, based on the more and more deep knowledge of transport properties of the materials.Many examples of industrial membranes can be cited.The principal uses of industrial and medical membranes are the following:

1) Hyperfiltration and desalination of sea-water

2) Separation of hydrocarbons by selective permeation

3) Packaging for foods and beverages

4) Polymeric coatings and encapsulants for electronic devices

5) Systems for controlled administration of drugs

There are,unfortunately,many examples of products designed and produced with an apparent lack of proper consideration of the solution or transport characteristic of the material.Particular environments can affect the performance and lifetimes of polymeric materials and this effect must be carefully examined before the use.For example the sorption of ambient vapours or liquids can plasticize the material with a consequent decrease in mechanical properties.In other cases the bottled beverage components,as CO_2 or alcohol,can be loss , determining a change of beverage characteristics.Therefore it is of the utmost importance to carefully evaluate the transport properties of the materials before their application.

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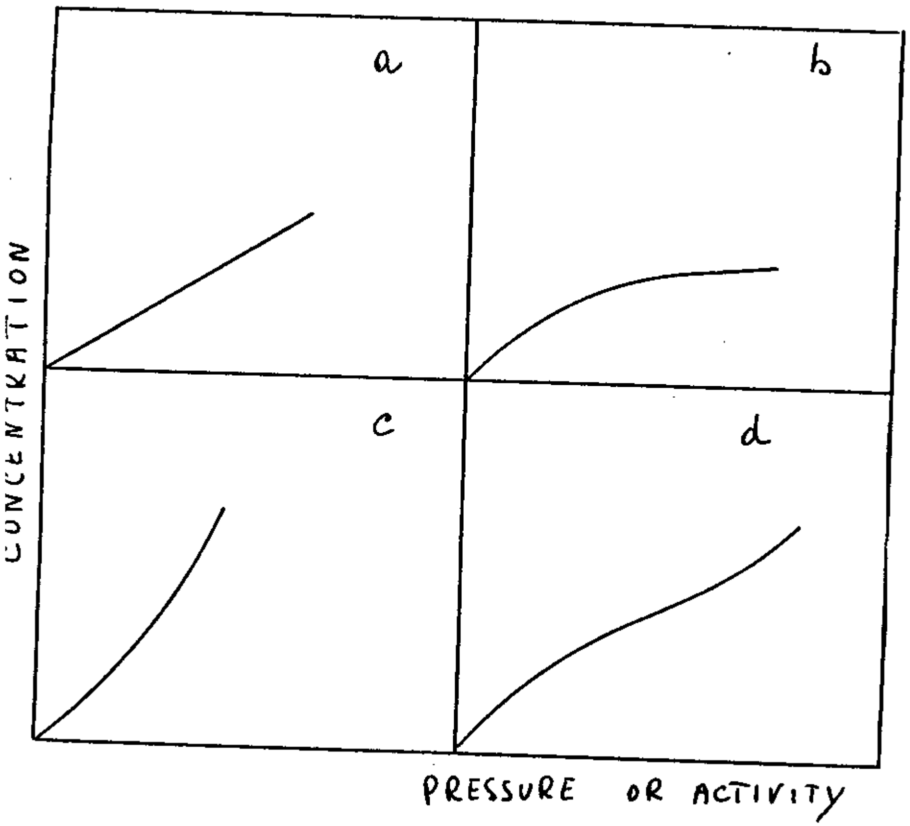

FIG. 1

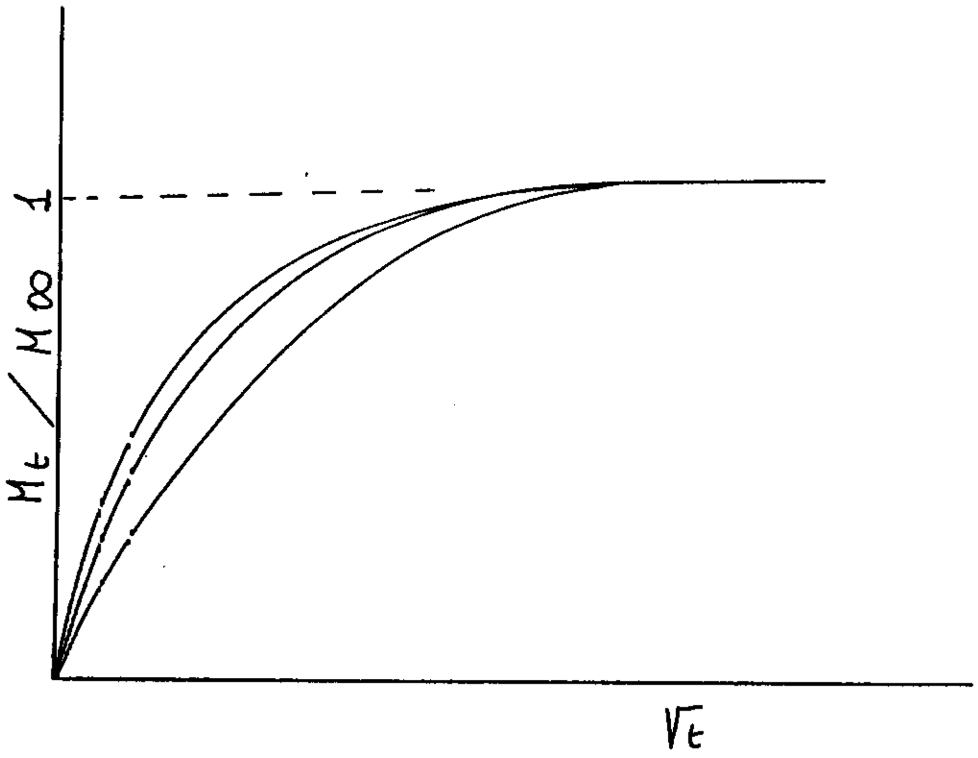

FIG. 2