



Transport phenomena through polymeric systems

Soney C. George¹, Sabu Thomas*

School of Chemical Sciences, Mahatma Gandhi University, Priyadarshini Hills P.O., Kottayam 686560, Kerala, India

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Abstract

Transport of gases, vapours and liquids through polymers is an important and in some cases, controlling factor in several applications such as protective coatings, membrane separation processes and packaging of foods and beverages. Therefore a better understanding of transport mechanisms in polymers is highly important in order to achieve significant improvement in these areas. This article provides a detailed review of current research in the field of transport phenomena and membrane assisted transport processes. Topics covered include the factors affecting transport processes and transport in various polymeric systems. The relationships between membrane characteristics, polymer structure and separation efficacy are treated in detail. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Transport; Permeation; Pervaporation; Vapour permeation; Gas permeation; Polymer; Polymer blend; Membranes

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* Corresponding author. Tel.: +91-481-598303; fax: 91-481-561190.

E-mail addresses: cec@giasmd01.vsnl.net.in (S.C. George),
sabut@vsnl.com (S. Thomas), mgu@md2.vsnl.net.in (S. Thomas).

¹ Present address. Department of Polymer Technology, Crescent Engineering College, Vandalur P.O., Chennai 600048.
Fax: +91-44-2376520.

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1. Introduction

Towards the end of the twentieth century, great attention has been focused on the field of diffusion, sorption and permeation because these basic phenomena play a vital role in several important areas of engineering and industry. These include protective coatings such as paints and varnishes, electronic devices and cable materials, packaging materials for foods and vegetables, biomedical devices, etc. [1–4]. Transport studies are of considerable importance when we come across problems like designing a barrier material or tubes for transporting liquids and gases.

Recently, a combination of improved economics and better technology has resulted in membrane products and this has resulted a new era in the commercial use of membranes for liquid and gas separation. The advantages of membrane separation over conventional processes, consists of reduced capital cost, lower energy consumption and lower installation costs due to its modular design and simplified operation [5]. Membrane separation techniques have already been used in some industrial applications like the desalination of brine, salt manufacturing from sea-water and oxygen enriched air [6]. Another technique of importance is pervaporation, which has been recently used for the separation of a wide variety of organic liquid mixtures [7,8]. In order to design highly efficient and economically viable barrier materials and membranes, the elucidation of the relationship between transport properties and molecular structure of polymers is necessary.

The aim of research in this field is to establish mechanisms and laws, relating solubility and transport in polymer membranes, to their molecular properties, the nature of the penetrants and the polymer morphology. Therefore, in most cases small molecules are used as a molecular probe for investigating the link between transport phenomena and polymer structure.

2. Fundamentals of transport phenomena

The transport of small molecules through a polymer membrane occurs due to random molecular motion of individual molecules [9]. The driving force behind the transport process which involves sorption, diffusion and permeation is the concentration difference between the two phases [9]. The transport process slowly tries to equalise the concentration difference or the chemical potential of the penetrant in the phases separated by the membrane. This process can be described in terms of Fick's first law of diffusion, according to which the flux J , in the direction of flow is proportional to the

concentration gradient ($\partial c/\partial x$) as

$$J = -D \left(\frac{\partial c}{\partial x} \right) \quad (1)$$

Here D is the diffusion coefficient. Eq. (1) is applicable to the diffusion in the steady state, i.e. when the concentration does not vary with time. On the other hand, Fick's second law describes the nonsteady state for transport process, which is given by the rate of change of the penetrant concentration ($\partial c/\partial x$) at a plane within the membrane, i.e.

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

This is an ideal case in which the membrane is isotropic and the diffusion coefficient is independent of distance, time and concentration. Depending on the boundary conditions, many solutions [10] are available for Eq. (2).

Strong polymer–penetrant interaction occurs with many organic penetrant molecules and hence D is dependent on concentration. Therefore, Eq. (2) becomes,

$$\frac{\partial c}{\partial t} = D \frac{\partial D(c)(\partial c/\partial x)}{\partial x} \quad (3)$$

Analytically this cannot be solved easily and hence another form of Eq. (4) is commonly used.

$$\frac{\partial c}{\partial t} = D(c) \frac{\partial^2 c}{\partial x^2} + \frac{\partial D(c)}{\partial c} \left(\frac{\partial c}{\partial x} \right)^2 \quad (4)$$

Generally experiments are conducted over relatively small intervals of c and the term $(\partial D(c)/\partial c)$ is negligible compared to $D(c)$. Then we get a mean or integral diffusion coefficient \bar{D} over a concentration range c_1 to c_2 , as given by

$$\bar{D} = \int_{c_1}^{c_2} D(c) dc/c_1-c_2 \quad (5)$$

where c_1 and c_2 are the concentrations of penetrant at the low and high concentration faces of the film, respectively.

In the steady state, diffusion flow is constant and the diffusion coefficient is independent of concentration. Then Eq. (1) may be integrated to give

$$J = \frac{D(c_1-c_2)}{h} \quad (6)$$

where h is the membrane thickness. The penetrant distribution between the penetrant and the polymer phase is described by the Nernst distribution law.

$$c = KC \quad (7)$$

where c is the sorbed concentration; C , the ambient penetrant concentration in contact with the polymer surface and K depends on temperature and c . In the case of transport of gases and vapours, pressure p is

used instead of surface concentration. According to Henry's law

$$c = Sp \quad (8)$$

where S is the solubility coefficient. The combination of Eqs. (6) and (8) gives the well-known permeation equation

$$J = \frac{DS(p_1 - p_2)}{h} \quad (9)$$

where p_1 and p_2 are the ambient pressures on two sides of a film of thickness h . The product DS is called the permeability coefficient P , so that

$$P = DS \quad (10)$$

In terms of permeability, the flux Eq. (9) can be written as

$$J = \frac{P(p_1 - p_2)}{h} \quad (11)$$

3. Factors contributing to transport processes

3.1. Nature of the polymer

The transport behaviour for a given penetrant varies from one polymer to another. Transport properties depend on the free volume within the polymer and on the segmental mobility of the polymer chains. The segmental mobility of the polymer chains is affected by the extent of unsaturation, degree of crosslinking, degree of crystallinity and nature of substituents. The glass transition temperature of polymers has a profound influence on transport properties. Polymers with low glass transition temperatures possess greater segmental mobility and will have higher diffusivity. This is clearly illustrated in Fig. 1 [11].

The considerable increase of D_0 with decreasing value of T_g is accompanied by a considerable decrease in the concentration dependence of the diffusion coefficient. For example, the diffusion coefficient of benzene in natural rubber, polyethylacrylate and polymethacrylate, with T_g values of 200, 250 and 280 K, respectively, increases by 2.9, 20 and 340 times on increasing the volume fraction of benzene from 0 to 0.1. Barrer et al. [12] have shown that the diffusion coefficient of krypton in silicone rubber at 25°C is $1.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ whereas in poly(vinyl acetate), at the same temperature it is $1.9 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$. This effect can be correlated with a considerable drop in T_g .

It is found that diffusivity is decreased when the extent of unsaturation in the polymer backbone is lowered by hydrogenation. Auerbach et al. [13] have reported a three-fold decrease in the diffusion coefficient for octadecane through polyisoprene, as the residual unsaturation was decreased from 100 to 37% by hydrogenation. This is because unsaturation in polymer chains provides for segmental mobility, whereas saturation tends to restrict it.

Barrer and Skirrow [14] have studied the diffusion of a series of alkanes through rubbers and reported that for low levels of crosslinking, the diffusivity decreased linearly with an increase in crosslink density. At higher levels of crosslink density, the rate of decrease of diffusivity levelled off.

The introduction of bulky or polar substituents on the polymer chain, influences the transport process.

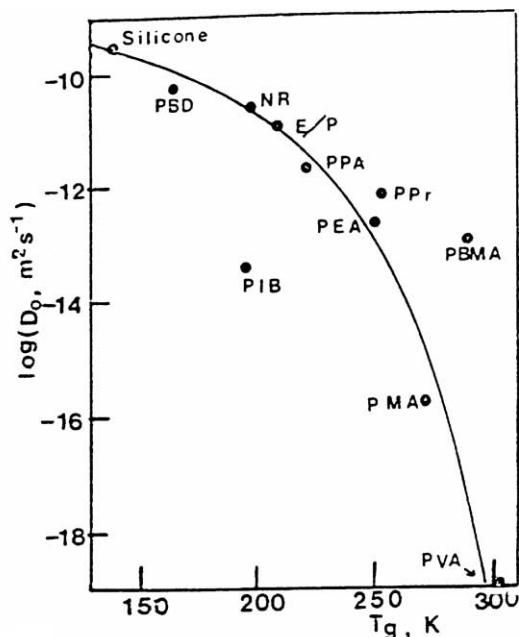


Fig. 1. Correlation of diffusion coefficient D_0 for benzene with the glass transition, T_g , of the diffusion medium. PBD = cis polybutadiene; NR = natural rubber; PEA = poly(ethylacrylate); PMA = poly(methylacrylate); PVA = poly(vinylalcohol); EP = ethylene propylene copolymer; PPA = polypropylacrylate; PPr = polypropylene; PBMA = polybutylmethacrylate; PIB = polyisobutene. Reprinted with permission from J. Paint Technol 1970;42:16. ©1970 Federation of Societies for Coatings Technology [11].

Van Amerongen [15] has reported that rubbers containing large numbers of substituent methyl groups have lower diffusivities. For instance, the low permeability of butyl rubber is due to the sluggish segmental motion of the polymer chains, caused by the steric hindrance of the two pendant methyl groups on every other main chain carbon atom. Data shown in Table 1 demonstrate that, for polymers with the same substitution pattern, it is the flexibility of the backbone that dominates permeation properties [16].

The Si–O backbone allows for rapid chain segment motion to occur in the silicone rubber (polymer C) and substitution of the Si–O linkage by Si–CH₂ (polymer B) dramatically reduces the permeability to a value even less than that of butyl rubber (polymer A). The insertion of a (CH₂)_n sequence into a siloxane backbone (polymer D) also leads to a decrease in permeability. Similarly, the Si–O backbone substitution of methyl by more bulky substituents decreases the permeability (polymer E). These decreases in permeability are mainly due to a decrease in permeant diffusivity, caused by an increasing rigidity of the polymer backbone and a decreasing free volume available for the diffusion of the permanent molecules. The substitution of bulky functional groups in the side chains appears to have a greater influence on decreasing diffusivity than substitution of these groups in the polymer backbone [16–18].

It was also reported that the polymer molecular weight, significantly influences the transport process. As polymer molecular weight increases, the number of chain ends decreases. The chain ends represent a discontinuity and may form sites for permeant molecules to be sorbed into glassy polymers. For instance, for a series of polystyrene samples, the diffusivity of a range of organic vapours (acetone, benzene, etc.) decreased by a factor of almost ten as molecular weight increased from 10,000 to 300,000 [19].

Table 1
The effect of side chain and main-chain substitution on oxygen permeability

Polymer	T_g (°C)	$P \times 10^{-17}$ (mol m ⁻¹ s ⁻¹ Pa ⁻¹) ^a
A	-76	0.84
B	-92	0.44
C	-123	437.0
D	-88	1.0
E	-28	0.14

^a At 35°C.

The permeability of permeants which interact weakly with functional groups present in a polymer can be expected to decrease as the cohesive energy of the polymer increases. For example, by increasing the polarity of the substituent group on a vinyl polymer backbone, oxygen permeability is reduced by almost 50,000 times, as shown in Table 2 [20].

The transport phenomenon is strongly related to the structure of the elastomers [21]. Penetrant mobility in the polymer and the sorption magnitude can be influenced by chain segmental mobility and interactions of different elastomers. For an increase of molecular size from C₈–C₁₆, the sorption rate and sorption magnitude decrease. In all solvents, at higher temperatures EPDM showed a lower uptake and this has been attributed to induced crystallinity at higher temperatures in the presence of penetrants.

Table 2
Effect of functional groups on oxygen permeability of vinyl polymers (CH₂CHX)_n

Functional group	$P \times 10^{-17}$ (mol m ⁻¹ s ⁻¹ Pa ⁻¹) ^a
H	1.3
Ph	1.1
Me	3.97×10^{-1}
F	3.96×10^{-2}
Cl	2.1×10^{-2}
CN	1.08×10^{-4}
OH	2.64×10^{-5}

^a At 23°C, 0% relative humidity.

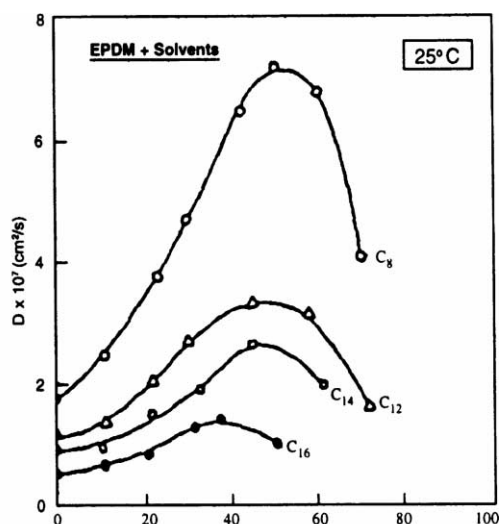


Fig. 2. Dependence of diffusion coefficient on concentration of solvents for EPDM membranes. Reprinted with permission from *Macromolecules* 1991:24:2598. ©1991 American Chemical Society [21].

The induced crystallinity reduces the free energy of mixing and hence the solvent uptake. Natural rubber also exhibited similar behaviour with 2,2,4-trimethyl pentane. The mechanism of sorption slightly deviates from Fickian to anomalous behaviour and this could be supported by the slight sigmoidal nature of the sorption curve. The concentration dependency of the diffusion coefficient was evident from the significant swelling as shown in Fig. 2 [21].

3.2. Nature of crosslinks

For the same polymer with the same crosslink density, transport phenomena depend on the nature of the crosslinks. Poh et al. [22] have studied the sorption behaviour of bulk and solution crosslinked natural rubber networks prepared by irradiation with γ -rays. They found that in benzene solutions, crosslinked networks swell more than the corresponding bulk crosslinked networks having the same crosslink density.

Unnikrishnan et al. [23] have investigated the effect of the nature of crosslinks on the diffusion and transport of aromatic hydrocarbons through natural rubber membranes. Natural rubber was vulcanised by four vulcanizing systems viz. conventional, efficient, dicumyl peroxide and a mixture consisting of sulphur and peroxide. All these samples under a common rheometric torque were subjected to swelling in various solvents to study the effect of the vulcanising system on diffusion. It was found that NR crosslinked with CV systems absorbs the highest amount of solvent whereas that crosslinked using a peroxide system takes the lowest. The sample crosslinked by mixed and EV systems exhibits intermediate behaviour. Representative diffusion curves are given in Fig. 3. The difference in the maximum Q_∞ values of NR with different crosslinking systems has been related to the different types of crosslinks present in them. The structure of networks formed during vulcanization is depicted in Fig. 4. The polysulfidic linkages in CV systems impart high chain flexibilities to the network and hence afford maximum solvent uptake. NR with the mixed system also has polysulfidic linkages along with C–C linkages. Hence this system stands second to CV system. For EV systems, less flexible mono or

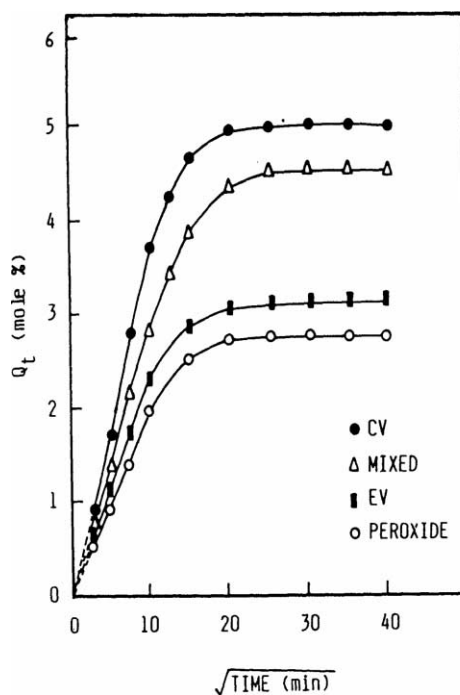


Fig. 3. Mole percent mesitylene uptake of natural rubber with different crosslinking systems at room temperature. Reprinted with permission from Polymer 1994;35(25):5504. ©1994 Elsevier Science Ltd [23].

disulfidic linkages are formed and hence this system shows lower Q_t values compared to CV and mixed systems. The stable C–C bonds formed with the DCP system shows the lowest Q_t values. Also, the effect of different fillers on the swelling nature of crosslinked NR was studied using carbon black and silica fillers. The silica filled sample took higher amounts of solvents than carbon filled samples. This is attributed to the fact that in carbon filled samples, the rubber binds tightly with carbon black which effectively binds the individual polymeric chains. Since the surface of silica is polar it can deactivate the accelerator, which leads to the ineffective curing of the sample. The χ values for the different systems indicate maximum-solvent interactions for the CV system (Table 3).

3.3. Effect of plasticisers

The addition of plasticisers to a polymer results in increased segmental mobility and usually in an

Table 3
Values of interaction parameter (NR toluene)

System	χ
Peroxide	0.30
EV	0.29
Mixed	0.28
CV	0.27

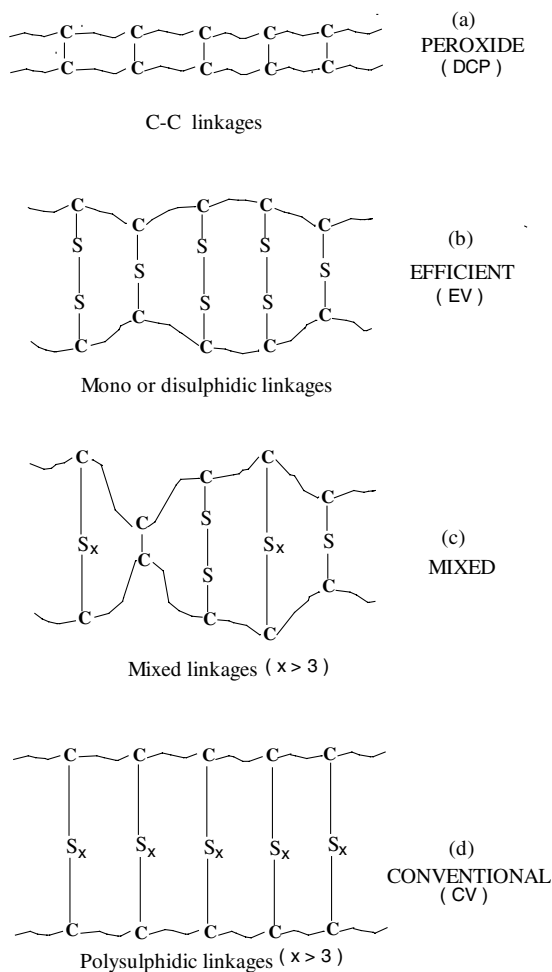


Fig. 4. Structure of the networks formed by different vulcanization techniques. Reprinted with permission from Polymer 1994;35(25):5504. ©1994 Elsevier Science Ltd [23].

increased penetrant transport. Detailed accounts on the effect of plasticizers and humidity have been given by Stannett et al. [24]. Barrer et al. [25] have reported the increase in diffusion coefficients for the transport of hydrogen and neon through poly(vinyl chloride) upon the addition of tricresyl phosphate as a plasticiser for the polymer. The plasticiser was found to lower the solubility coefficient.

3.4. Nature of the penetrant

The size and shape of penetrant molecule will influence its rate of transport within the polymer matrix. A decrease in diffusivity with an increase in the size of the penetrant has been reported by many investigators [26,27]. Kim et al. [28] have reported a decrease in equilibrium penetrant uptake with increasing penetrant chain length for the transport of alkanes from heptane to dodecane through cross-linked polystyrene. The permeant's shape also has a noticeable effect on permeability. For instance,

flattened or elongated molecules have higher diffusion coefficients than spherical molecules of equal molecular volume [19,29]. Generally, permeant size and shape effects are much more marked in glassy than in rubbery polymers. This arises from the differences in the permeant–polymer mixing processes. In rubbery polymers, energy is required to generate sites for the permeant molecules to occupy, but since increasing permeant size tends to increase the heat of sorption, it follows that larger permeant molecules will be readily sorbed leading to enhanced plasticisation of the polymer chains. Consequently, while smaller permeants will have a greater diffusion coefficient, the polymer will be less plasticised, whereas the lower diffusion coefficient of the larger permeants will be compensated for by the higher degree of sorption. The overall effect is to minimise any differences in the permeation coefficients for large and small permeants.

3.5. Fillers

The diffusion and transport in filled polymers depend upon the nature of fillers, the degree of adhesion and their compatibility with the polymer matrix. If the inert filler used, is compatible with the polymer matrix, the filler will take up the free volume within the polymer matrix and create a tortuous path for the permeating molecules [30]. The degree of tortuosity is dependent on the volume fraction of the filler and the shape and orientation of the particles. When the filler is incompatible with the polymer, voids tend to occur at the interface, which leads to an increase in free volume of the system and consequently, to an increase in permeability. Coran et al. [31] studied the transport of solvents in unidirectional rubber–fibre composites and concluded that fibres restrict the solvent uptake. Equilibrium swelling in solvents was found to be a very good technique for assessing rubber–fibre adhesion in fibre filled composites. Lowering of equilibrium swelling in fibre filled samples indicates excellent fibre–rubber adhesion.

Das [32] reported that restricted equilibrium swelling is a true measure of adhesion between short fibres and rubber. Varghese and co-workers [33] used equilibrium swelling as a probe for investigating the adhesion between short sisal fibre and natural rubber. The restriction to elastomer swelling, exerted by the sisal fibre, as well as the anisotropy of swelling of the composite have been confirmed from diffusion experiments. The swelling decreased with an increase of fibre content and also with the addition of bonding agents. They have also found from diffusion studies that chemically treated fibres have better adhesion to natural rubber than untreated fibres.

3.6. Temperature

The variation of diffusivity, sorptivity and permeability coefficients with temperature is described by the following Arrhenius relationship [34,35]

$$D = D_0(e^{-E_D/RT}) \quad (12)$$

$$S = S_0(e^{-\Delta H_s/RT}) \quad (13)$$

$$P = P_0(e^{-E_p/RT}) \quad (14)$$

where E_D and E_p are the activation energies of diffusion and permeation, respectively, ΔH_s is the heat of solution of the penetrant in the polymer and D_0 , S_0 and P_0 are the pre-exponential factors. Both E_p and E_D

are related as follows

$$E_p = E_D + \Delta H_s \quad (15)$$

The enthalpy of sorption ΔH can be computed using Van't Hoff relation

$$\log K_s = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad (16)$$

In this equation, K_s is the thermodynamic sorption constant and ΔS the entropy of sorption. In most cases ΔH_s and ΔH determined by Eqs. (15) and (16) are approximately the same.

There are reports relating to the deviations from the above relations, especially in the region of the glass transition temperature of the polymer concerned, where a break between two straight lines in the Arrhenius plot is often observed. The calculated activation energy values are normally greater above T_g than below it. A typical example is the data of Mears [36] for the diffusion, solubility and permeation of hydrogen, helium, oxygen, neon and argon through poly(vinyl acetate).

4. Transport phenomena in different polymeric systems

4.1. Diffusion in rubbery polymers

Important characteristics of rubbery polymers are unsaturation, segmental mobility and the large amount of free volume between molecules. Hence smooth and easy diffusion of small molecules through rubbery polymers is usually observed. Owing to its two phase-morphology, the transport of organic solvents through polyurethane (PU) membrane is highly interesting. Hung and Autian [37] studied the transport behaviour for PU with a series of aliphatic alcohols in the temperature range of 24–50°C by using the thermogravimetric sorption method. The diffusivity values were calculated from the desorption curves by means of an integrated form of Fick's relation. The diffusion coefficient, D , was found to increase with temperature and decrease with an increase in the molecular weight of penetrants. On the other hand, the branched alcohols exhibited lower D values as expected. The activation energies (E_D) for diffusion were also calculated. The E_D values increase with an increase in molecular size and the diffusion results were analysed on the basis of Eyring hole theory [38].

Transport studies on the interactions of a wide range of organic liquids, having a variety of structural/functional groups, with polyurethane membranes have also been reported [39]. In this analysis, the effect of temperature, molecular size and the polarity of the solvent on the interactions were all examined. Among the solvents used, chlorobenzene exhibited a strong affinity for polyurethane. But hexane, the symmetrical nonpolar solvent showed less interaction with the PU membrane. The diffusion coefficient was found to follow an inverse relationship with the size of the molecule.

Hopfenberg and co-workers [40] have reported steady state permeation rates concerning equilibrium sorption for a series of alcohols (C_1 – C_7) in a polybutylene adipate polyurethane polymer membrane. Solubility coefficients as well as diffusion coefficients were satisfactorily correlated with diffusant sizes. Owing to the steric hindrance, branched alcohols have lower solubility coefficient values. The diffusivity exhibited concentration dependent behaviour.

The rate of absorption of benzene by open cell polyurethane foam of varying sizes has been investigated [41]. The rate of absorption was found to depend on the size of the cell. In order to estimate matrix diffusivities and pore mass transfer coefficients, a dual resistance model was used. There was a good agreement between pore mass transfer coefficients with the order of magnitudes of the steady state resistance for pore diffusion. Therefore, bulk flow is found to be important in the absorption process. Experimental results suggest that the bulk flow was more rapid than pore diffusion. On the basis of experimental results, it was concluded that pore diffusion is more important than bulk flow in foams, giving resistant absorption behaviour, which is characteristic of closed cell foams.

The sorption and diffusion of a series of liquids through polyurethane membrane showed how this behaviour is affected by the choice of solvent and the heterophase nature of the polymer [42]. Sorption experiments in *n*-heptane liquid and incremental sorption experiments in *n*-heptane vapour showed normal Fickian behaviour. With increasing polarity of liquids, the swelling increases to a maximum level. The molar mass between crosslinks computed from the Flory–Rehner equation assuming complete phase segregation varied with different liquids. Oberth [43] developed a new swelling model for determining crosslink density of polyurethane elastomers. The model is based on the assumption that every element in the polymer will solvate to the same extent, regardless of whether it belongs to a short or long chain.

The interactions of industrially important solvents with commercially available polyurethanes have been studied in detail [44]. The interaction of halogen substituted organic penetrants with a polyurethane membrane over the temperature interval of 25–60°C has been reported. Sorption data have been interpreted in terms of the percentage weight gain of the polymer with respect to time. Except for trichloroethylene, sorption was found to increase with an increase of temperature. This might be due to the specific interactions of trichloroethylene with the hard segment part of the polyurethane. The diffusivity and permeability values were found to be higher for trichloroethylene and 1,2-dichloroethylene compared to other penetrants, but the solubilities of these two penetrants were comparable.

Lawandy and Helaly [45] investigated the penetration rate of chloroform in chloroprene rubber vulcanisate with different carbon black type and loading. They observed an increase in the penetration rate with the increase in loading percentage. An inverse relationship was noticed between the particle size of carbon black and the penetration rate, at higher degrees of equilibrium. This was attributed to the wrinkles formed at the surface of the rubber at high equilibrium swelling. Chiang and Sefton [46] used diffusion analysis to investigate the morphology of styrene–butadiene–styrene (SBS) triblock copolymer. Unlike the diffusion process in conventional rubber, they found that the diffusion of cyclohexane vapour in SBS thermoplastic elastomer exhibits non-Fickian time-dependent characteristics. The time-dependent diffusion was attributed to the inability of the polymer molecules to respond instantaneously to the change in concentration. This slow response was due to sorption by the interfacial region at a temperature below its glass transition. The equilibrium diffusion coefficient was estimated to be $3.2 \times 10^{-7} \text{ cm}^2/\text{s}$ regardless of the casting surface. According to the sorption measurements, the casting surface did have an effect on the approach to equilibrium. The results indicated a close packing of the molecules and hence a decreased diffusion coefficient for teflon and glass cast films, because of internal stresses left within the films during casting.

The integral absorption and desorption of *n*-hexane vapour by styrene–butadiene block copolymers were studied as a function of film thickness and vapour pressure at 25°C by Odani et al. [47]. These

studies indicated that S–B block copolymer films having two different types of morphologies exhibited two non-Fickian features: the thickness anomaly in the reduced absorption and desorption curves and the two-stage absorption curve at a certain concentration. The segmental motions in the PB phase of the copolymers are more restricted than in the PB homopolymer, even at a temperature well above the glass transition of the PB blocks. The chain immobilisation effect and the geometric impedance effect due to the presence of impermeable PS domains interfere with the transport of penetrant molecule in the copolymer solid.

The mutual diffusion coefficients for styrene butadiene rubber (SBR)-*n*-nonane system by sorption method has recently been studied [48]. The mutual diffusion coefficients were correlated with the free volume theory. Guo et al. [49] designed an experimental method based on a gravimetric permeation cell and successfully used this for measuring the diffusivities and permeabilities of several rubber-solvent systems. For the four solvents diffusing in the same rubber, the diffusion coefficients followed the order, chloroform > benzene > ethyl benzene > *o*-xylene. This is consistent with the effect of molecular geometry. The molecule with a greater effective diameter shows a slower diffusion rate in a given polymer. The diffusion in different rubbers follow the trend: silicone > natural > bromobutyl. This may be related to the difference in fractional free volumes and polymer chain flexibilities in these rubbers.

The validity of the swelling method for the determination of the interaction parameter using the Flory–Rehner theory and the phantom network assumption has been a subject of investigation recently [50]. Poly(dimethyl siloxane) was used for this study. Experiments were carried out based on the assumption of the additivity of the free energy of mixing and on the elastic free energy of the Flory–Rehner model. It was reported that the interaction parameter may have some dependence on crosslink density in addition to polymer concentration.

Schneider and co-workers [51] have investigated toluene diffusion in butyl rubber. They measured the sorption isotherms and the polymer mass-fixed diffusion coefficient, D_1 , for toluene in butyl rubber by the incremental sorption method. The increase in D_1 with concentration is strongly exponential to a concentration of 30% and then begins to level out.

The applicability of Flory–Rehner theory of swelling has been demonstrated by differential swelling measurements on two poly(dimethyl siloxane) (PDMS) networks [52]. The two elastomers are more or less similar in their structure except for the chemical nature of their crosslinks. The samples were swollen in benzene and cyclohexane at 20 and 30°C. The reduced dilation moduli of the two samples parallel to one another in a given solvent at a fixed temperature reveal that solvent and temperature dependences are not encompassed by any known theory.

The molecular transport of organic liquids through a series of rubber membranes has been studied by Thomas et al. [53–56]. They investigated the effects of the nature of crosslinks, penetrant size and temperature on diffusion behaviour in different polymeric membranes.

4.2. Diffusion in glassy polymers

Glassy polymers are characterised by hard and brittle moiety with restricted chain mobility. Rotation about the chain axis is limited and motion within the structure is largely vibratory within a frozen quasi-lattice. These dense structures have very little void space (0.2–10%). Therefore diffusion in glassy polymers is more complex compared to that in rubbery polymers.

Choy et al. [57] investigated the toluene diffusion in highly oriented polypropylene with draw ratios

from 1 to 18. Drawing converted the initially spherulitic materials into a fibrous structure with many taut tie molecules lying mainly on the outer boundary of the microfibrils. Therefore the free volume and sorption sites were reduced and the microfibrils become less and less permeable as the draw ratio increases. The diffusivity shows an exponential increase with toluene concentration but the concentration dependence becomes weaker with increasing draw ratio indicating that the severely constrained chain segments in the drawn samples have much less freedom to mix with penetrant molecules. Annealing releases the toluene molecules and thus restores the sorption and diffusion properties to values corresponding to completely relaxed amorphous component, i.e. to values even higher than those of the undrawn but quenched material.

Orchard and Ward [58] have reported that when the polyethylene tubes were immersed in toluene (liquid) a change in weight was obtained. They have estimated the diffusion rates from these values. They also compared the drawn and undrawn tubes of isotopic homopolymer and copolymer feed stocks. The equilibrium uptake values of the drawn tubes were at least three times lower than those of the feed stock with diffusion coefficient reduced by a factor of twelve or more. New and efficient techniques for estimation of diffusion parameter have been proposed by Ravetkar and co-workers [59]. They used the moments technique for estimating absorption parameters. The validity of these techniques has been demonstrated by the analysis of the data on adsorption of polyacrylamide.

The self-diffusion of benzene, toluene and ethyl benzene in polystyrene using the Vrentas–Duda free volume diffusion model [60,61] has been reported [62]. Zielinski and Duda [63] found that predictions of solvent self-diffusion over ranges of temperature and concentration are in much better agreement with experimental observation than mutual-diffusion coefficients. Diffusion coefficient predictions suggest an exponential concentration dependence of the activation energy required to overcome attractive forces, E . Without the use of any diffusion data, approximating E as zero over the entire concentration range yields self-diffusion coefficient predictions which are in good agreement with experimental data.

The self-diffusion coefficient of dodecane in crosslinked polystyrene by means of pulsed gradient spin echo nuclear magnetic resonance (PGSE-NMR) spectroscopy has been measured [64]. By using the free volume model of Fujita and Vrentas–Duda, the concentration and temperature dependence of the diffusivity was analysed. Parameters describing the Fujita model were determined from fitting diffusion data to the PVT behaviour of the system. From the analysis of the viscosity of dodecane, the viscoelastic relaxation properties and the glass transition temperature of polystyrene were determined. The parameters describing the Vrentas–Duda model were determined from the diffusion coefficient of the system. Both the Fujita and Vrentas–Duda models described the concentration and temperature dependence of the diffusion coefficient. Diffusion behaviours of two polyimides (PIS) synthesised from 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), 4,4'-oxydianiline (ODA) and 4,4'-diamino diphenyl sulfone (DDS) were investigated by Moon and Lee [65].

The weight uptake of penetrants *n*-methyl-2-pyrrolidone (NMP) and DMSO showed a linear relationship with time. The mechanism of this phenomenon was considered as the case-II diffusion (nonFickian). The polyimine films of the BTDA system had a better affinity to NMP than DMSO since the solubility parameter difference between BTDA-based PIS and NMP is less than five.

Vrentas and Vrentas [66] proposed an equation describing sorption behaviour in polymer–penetrant

systems. This equation is based on a model that has been formulated for describing the volumetric and sorption behaviour of a system composed of a glassy polymer and a penetrant. Later Vrentas and Vrentas [67] evaluated the predictive capabilities of a sorption equation for describing the sorption behaviour of three glassy polymer penetrant systems. They also examined the factors determining the shapes of isotherms for glassy-penetrant systems. Recently, Dragan et al. [68] reported the sorption of phenol, *p*-toluene sulfonic acid (P-TSA), Na-P-toluene sulfonate (Na-P-TS), 1,2-dihydroxy-3,5-benzene disulfonic and disodium salt (Tiron), and 3-hydroxy-4(sulfonaphthylazo)-5,7-naphthalene-disulfonic acid trisodium salt through the macroporous anion exchangers with acrylamide structural units. The maximum specific sorption of PTSA was almost identical with the total exchange capacity for both the weak and strong basic anion exchangers. The sorption of Na-P-TS is strongly related to the functional group structure of the anion exchangers.

Brown and co-workers [69] calculated diffusion coefficients of methylene chloride, chloroform, benzene and 2,2,4-trimethyl pentane in 1,4-polybutadiene having *trans* contents between 2 and 100%. They observed that for amorphous polymers (*trans* contents less than 70–80%) the diffusion at zero penetrant concentration decreases with increasing *trans* content and with increasing size of the diffusant.

Spirakis and Rogers [70] have studied the factors contributing to the solubility and diffusivity of penetrants through amorphous polymers. They found that the sorption kinetics change progressively from Fickian to non-Fickian to case II or super case II transport as a function of polymer composition.

4.3. Diffusion in polymer blends

The diffusion and transport through polymer blends depend upon its composition, miscibility and phase morphology. The blends may be either heterogeneous or homogeneous. In homogeneous blends, the diffusion process is influenced by the interaction between the component polymers [71–73] while for heterogeneous blends, interfacial phenomena and the rubbery or glassy nature of the phases are important [74]. Most polymer blends, however, are heterogeneous and consist of a polymeric matrix in which the second polymer is embedded. Consequently, the effects on permeability are very dependent on the degree of heterogeneity of the system and therefore on the method of formation [75]. The nature and type of polymers used are very important.

The most extensive study of the permeability of rubber blends was perhaps the early work of Barbier [76]. Mesrobian and Ammondson [77] reported the permeability of *n*-heptane and methylsalicylate through polyethylene–nylon blends. Cates and White [78–80] were among the first to report the sorption behaviour of water in blends of polyacrylonitrile and cellulose, silk and cellulose acetate, respectively. The sorption of water in PAN-cellulose acetate and PAN-cellulose varied linearly with blend composition. However in the case of PAN-silk blend, a complicated sorption behaviour was obtained. Saltonstall and co-workers [81] have reported the desalination of sea water through membrane from blends of cellulose triacetate and cellulose diacetate. Cabasso et al. [82] have investigated the sorption of benzene–cyclohexane mixtures in polymer blend membranes composed of polyphosphonate and acetyl cellulose. The authors state that this blend represents a miscible pair. The blend selectively absorbs benzene from

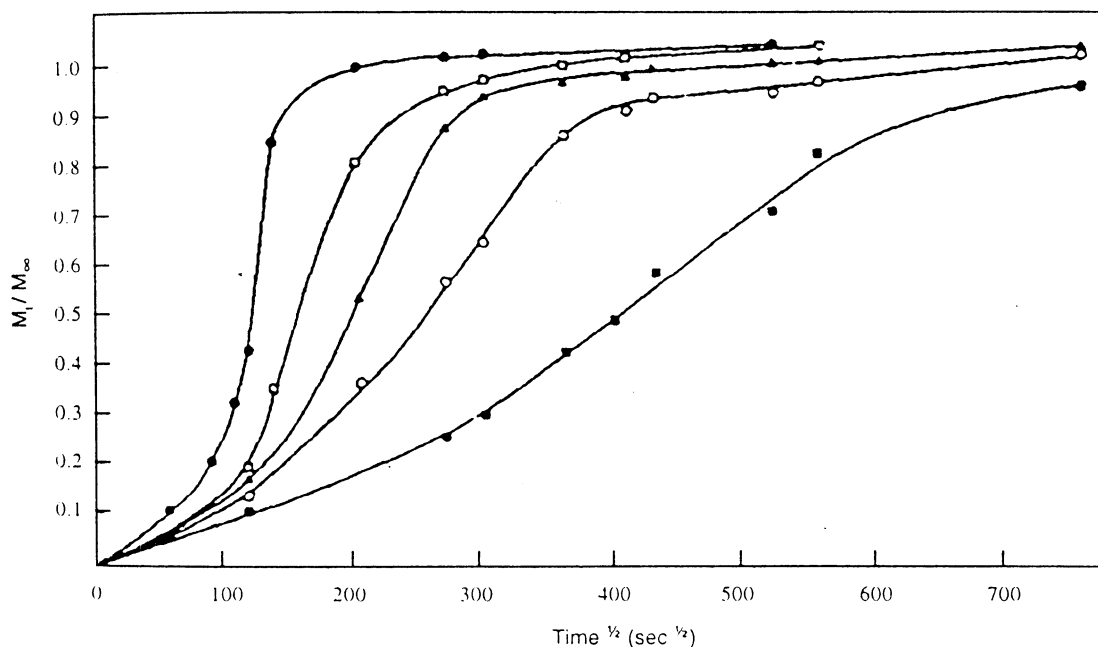


Fig. 5. Fractional sorption vs. \sqrt{t} for various poly(phosphonate)/cellulose acetate (P/A) blends determined at 30°C from 1/1 (w/w) benzene/cyclohexane mixture: (\square) P/A 50, (\blacksquare) P/A 40, (\diamond) P/A 30, (\blacklozenge) P/A 20, (\bullet) A (the numbers indicate wt% of P). Reprinted with permission from J Appl Polym Sci 1974;18:2117. ©1974 John Wiley & Sons, Inc. [82].

benzene–cyclohexane mixtures. They indicated that there was a dramatic concentration dependence of the diffusion coefficient with the increasing concentration of benzene in the blend membrane. Fig. 5 represents the fractional sorption of benzene from benzene–cyclohexane mixture into poly(phosphonate)-acetyl cellulose blends [82].

The sorption kinetics and equilibrium of normal alkanes in solution cast blend films of miscible atactic polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) has been reported [83–86]. The authors systematically examined the effects of temperature, penetrant activity, blend composition and thermal history on the sorption kinetics and equilibria of *n*-hexane in the PS–PPO blends. This blend system has been reported to be compatible over the entire range of blend composition.

The molecular transport of alkanes through thermoplastic blends of ethylene–propylene random copolymer and isotactic polypropylene has been investigated [87]. For all liquids, equilibrium penetrant uptake and degree of penetrant overshoot have been influenced by factors such as penetrant size and shape, polymer morphology and temperature. The diffusivity values of 2,2,4-trimethyl pentane at all temperatures were considerably lower than the corresponding values for a linear molecule of similar size, namely, *n*-octane. This is attributed to the rigidity of 2,2,4-trimethyl pentane. The observed overshoot effect is attributed to the complicated two-phase polymer morphology. Also sorption (S)–desorption (D)–resorption (RS)–redesorption (RD) experiments have been performed to determine the sorption equilibrium and transport parameters. Very recently in this laboratory, a series of transport studies have been conducted based on natural rubber/epoxidised natural rubber [88], nitrile rubber/ethylene–vinyl acetate

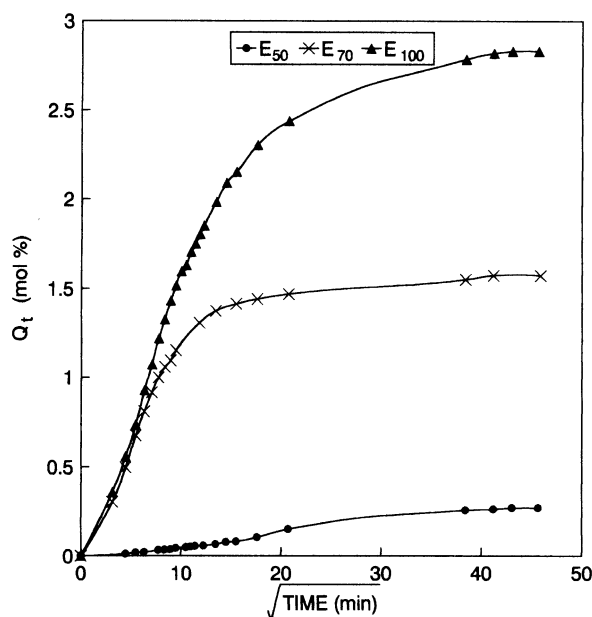


Fig. 6. Transport behaviour of nylon/EPR blends. Reprinted with permission from J Polym Sci, Polym Phys Ed 2000;38:2136. ©2000 John Wiley & Sons, Inc. [93].

copolymer [89], natural/polystyrene [90], nitrile rubber/polypropylene [91], styrene–butadiene rubber/natural rubber blends [92] and ethylene–propylene rubber/nylon blends [93].

The transport behavior of nylon/EPR blend is given in Fig. 6 [93]. The mol% benzene uptake of different blend compositions is depicted here. The maximum solvent uptake was observed for E_{100} and the minimum by E_{50} . For pure nylon and E_{30} , practically no solvent uptake could be observed. The mol% solvent uptake increases in the order E_{50} , E_{70} and E_{100} . It is very clear that the mol% solvent uptake increases with increase of rubber content in the blend composition. As is evident from Fig. 6 the diffusion behavior of E_{50} blend is different from that of E_{70} and E_{100} . The blends E_{70} and E_{100} have similar sorption behavior even though the maximum uptake is significantly large in the case of E_{100} .

The mol% solvent uptake of E_0 and E_{30} systems are negligible. Pure nylon (E_0) is highly crystalline and hence it is denser. Therefore free volume available is small. Hence the solvent uptake in nylon 6 is nil. The lack of sorption of solvent through E_{30} could be explained on the basis of the morphology of the system. SEM photograph of the morphology are given in Fig. 7. As shown in Fig. 7(a), in E_{30} blend, EPR is dispersed as domains in the continuous nylon matrix. The continuous nylon matrix restricts the swelling and hence the solvent uptake is negligible in this system, but in E_{50} , an interpenetrating morphology was observed. Here both EPR and nylon form a co-continuous morphology. In E_{70} , nylon is dispersed as domain in the continuous EPR matrix. The volume fraction of the crystalline phase decreases with increase of rubber content in E_{50} and E_{70} systems. This factor, together with the morphology of the systems significantly accelerate the swelling process in these two systems. The influence of blend morphology on the transport process is clearly shown in the schematic model given in Fig. 7(b).

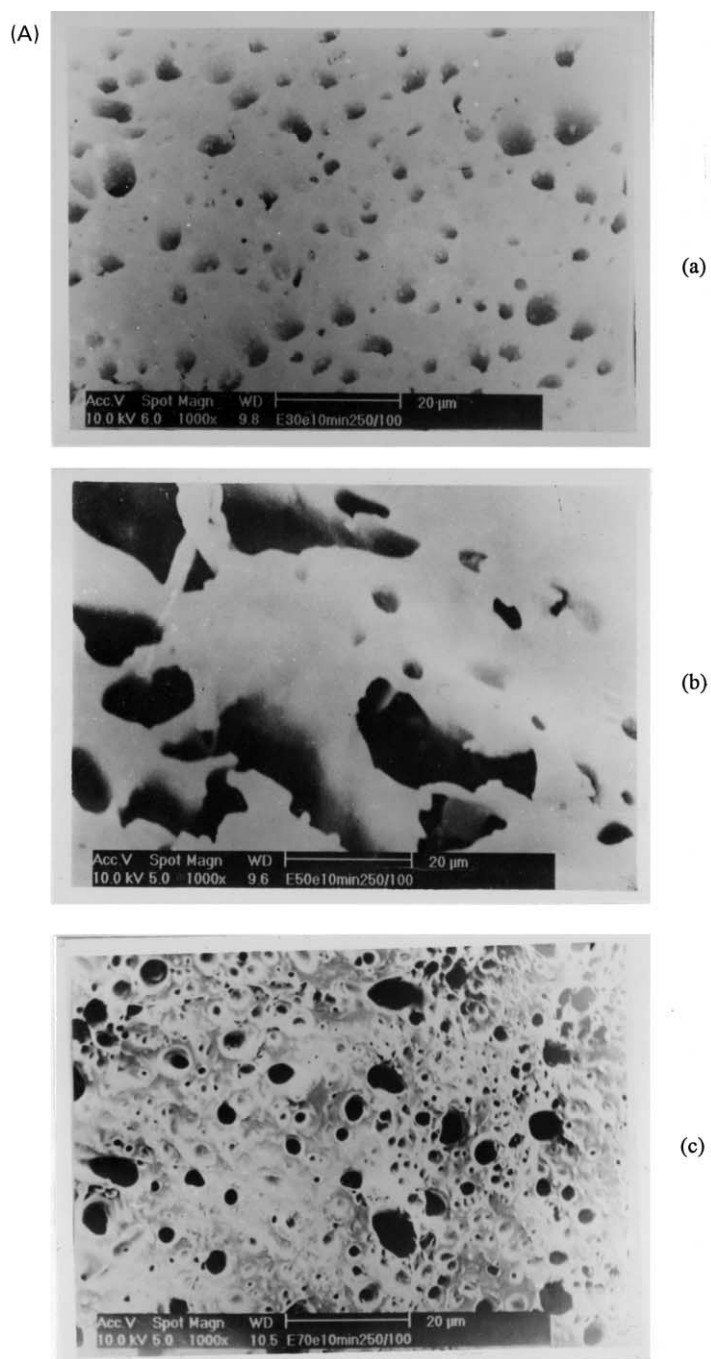


Fig. 7. (A) SEM photographs of morphology of nylon/EPR blends: (a) E_{30} ; (b) E_{50} ; (c) E_{70} . (B) Schematic model exhibiting the influence of blend morphology on transport process. Reprinted with permission from J Polym Sci, Polym Phys Ed 2000;38:2136. © 2000 John Wiley & Sons, Inc. [93].

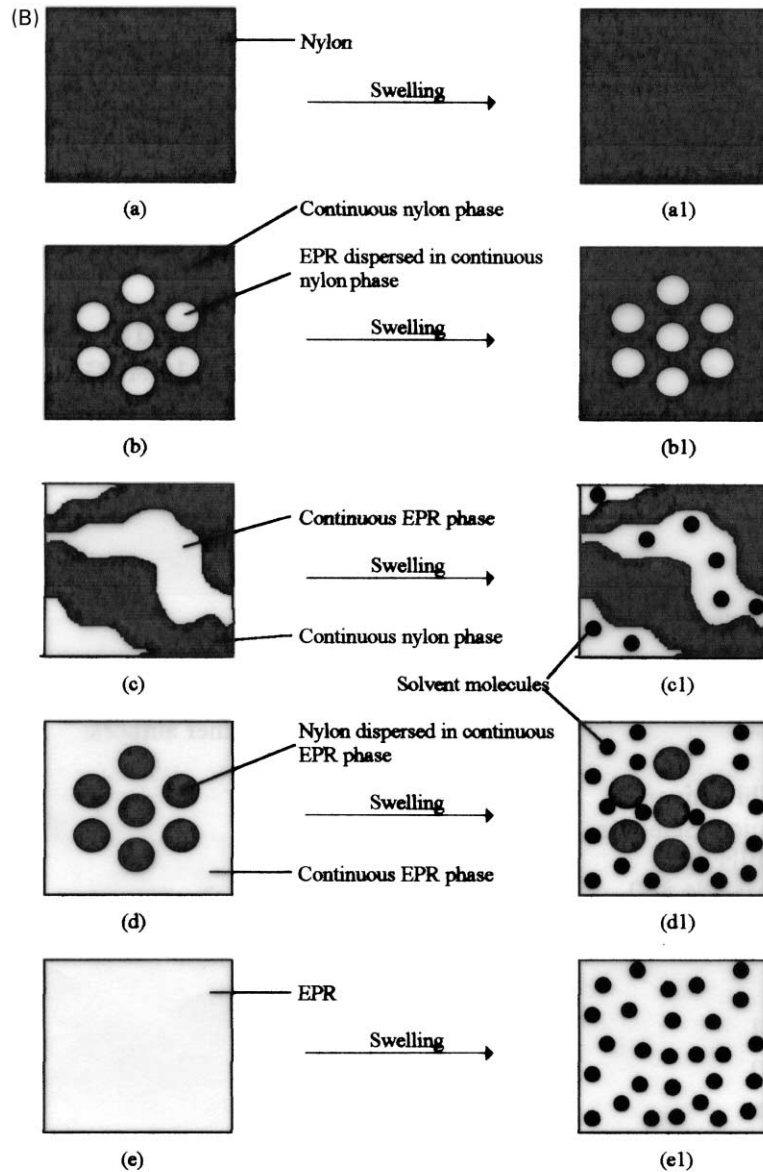


Fig. 7. (continued)

5. Membrane based transport processes

The feasibility and success of several transport processes depend upon the nature of the membranes used. The development of membranes and its utilisation for the separation of liquid and gas mixtures is an important emerging technique in membrane science and technology. The membrane morphology dictates the mode of permeation and separation, as shown in Fig. 8 [94]. The basic morphologies are

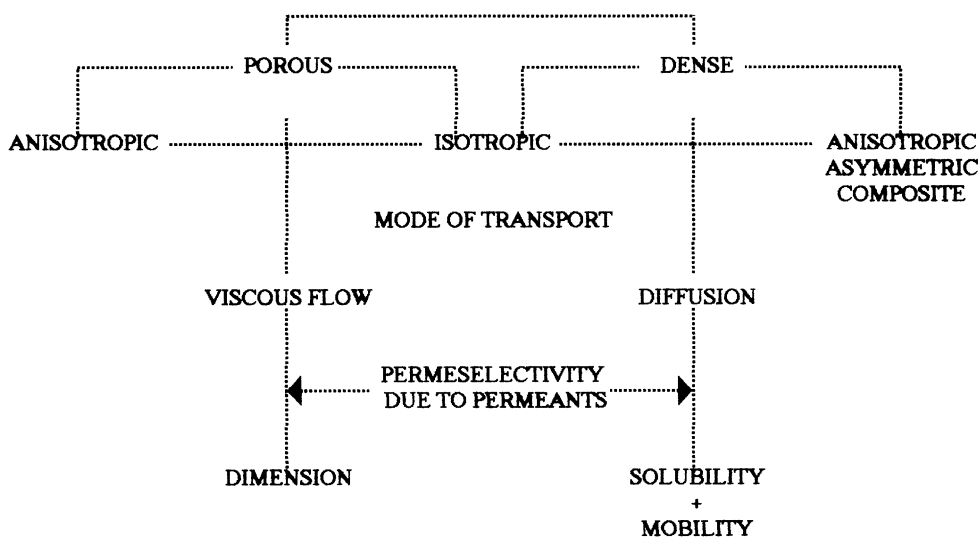


Fig. 8. Configuration, transport and permselectivity employed in membrane science and technology. Reprinted with permission from Encyclopaedia of Polymer Science and Engineering, vol. 9, 1986, p. 513. © 1986 John Wiley & Sons, Inc. [94].

isotropic (dense or porous) and anisotropic with a tight surface extending from a highly porous wall structure. The tight surface can be dense selective skin, permitting only diffusive transport or a porous skin, allowing viscous flow of the permeates. The membrane separation is achieved by the manipulation of these basic morphologies.

5.1. Liquid separation by pervaporation

Membranes can be used effectively to separate liquid mixtures in competition with traditional chemical processes such as distillation, absorption, liquid extraction and fractional crystallisation. Pervaporation process is an emerging membrane separation technique widely used for the separation of organic liquid mixtures. This technique attracted the attention of specialists in chemical, biochemical and petrochemical industries as an energy saving and environment friendly technology.

In pervaporation process, a thin polymer film is brought into contact with the liquid mixture (feed) and the permeant dissolves and permeates through the membrane by a diffusion mechanism, along a concentration gradient. The permeate vapour can be condensed and collected or released as desired. The chemical potential gradient across the membrane serves as the driving force for the process (Fig. 9) [95]. The driving force can be created by applying a vacuum on the permeate side to maintain the permeate vapour pressure lower than the partial pressure of the feed liquid. The vacuum pervaporation is the most widely utilised mode of operation, while several other processes such as inert purge pervaporation, thermal pervaporation, perstraction or osmotic distillation, saturated pressure driven pervaporation and electrically induced pervaporation are also available [96–99].

Though pervaporation is one of the most popular areas of current membrane research, the concept of pervaporation separation is not new. The phenomenon of pervaporation was first observed by Kober [100] who originated the term in a publication reporting selective permeation of water from aqueous solutions of

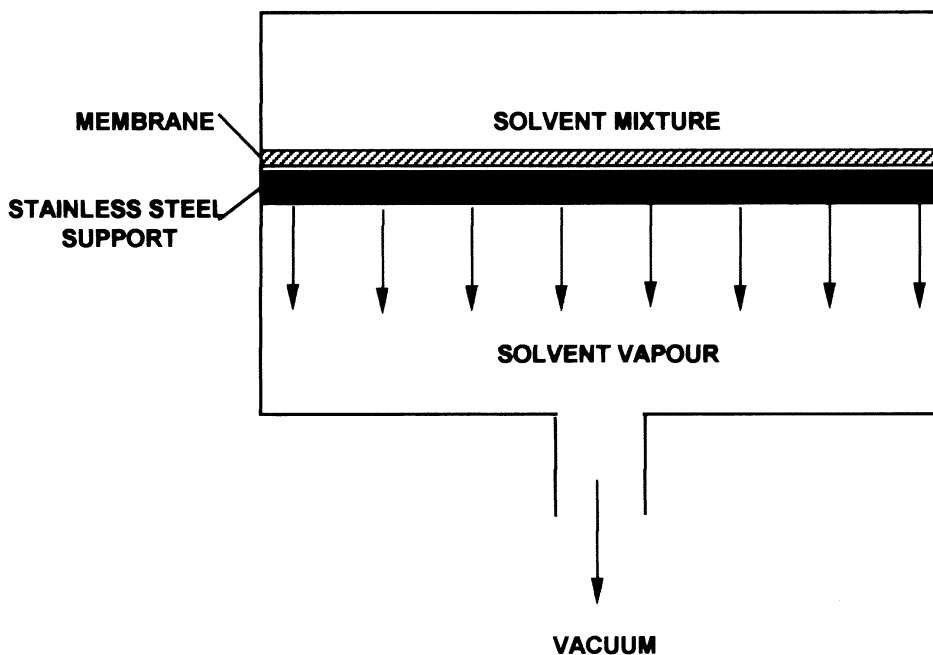


Fig. 9. The principle involved in pervaporation process. Reprinted with permission from *Trans IChemE* 1991;69:335. ©1991 Institution of Chemical Engineers [95].

albumin and toluene through cellulose nitrate films. The usefulness of pervaporation for separation and concentration was recognised by Farber [101]. However, the first known quantitative work on pervaporation was published by Heisler et al. [102] for the separation of water/ethanol mixtures using a cellulose membrane. It was the work of Binning and co-workers [103–105] that established the principles and highlighted the potential of pervaporation technology. In the following years, substantial work was done that widened the research scope to many liquid mixtures and a variety of membranes.

Membranes made of both synthetic polymers and derivatives of natural polymers have been tested for the separation of various liquid mixtures. The applications of pervaporation can be classified into three categories (1) dehydration of organic solvents and their mixtures [106,107], (2) removal of organic compounds from aqueous solutions [108,109] and (3) separation of organic liquid mixtures.

Various polymer membranes were developed for selective removal of ethanol and chloroform from aqueous binary solution [110]. Flat sheet membranes were cast from polymer solutions and evaluated for their sorption, diffusion and pervaporation of organics from dilute aqueous solutions. Selective sorption of organics dominate pervaporation selectivity of different polymers. The ionomeric membranes of perfluorosulfonic acid polymer allow selective pervaporation of polar organic compounds from their azeotropic mixtures with less polar compounds [111]. It is also noticed that fluxes increased with increasing alcohol content of the feed and with temperature. But the selectivity of more permeating component remained reasonably constant around azeotropic point.

Pervaporation process can be successfully used as a tool for the treatment of effluents [112]. Brun et al. [113] sorbed dilute aqueous solutions of benzene and chloroform on styrene butadiene rubber and nitrile

rubber. Several interesting studies on the performance of pervaporation as a tool for the treatment of effluents could be found in the literature [114–116].

The permeation and separation of benzene cyclohexane mixtures through liquid-crystalline polymer membrane has been reported [117]. The side-chain liquid crystalline polymer (LCP) was synthesised by the addition of the mesogenic monomer to poly(methyl siloxane) using platinum catalyst. They found that permeation rate increased with increasing benzene concentration in the feed solution and permeation temperature. The effect of membrane thickness on the removal of trace organics from aqueous solutions has been reported [118]. They have used a resistance-in-series model for describing the pervaporation performance of elastomeric membranes. The water fluxes are inversely proportional to the thickness of the actual separating layer and they depend strongly on the type of elastomer used.

The pervaporation performance of poly(alkyl methacrylate) [119] cross linked with ethylene glycol dimethacrylate (EGDM) membranes was investigated for the separation of benzene–cyclohexane mixtures by Uragami and co-workers. The crosslinked poly(alkyl methacrylate) membranes exhibited benzene permeability for the benzene–cyclohexane mixtures and the permeation rate increased with increasing benzene in the feed solution.

Luo et al. [120] prepared a membrane by blending cellulose acetate butyrate with cellulose acetate propionate. The properties of these membranes were evaluated by the pervaporation separation of ethyl tert-butyl ether and ethanol mixtures. The experimental results showed that the selectivity and the fluxes of this membrane depend on the blend ratio and on that of the processed feed mixtures.

The high pervaporation performance of crosslinked poly(vinyl alcohol)–poly(acrylic acid) blends in the pervaporation and differential permeation of water–alcohol mixtures has been reported [121]. Instead of a decrease of permeation flux, an increase in the permeability was observed with PAA crosslinked membranes at low PAA contents. Oliveria et al. [122] developed membranes from polyacrylonitrile and polyacrylonitrile-graft-poly(ethylene oxide) blend for separation of water/ ethanol mixtures by pervaporation.

Recently a membrane based on 2,3-(epoxy propyl)-methacrylate chemical modified polyurethane was developed for the separation of an aqueous alcohol solution by pervaporation [123]. The effects of feed composition degree of grafting and operation temperature on the pervaporation performance for the ungrafted and grafted membranes were investigated. The membranes were water permselective because of the hydrophilicity. The water permselectivity was increased with increasing degree of grafting. The separation factor and the permeation rate of PU-g-EPMA membranes were higher than that of the ungrafted PU membrane for aqueous alcohol solution. The PU-g-EPMA membrane with a 83.0% degree of grafting gives the best result for the separation factor and permeation rate i.e. 209 and 203 g/m² h, respectively. Recently Thomas et al. have extensively worked on the separation of organic liquid mixtures using various polymer membranes such as natural rubber [124], poly(ethylene-co-vinyl-acetate) [125], epoxidised natural rubber [126], epoxidised natural rubber/natural rubber blends [127], and styrene–butadiene rubber/natural rubber blends [128–129]. The effects of nature of crosslinks, feed composition, molecular size of the permeant and dosage of the crosslinking agent and role of blend morphology on the pervaporation performance were examined.

A proper understanding of the membrane separation mechanism may provide direct information on the research and development of an appropriate membrane. There are two approaches to describe the mass transport in pervaporation (1) the solution–diffusion model and (2) the pore flow model. The solution diffusion model is accepted by several researchers [130–132]. According to this mechanism, pervaporation consists of three consecutive steps (i) sorption of the permeant from the feed liquid to the

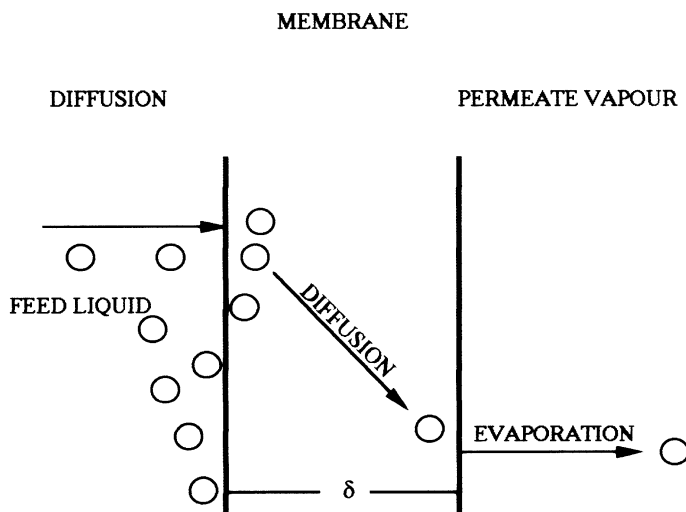


Fig. 10. Solution–diffusion transport model. Reprinted with permission from J Membr Sci 1995;107:1. ©1995 Elsevier Science Ltd [132].

membrane, (ii) diffusion of the permeant in the membrane and (iii) desorption of the permeant to the vapour phase on the downstream side of the membrane (Fig. 10) [132].

In general, the solubility and diffusivity are concentration dependent. Recently, Matsuura and co-workers [133–135] have proposed a transport model applicable to pervaporation on the basis of the pore flow mechanism. It is assumed that there are bundles of straight cylindrical pores on the membrane surface. The mass transport by the pore flow mechanism consists of three steps.

- (a) Liquid transport from the pore inlet to a liquid–vapour phase boundary,
- (b) evaporation at the phase boundary and
- (c) vapour transport from the boundary to the pore outlet (Fig. 11) [135].

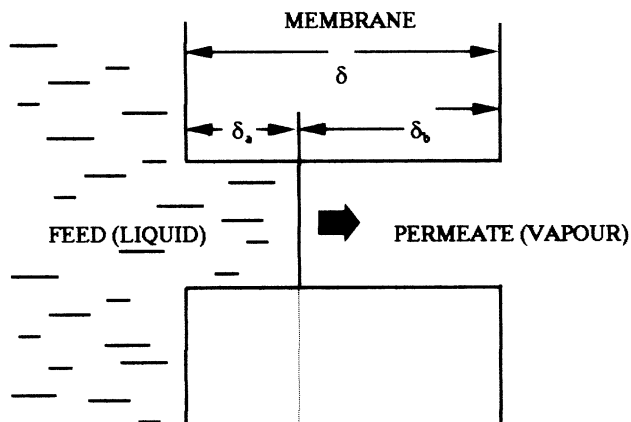


Fig. 11. Pore-flow model. Reprinted with permission from J Membr Sci 1991;59:151. ©1991 Elsevier Science Ltd [135].

The distinguishing feature of the pore flow model is that it assumes a liquid–vapour phase boundary inside the membrane and pervaporation is considered to be a combination of liquid transport and vapour transport in series. At present, it would be recognised that the two models represent two different approaches to the description of pervaporation transport.

5.2. Vapour permeation

Vapour permeation has emerged as a new industrial membrane technology. In vapour permeation, transport of a condensable vapour through a dense membrane consecutive to an activity gradient takes place. This process offers the unique feature of studying the transport process of a single permeant through a dense membrane under various upstream activities [136]. Such characteristics can by no means be obtained by liquid permeation, where the modification of the upstream activity of a component can only be achieved by adding another compound to the mixture. The activity of both components is modified in this case in compliance with the Gibbs–Duhem relation, which complicates transport analysis. On the contrary, coupling phenomena are not to be considered with pure vapour permeation results. Furthermore, the calculation of upstream solvent activity demands the use of somewhat complicated vapour liquid equilibria methods. In the case of pure solvent vapour permeation, upstream activity can be easily calculated, provided upstream pressure is precisely monitored [137]. This process offers direct practical conclusions for the understanding and rational design of volatile organic components (VOC) vapour recovery from contaminated air streams [138,139]. This technique also offers significant opportunities for energy saving and solvent release, compared to classical VOC control processes such as incineration, oxidation or active carbon absorption.

For VOC vapours recovery, as well as organic extraction from aqueous streams by pervaporation, a

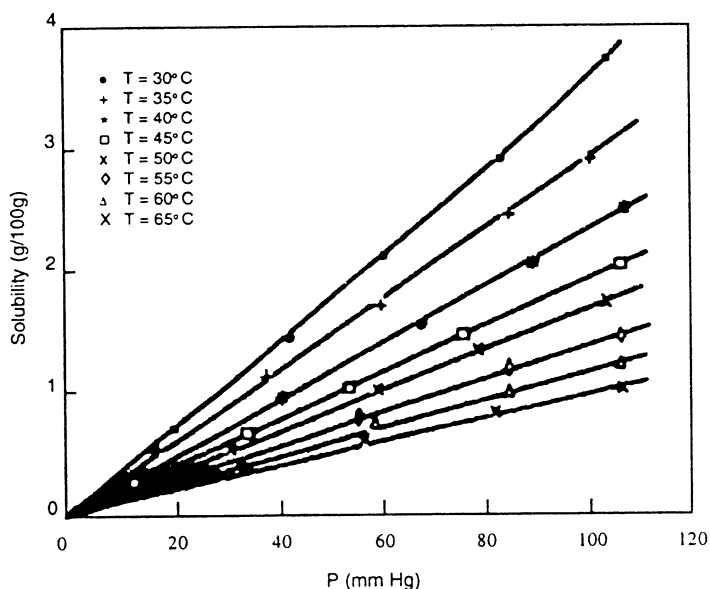


Fig. 12. An adsorption isotherm for *n*-hexane–PP systems. Reprinted with permission from J Membr Sci 1996;113:57. ©1996 Elsevier Science Ltd [142].

membrane material showing high organic vapour permeabilities, but low air and water permeabilities is required in order to set up a competitive process, while several elastomeric materials, well known for their high permeabilities as well as organophilic behaviour, have been already proposed for this purpose [140]. Dense poly(dimethylsiloxane) (PDMS) membranes, commonly named silicone rubber, offer a good compromise in most cases and are widely used [141]. Castro et al. [142] analysed the sorption data of hydrocarbon vapours in polyethylene and polypropylene films using, Flory–Huggins, Michael–Haussein and Flory–Rehner theories. Predictions of penetrant activity values through these theories fit quite well the experimental results, with errors ranging between 4.7 and 10.8%. A typical adsorption isotherm for *n*-hexane–polypropylene is shown in Fig. 12 [142]. As can be seen, the solubility depends on temperature and almost linearly on pressure. Duncan and Koros [143] have measured the permeabilities and diffusivities of methyl chloride and benzene vapours at low activities in 2 mil thick teflon membrane in a continuous flow permeation cell. The permeability and diffusivity were independent of penetrant partial pressures and the permeation process was described by Henry's law and the sorption by Fickian diffusion model. The diffusion and permeation coefficients of *n*-alkanes (from carbon atom numbers 12 to 32) have been measured by the pouch method for LDPE, HDPE, polypropylene copolymer and polypropylene homopolymer [3,144–146].

Salwinski et al. [147] developed a method for simultaneous determination of diffusivity (*D*), permeability (*P*) and sorptivity (*S*) of organic vapour through polymers from the mass transport. A kinetic equation was developed to estimate the loss of vapour under constant pressure in relation to mass transfer near zero pressure. Sorption of methanol vapours in estrofol and polythermopolyester films was investigated [148]. The sorption capacities of degassed and non-degassed films were similar. The permeation of propane, propene, ethane and ethylene through 0.0051 cm thick polyethylene films was determined from 25 to 30°C [149]. The sorptivity and diffusivity of acetylene, ethylene, ethane, propane, butane, pentane and xenon in poly(trimethyl vinylsilane) were determined by the sorption–desorption method in the pressure range of 0–700 Torr [150].

The permeability coefficients of benzene vapours in air from the measured values of solubility and diffusivity for natural rubber, neoprene, a blend of natural rubber and neoprene, butyl rubber, poly(vinyl chloride) and polyethylene membranes were calculated [151]. The permeability for natural rubber at room temperature was $4.2 \times 10^1 \text{ cm}^2/\text{s}$ for 10 ppm concentration of benzene vapour in air.

Vapour sorption technique is also a good tool for the thermodynamic characterisation of polymer blends. Analysis of equilibrium sorption of a vapour by the blend can provide information regarding polymer–polymer interactions [152–154]. The amount of vapour sorbed is related to its interaction with the blend. By comparing this interaction with the interaction between the vapour and each of the pure polymers it is possible to obtain information about the interaction between the polymer components of the blend.

Geuskens [155] has investigated the morphology of polyethylene–silicone blends by combining scanning electron microscopy with measurements of permeability to methanol vapour and selective extraction of the silicone phase by diethylether. He found that in polyethylene–silicone blends, SEM and permeability measurements are complementary sources of information regarding the morphology of the blends. SEM is useful to characterise the microstructure of the blends at low silicone content. He also found that the permeability measurements are useful to determine how phase inversion proceeds and what composition of the blend corresponds to the maximum level of co-continuity of the two phases. Recently Thomas and coworkers investigated the permeation of chlorohydrocarbon vapours through various blend membranes such as epoxidised

natural rubber/natural rubber [156], styrene–butadiene rubber/natural rubber [157] and nylon/ethylene propylene rubber [158].

5.3. Gas permeation

Gas transport through polymers is an area of growing interest as materials with unique transport properties continue to find use in new, specialised applications ranging from extended life tennis balls [159] to natural gas separation systems. The ability to relate polymer molecular structure to gas transport properties is crucial in any attempt to rationally design materials for specific permeability applications such as gas barriers. Historically, the availability of experimental permeability data has been limited mostly to common/commercial polymers [160] and the information demonstrated that gas transport rates of polymers may vary by many orders of magnitude. A variety of techniques have been used to measure gas permeation through polymer membranes. The most common method utilises a Dow permeation cell wherein the film is sealed in the cell. The downstream side of the chamber is evacuated and the test gas is passed upstream at a given pressure to reach equilibrium with the film while maintaining vacuum on the downstream side. The film must be dry since the method does not differentiate between the test gas permeating the polymer sample and water vapour.

Traditionally the behaviour of gas transport through a gas separation membrane was presumably dominated by the diffusion of absorbed molecules. The gas flux was driven by the concentration gradient of absorbed molecules in polymer matrix. This leads to a simple model which is known as the solution diffusion model [161–165]. The permeating species interacts with the polymer matrix and selectively dissolves in it, resulting in diffusive mass transport along a chemical potential gradient. Besides solution diffusion model, there are viscous flow, Knudson flow and molecular sieving for explaining gas transport through porous membranes. As illustrated in Fig. 13 the mechanism of flow of gas molecules depends upon the size of the pores in relation to the mean free-path of the gas molecules [166]. In viscous flow, flow is inversely proportional to the viscosity of the fluid (gas). In contrast, flow is inversely proportional to the square root of the molecular mass of diffusing species in Knudson flow [167]. Ultra micro porous molecular sieving membrane has higher productivities and selectivities than solution diffusion mechanics [168,169].

The gas sorption to a homogenous polymer has been classified into two categories. For sorption to a

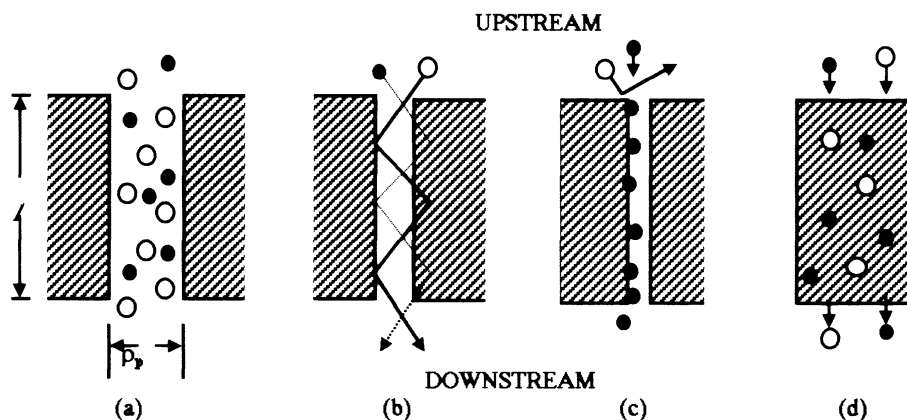


Fig. 13. Mechanism of flow of gas molecules: (a) viscous flow, (b) Knudson flow, (c) molecular sieving and (d) solution–diffusion [165].

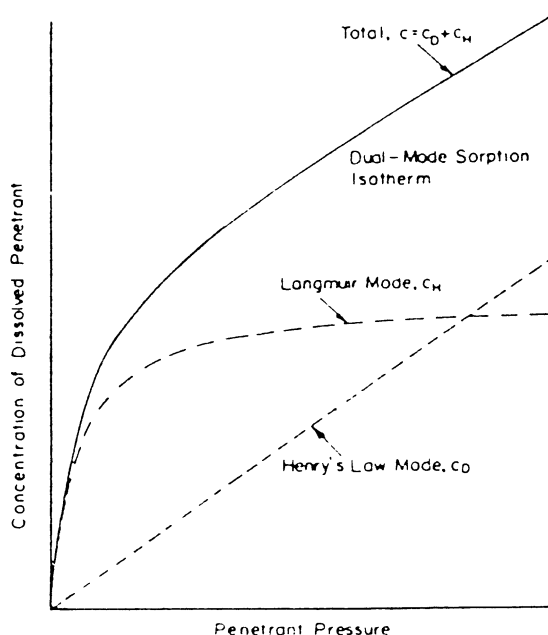


Fig. 14. Typical dual-mode sorption isotherm and its components. Reprinted with permission from Barrier Polymers and Structures, ACS Symposium Series No. 423, 1990. ©1990 American Chemical Society [175].

rubbery polymer membrane, the sorption behaviour was described by Henry's law. Recently, a more complex BET-type sorption isotherm which describes multilayer sorption has also been discussed. For sorption to a glassy polymer membrane, the sorption isotherm has been characterised by many authors using a dual sorption model. This combines two isotherms, a Henry-type isotherm for matrix absorption and a Langmuir-type isotherm for site sorption [170–174] (Fig. 14) [175]. The gas transport behaviour for glassy polymer is then described by a so-called dual mobility model, [176,177] which assigns two different diffusivities to the molecules absorbed by different mechanisms, Langmuir and Henry's sorption. This model described well, the pressure dependency of gas permeability of a wide range of glassy polymer membrane [178–180] and reasonably related the gas solubility to its permeability.

The difference in the transport and solution behaviour of gases in rubbery and glassy polymers is due to the fact that, the latter is not in a state of true thermodynamic equilibrium [181,182]. Rubbery polymers have very short relaxation times and respond very rapidly to stress that tend to change their physical conditions. Thus a change in temperature causes an immediate adjustment to a new equilibrium state. A similar adjustment occurs when small penetrant molecules are absorbed by a rubbery polymer at constant temperature and pressure and adsorption equilibrium is very rapidly established.

On the other hand, glassy polymers have very long relaxation times. Therefore, in the presence of a penetrant, the motions of whole polymer chains or of portions thereof are not sufficiently rapid to completely homogenise the penetrant's environment. Penetrant (gas molecules) can thus potentially sit in holes or irregular cavities with very different intrinsic diffusional mobilities.

Gas separation by permeation through membranes has been suggested for many years [183,184]. For the efficient separation of gas mixtures, the membranes should have a high selectivity for a particular gas over other gases. However, with homogenous membranes, high selectivity is usually associated with low

permeability, as in the case of membranes used for enrichment of air [185]. On the other hand, porous membranes usually have very high permeabilities but their selectivity is generally low. Kanitz and Huang [186,187] investigated the permeation of gases through poly(ethylene styrene) grafted copolymer membranes prepared by γ -ray irradiation. They also studied separation of nitrogen and methane gases in air using vacuum-irradiated polyethylene and teflon films. Rogers [188] studied the permeation and separation of helium and nitrogen gases through grafted methyl methacrylate and polyisoprene membranes.

Haraya and Hwang [189] have conducted permeation studies in a series of polymers for selecting appropriate polymers for the separation of O_2/Ar mixtures. The gas permeabilities and diffusivities in all the polymers tested are in the order $O_2 > Ar > N_2$. Higher permselectivities are observed in glassy polymers than in rubbery polymers. Permeability ratios for O_2/N_2 in glassy polymers are strongly affected by the contribution of the diffusivity ratios. Recently, Lai and co-workers [190] studied the transport phenomenon of oxygen and nitrogen across a pure polycarbonate and a cobalt(III) acetylacetonate $[Co(acac)_3]$ containing polycarbonate membrane. $Co(acac)_3$ was added into a polycarbonate membrane to enhance its oxygen solubility. It was found that oxygen permeability increased slightly with respect to pressure.

The gas transport in polymer blend is directly affected by the morphology [191,192] and chemical uniformity of the material. For instance, the enhancement of the permselectivity of a membrane composed of a miscible polymer pair, over that of membrane composed of the parent polymers, was demonstrated with poly(dimethylphenylene oxide)-polystyrene blend [193]. Using the ratios of the permeabilities of the pure gases, the separation factor for the gas pairs $He-CH_4$ and CO_2-CH_4 was estimated. For both pairs, the

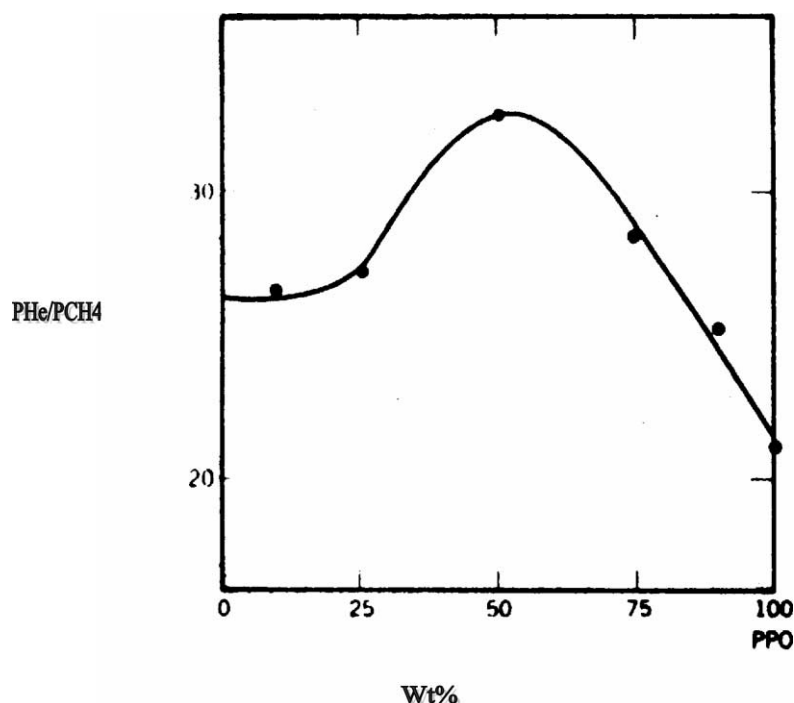


Fig. 15. Separation factor for $He-CH_4$ pair at 1010 kPa (10 atm) $35^\circ C$, as computed from the permeability coefficient of the pure gases in PPO-PS blends. Reprinted with permission from Polymer 1985;26:2055. ©1985 Elsevier Science Ltd [193].

estimated separation factor passes through a prominent maximum, indicating that the blend membrane is significantly more selective than expected from the behaviour of a two-polymer component (Fig. 15) [193].

Ranby and co-workers have reported the most extensive experimental study of permeability behaviour in polymer blend systems [194–196]. Ranby focused his early work on mechanical blends of poly(vinyl chloride) (PVC) with ethylene–vinylacetate copolymers (EVA) and with acrylonitrile–butadiene copolymers (NBR), respectively. The effect of varying vinyl acetate content on the miscibility of the resulting blends and in turn, on the transport behaviour was the primary focus of the study. Recently from our laboratory Thomas and coworkers reported on the gas transport properties of natural rubber/epoxidised rubber blends [197] and styrene–butadiene rubber/natural rubber blends [198]. The permeabilities of the pure polymers and blends were determined with nitrogen and oxygen. Even though several polymer membranes are available for separation process, nowadays only a few of them exhibit high selectivity and permeability. Hence the pursuit is still going on in both laboratory and academia for the development of membranes with high permeability and high selectivity.

6. Conclusions

The results presented in this review consist of a detailed investigation of the transport of small molecules through the polymer membranes. Transport process through polymeric systems depends upon several factors such as nature of the polymer, polymer molar mass, nature of crosslinks, plasticisers, temperature and crosslink density. Among the different parameters discussed above, nature of polymer itself is the predominant factor that influences the transport process strongly. The factors such as free volume within the polymer and segmental mobility directly influence the transport process whereas the extent of unsaturation, crosslinking, degree of crystallinity and the nature of substituents are the factors that alters the polymer structure and hence indirectly influence the transport process. Different types of crosslinks formed during the curing process also affect the transport behaviour. The size and shape of penetrant molecule will influence the rate of transport within the polymer matrix. Diffusivity was decreased with increase in the size of the penetrant. Permeation rate was decreased with increase of crosslink density. The key element in the separation process is the development of membrane itself. Transport characteristics as well as the separation characteristics are strongly influenced by blend morphology. Transport of small molecules through the polymeric membrane influences several industrial processes. The molecular diffusion process is a key step in the design process and often governs the utility and manufacture of commercial products. These include the controlled release of drugs, fertilisers and pesticides. The physical properties and appearance of coatings can be modified by trace amounts of volatile components. The use of new and more sophisticated experimental techniques such as NMR spectroscopy, inverse gas chromatography and neutron diffraction has a significant role in future research. These techniques will yield new insights into the mechanism of small molecules in elastomers and blends. The development of synthetic membranes is closely linked to the progress of separation industry. The membranes are used to separate or chemically convert and modify the permeate stream. This technology could revolutionise the biochemical, pharmaceutical and other chemical industries.

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