TRANSPORT OF ALIPHATIC HYDROCARBON LIQUIDS THROUGH CONVENTIONALLY VULCANISED NATURAL RUBBER FILLED WITH DIFFERENT TYPES OF SILICA FILLER

PROJECT REPORT

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SCIENCE AND TECHNOLOGY

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CERTIFICATE

This is to certify that the project entitled **Transport of Aliphatic Hydrocarbon Liquids through Conventionally Vulcanised Natural Rubber Filled with different types of silica filler** submitted by **Sheela Joseph** for the award of the degree of Master of Technology of Cochin University of Science and Technology, was done by her under the joint guidances of Dr. Sabu Thomas, Reader, School of Chemical Sciences, Mahatma Gandhi University, Kottayam and Dr.M.G. Kumaran, Joint Director, Rubber research Institute of India, Kottayam.

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*This is to certify that this project report on **TRANSPORT OF ALIPHATIC HYDROCARBON LIQUIDS THROUGH CONVENTIONALLY VULCANISED NATURAL RUBBER FILLED WITH DIFFERENT TYPES OF SILICA FILLER** submitted by **Mrs. SHEELA JOSEPH** was carried out under our joint supervision and guidance during the period of February 1995 to July 1995 at Rubber Research Institute of India, Kottayam. This report is for the partial fulfilment of the Master of Technology Degree in Polymer Technology of Cochin University of Science and Technology, Cochin. It is also certified that this work has not been presented for any other degree.*

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Chapter 1

INTRODUCTION

INTRODUCTION

One of the important features of polymeric materials is their ability to dissolve molecules of gas, vapour, liquid and sometimes solute and to allow the transport of these molecules through the solid phase. This is in marked contrast to metals, glasses and ceramics which are essentially impermeable. The property of transport has many practical applications and sometimes unwelcome repercussions.

The first observation of transport phenomena in polymeric materials was that of Grahams[1] who in 1829 reported that a wet pig bladder inflated when placed in an atmosphere of carbon dioxide. The discovery that a rubber membrane is permeable to gases was made by Mitchell in 1831.[2] It was shown that the rate of permeation varied for different gases and that the gases penetrated most rapidly were those most easily condensed and most soluble in water and other liquids. In 1866 Graham published a paper in which all these ideas are given.[3] Graham drew attention to the greater similarity of rubber to the liquid rather than the solid state and postulated that the permeation was a three stage process comprising condensation and solution at one face of the film, diffusion as a liquid to the other face followed by dissolution and evaporation. The increasing rate of permeation with temperature was attributed to an increase in the softness of liquid nature of the rubber.

Molecular transport of organic chemicals into elastomers has been an active area of research over the past two decades in view of its importance in several discipline such as chemical pond lining, polymer processing and membrane science phenomena.[4,5] Most polymer products when brought into contact with organic chemicals show a reduction in polymer property due to swelling and relaxation of chain segments.

Polymer films are widely employed as protective barriers. For example metals are painted to prevent corrosion. Paper is coated to render it moisture resistant or foods are packaged to reduce their rate of deterioration. In these applications the permeability of the films can be a major consideration. In the case of rubber tubes and hoses, when they are come in contact with organic oils and fuels the swelling and deterioration of the tubes is a major problem. This infact depends of the permeability of the rubber to these liquids.

In the field of chemical engineering, polymer films are often used to effect the separation of mixtures. For example the extraction of helium from natural gas, the drying of solvents and desalination of sea water.[6] More recently the feasibility of using fluorinated polymers in pollution control systems has been examined. Promising results for the selective permeation of hydrocarbons have been obtained.[7]

Polymer films may be used to control the rate at which a substance is released into its environment. This property is exploited by the pharmaceutical industry in the production of sustained-release dosage forms.[8] A good example is the cold cure capsule which contains tiny drug-containing polymer particles. The thickness of the polymer coat contains the rate at which the drug is released from the particles. Several components can be included in one capsule and each can be released at varying rates to give the optimum therapeutic effect. The degree of selectivity achieved by a polymer depends on its ability to discriminate on the basis of size, shape, polarity, charge or other factors and this is often highly dependent on preparation, conditioning and operating conditions.

Some times a polymer film may be used in situations where its limited permeability is a hindrance. This arises for instances when a charcoal adsorbent is coated by binder attaching it to the fabric of protective clothing or when it must be coated with a hydrophilic material to make it biocompatible and hence suitable for use in clinical heamoperfusion.[9] In these cases the polymer employed must have a high permeability to the absorbates for the charcoal to be utilized efficiently.

The transport properties of a polymer will be affected by both the method of preparation and the subsequent processing characteristics. The main processing properties which affect the transport properties are molecular weight, degree of dispersity, extent of chain branching, degree of crystallinity etc. These are determined principally by the polymerisation process. A change in any one of these characteristics usually has some effect on the transport properties of the polymer. These effects have been studied systematically by many workers.

1.1 Diffusion

The transport behaviour of organic liquids in polymers has been studied extensively for many years and reviewed by several authors.[10-15] Diffusion is the process by which matter is transported from one part of a system to another by random molecular motion. In this content "matter" refers to gases, vapours, liquids and solutes and the system is the polymer film through which they may diffuse. The tendency of the transport process is to equalise the chemical potential of the penetrant in the phases separated by the film. The chemical potential is usually expressed in terms of penetrant concentration or pressure.

Suppose that the film is initially free from penetrant. when one phase is exposed to a penetrant there will be an accumulation within the film and after a period of time the rate of dissolution from the opposite face will rise from zero to a constant value. This is known as the transient state of permeation. When the constant rate of dissolution is attained a steady state of permeation prevails.

Solvent diffusion is needed for the development of detailed analysis of mass transfer problems involving polymer penetrant systems.

1.2 Fick's law

In 1855 Fick formulated a law of diffusion based on Fourriers law of conduction of heat due to a close analogy between the process of diffusion of a penetrant and the flow of heat through a solid. The law states that the rate of diffusion in any direction is proportional to the concentration gradient of the penetrant in that direction.

If we denote the change of concentration for a small distance ∂x by ∂c, the concentration gradient is $\partial c/\partial x$ and the quantity (J) of the penetrant diffusing in unit time through unit area (flux) is given by the relation

$$J = -D\ \partial c/\partial x \qquad (1.1)$$

where D is the diffusion coefficient or diffusivity. Solvent diffusion in rubbery polymers also obey Ficks law.

1.3 Determination of diffusion coefficient

The simplest technique for determining the diffusion coefficient is based on Fick's law of diffusion. consider a membrane of thickness x whose surfaces at $x = 0$ and $x = 1$ are maintained at constant concentrations C_1 and C_2 respectively. At the beginning of the experiment both the rate of flow and the concentration of permeant at any point in the membrane vary with time. Once equilibrium is established, however, the concentration changes linearly through the membrane from C_1 to C_2. The flux, J, of the material diffusing through unit area of the material per unit time is given by

$$J = D\ \left(\frac{C_1 - C_2}{x}\right) \qquad (1.2)$$

Generally C_2 is kept at zero by use of a high vacuum and the membrane thickness and the surface concentration C_1 are known. The diffusion coefficient or diffusivity D can be obtained from a single measurement of the film J. It should be noted that D in this instance is dependent upon the sorbed concentration C which itself varies through the polymer.

In many practical systems however the surface concentration is not always known with accuracy and it is conventional to express the flux per unit area J in terms of the concentrations of the external phases C^{ext}, by

$$J = P \left(\frac{C_1^{ext} - C_2^{ext}}{x}\right) \tag{1.3}$$

where P is termed the permeability, permeability-coefficient or permeability constant.

If there is a linear relationship between the concentration of the external phase and the corresponding surface concentration. i.e., if Henry's law is obeyed then

$$C = SC^{ext} \tag{1.4}$$

where S is the solubility constant and it follows from equations 2, 3 and 4 that

$$P = DS \tag{1.5}$$

For the unsteady state condition where the concentration gradient of permeant across the membrane varies with time, the rate of change of permeant concentration at any point (assuming unidirectional flow and that D is a constant independent of x, t and c) is given by Fick's law

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \qquad (1.6)$$

Depending on the boundary conditions there are many solutions to equations (1.1 and 1.6).

Glassy polymers however because of their time dependent response exhibit non Fickian or anomalous diffusion kinetics. It is well known that the phenomenon of transport through rubbery polymers is controlled by polymer structure, its crosslink density, mode of crosslinking presence of fillers, penetrant size, temperature, etc.

1.4 Concentration and time dependence of D

In many instances where swelling of the sample occurs both D and S become concentration and time dependent. The sorption behaviour can be measured from the rate of transport of penetrant through a film as a function of time. Typical experimental procedures utilize thin films of the polymer soaked in the penetrant at constant temperature and pressure. Solution of the penetrant occurs at the surface of the film followed by diffusion towards its centre. The resulting weight increase is measured as a function of time and plotted Q_t (percentage molar uptake of the solvent) against $\surd t$ (time) for Fickian diffusion. A typical isotherm for Fickian diffusion is shown.

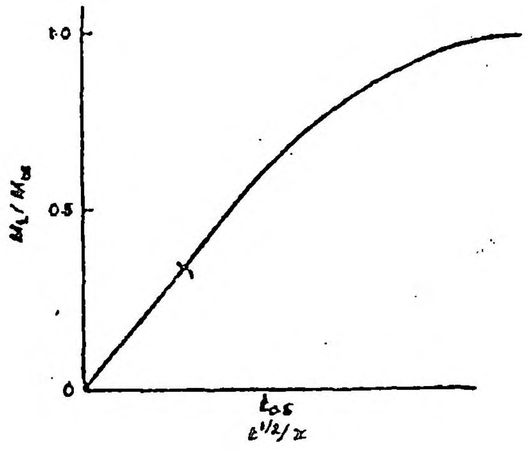


Figure 1.1. A typical isotherm observed for Fickian diffusion.

Uptake of penetrant continues until equilibrium with the solvent phase is attained. If the solvent concentration is reduced penetrant will desorb from the film and the weight loss can be monitored. In common with most permeation experiments the film is normally free from penetrant at the start of the experiment. It may however be preequilibrated to a non-zero concentration. This procedure which is termed interval sorption permits the calculation of a mean diffusion coefficient between the concentrations of the initial and final equilibria. It therefore provides a means of estimating the concentration dependence of the diffusion coefficient. In a Fickian behaviour the plots of Q_t versus $\surd t$ should increase linearly up to about 50% sorption. From the slope of these curves we can calculate the diffusion coefficient using the equation.[15,16]

$$\frac{Q_t}{Q_\infty} = 4\left[\frac{Dt}{h^2}\right]^{\frac{1}{2}} \left[\frac{1}{\surd\pi} + 2\sum_{n=0}^{\infty}(-1)^n \text{ierfc}\left[\frac{nh}{2(Dt)^{\frac{1}{2}}}\right]\right] \qquad (1.7)$$

where Q_t and Q_∞ are the masses sorbed at time t and equilibrium, respectively, h the film thickness and 'ierfc' is the inverse complementary error function.

The equation (1.7) is only valid under the following conditions. (i) The film sample should immersed in the penetrant such that both faces are exposed simultaneously to the same concentration (ii) Solution of the penetrant occurs at the faces of the film followed by diffusion towards its centre. (iii) This condition is usually satisfied by the polymers at temperature well above their glass transition temperature.

For shorter time equation (1.7) can be simplified as

$$\frac{Q_t}{Q_\infty} = \frac{4}{\surd\pi}\left[\frac{Dt}{h^2}\right]^{\frac{1}{2}} \qquad (1.8)$$

If the Q_t values are plotted against $\surd t$ then slope of the curve (θ) is $\dfrac{Q_t}{\surd t}$. Then from equation (1.8)

$$D = \pi \left[\frac{h\theta}{4Q_\infty} \right]^2 \qquad (1.9)$$

In the sorption experiment the usual procedure is to plot the Q_t values against $\surd t$ and calculate the diffusion coefficient D from the initial linear slope. Equation (1.8) can be generated as

$$\frac{Q_t}{Q_\infty} = kt^n \qquad (1.10)$$

K is a parameter which depends on the structural characteristics of the polymer in addition to its interaction with solvent molecules. The value of n is indicative of the type of transport mechanism. The value of n normally lies between 0.5 and 1. If n is close to 0.5, the mechanism of diffusion is regular Fickian, where diffusion coefficients are functions of concentration only, when n=1 the mechanism is said to be case II (relaxation controlled transport), when $0.5 < n < 1$ the mechanism of transport is considered to be anomalous. The values of n and k can be calculated by least squares analysis.

In the instance of Fickian diffusion ($n = \frac{1}{2}$) and it is possible to determine D from $t_{0.5}$ which is time taken for half the amount of solvent absorbed at equilibrium.

i.e., $$D = \frac{0.04939\ h^2}{t_{0.5}} \qquad (1.11)$$

For Fickian behaviour the plots of Q_t versus $t^{\frac{1}{2}}$ should increase linearly up to about 50% sorption. Deviations from the Fickian sorption are associated with the time taken by the polymer segments to respond to a swelling stress and rearrange themselves to accommodate the solvent molecules. This usually results in the sigmoidal shapes for the sorption curves.

The concentration dependence of the diffusivity D arises from the presence of permeant molecules within the polymer which weakens the interactions between adjacent polymer chains which in turn leads to the commonly observed effects of plasticization. Hence the rate of diffusion increases.

The importance of the concentration dependence of D is shown by the magnitude of the change in D for even small increases in permeant concentration. The exponential dependence found for the benzene poly(vinyl acetate) system is a consequence of an almost thousand fold increase in D for an increase in permeant volume fraction from 0 to 0.1. However in the benzene poly(dimethyl siloxane) system D is virtually independent of concentration.[18] For benzene natural rubber system there is only about a three fold increase over the same concentration range.[19] Clearly the variation of permeant diffusivity with concentration is very dependent on the polymer system studied. However generally it appears that this variation is greater for glassy polymers than for rubbery polymers.

It is well known that the phenomenon of transport through rubbery polymers is controlled by the structure of the polymer, nature of penetrant, presence of fillers, temperature, presence of plasticizers, etc.

1.5 Temperature dependence of transport properties

Temperature activates diffusion, sorption and permeation.[20] At moderate temperatures the temperature dependency is given by the Arrhenius relationships.[21]

$$D = Do \exp (-E_D/RT) \tag{1.12}$$

$$S = So \exp (-\Delta Hs/RT) \tag{1.13}$$

$$P = Po \exp (-E_P/RT) \tag{1.14}$$

Generally the equations can be written as

$$\log X = \log Xo - \frac{Ex}{2.303\ RT} \qquad (1.15)$$

where X represents D or P. D is the diffusion coefficient, P permeation coefficient and S sorption coefficient. E_X is the activation energies E_D or E_P. E_D is the activation energy for diffusion and E_P for permeation which depends upon the transport process under consideration. From the slope of the least square fit of the linear plot of log X vs 1/T one can get the values of E_X. X_0 is a constant representing either D_0 or P_0 which are diffusion and permeation coefficient extrapolated to zero permeant concentration in the above said graph. R is the gas constant and T is temperature in kelvin. The activation energy is a measure of the energy expended against the cohesive forces of the polymer forming the gaps through which diffusion will occur. The diffusivity D is a kinetic parameter which is related to polymer-segmental mobility. The values of E_P and E_D vary with the size of the penetrant molecule. But the increase in activation energy is not uniform with increase in penetrant size. The heat of sorption can be calculated using the equation[21]

$$\Delta H_S = E_P - E_D \qquad (1.16)$$

and this gives additional information about molecular transport.

The value of heat sorption tells us whether Henry's law type dissolution process or Langmuir type holes fitting process predominates.[22] Positive values of ΔHs indicates predominance of Henry's law type sorption mechanism and negative value of ΔHs suggests Langmuir type sorption. In Henry's law model site formation within the polymer matrix occurs followed by the dissolution of the penetrant into that site. The site formation of segmental motion of polymer chain makes an endothermic contribution. In Langmuir mode the site already exists within the polymer matrix and only sorption by hole-filling which is exothermic occurs. The positive value of ΔH_s suggests that sorption by Henry's law mode.

Larger molecules usually do not fit into the holes or free space already available in the polymer matrix. They really require more energy to create additional space which are known as "Eyring holes" within the polymer matrix.[23]

1.6 Nature of the polymer and transport behaviour

The diffusion of a penetrant molecule through a polymer matrix can be visualised as a series of jumps through a mass of tangled polymer chains and cavities. The overall diffusion process results from the movement of penetrant molecules from cavity to cavity under the influence of a concentration gradient. So it depends on the number and size of the cavities of the polymer matrix, the energy required to disrupt the polymer and polymer and penetrant interactions in order that the surrounding chain can rearrange themselves to allow the passage of the diffusing molecule. In other words, it basically depends on the structure of polymer and penetrant and the glass transition temperature (Tg) of polymer. The main structural features that control the transport properties are glass transition temperature, molecular weight, density, crystallinity, crosslinking, flexibility, orientation, etc.

a) Glass transition temperature (Tg)

The glass transition temperature of the polymer has a very marked influence on the transport properties. This is most clearly shown by the increase in Do with increasing Tg as shown in Figure 1.2.

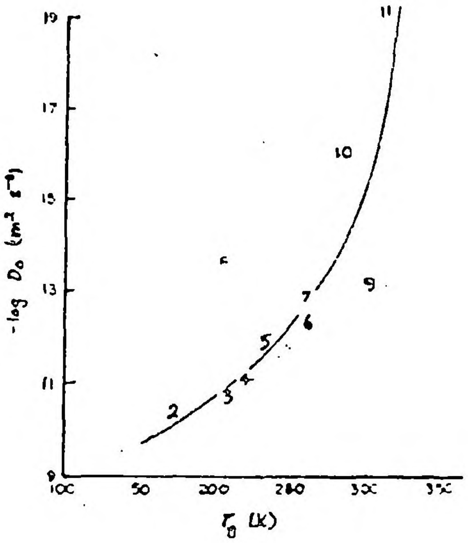


Figure 1.2. Increase in D_0 with decreasing Tg: 1, silicon rubber; 2, cis-polybutadiene; 3, natural rubber; 4, ethylenepropylene rubber; 5, poly(propyl acrylate); 6, polypropylene; 7, poly(ethyl acrylate); 8, polyisobutylene; 9, poly(butyl methacrylate); 10, poly(methyl acrylate); 11, polyvinyl alcohol).

b) Molecular weight

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 polymers. For example the diffusivity of a range of organic vapours (acetone, benzene, etc.) through polystyrene of different molecular weight decreased by a factor of almost ten as molecular weight increased from 10,000 to 3,00,000.[24] However in other systems, molecular weight has been found to have no influence on the transport of liquid permeants.

c) Density

Density of a polymer is a measure of the amount of free volume within a polymer. A reduction in density in series of polymers results in an increase in permeability.[25]

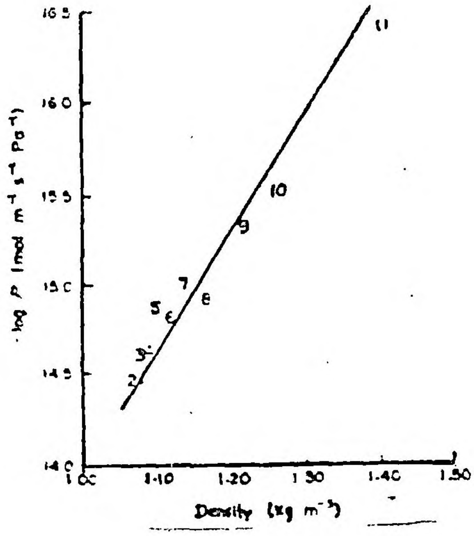


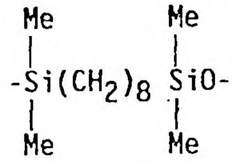
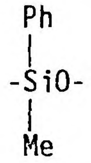
Figure 1.3. Correlation between polymer density and helium permeability P through polyethylene at 25^{0}C. 1, poly(tetramethyl-bis-L terephthalate) (1); 2, poly(tetraisopropyl-bis-A sulfone) (2); 3, poly(2,6-dimethyl-1,4-phenylene oxide) (3); 4, polytetramethylcyclobutanediol carbonate) (4); 5, poly(tetramethylObis-A carbonate) (5); 6, poly(tetramethyl-bis-L sulfone) (6); 7, poly(tetramethyl-bis-A terephthalate) (7); 8, polytetramethyl-bis-A sulfone) (8); 9, poly(bis-A carbonate) (9); 10, poly(bis--A sulfone) (10); 11, poly(ethylene terephthalate) (11).

Figure 1.3 shows a generally good correlation between polymer density and helium permeability. But three polymers do not fit well. This may be due to experimental error. But if we consider the case of butyl rubber it cannot be fit into the above curve. The density and permeability of butyl rubber are 0.93 kgm^{-3} and 2.8 x 10^{-15} mol m^{-1} S^{-1} Pa^{-1} respectively But butyl rubber is less permeable to helium than poly(phenylene oxide)(PPO) but it is well above its Tg (-76^{o}C) whereas Tg of PPO is 220^{o}C. Since the solubility of helium in both the polymers is low swelling effect cannot be invoked to explain this apparent anomaly. The low permeability of butyl rubber can be explained on the basis of the sluggish segmental motion of polymer chains caused by the steric hindrance of the two pendant methyl groups on every other main chain carbon atom.

d) Flexibility of polymer chain

In polymers with the same substitution pattern it is the flexibility of the back bone that dominates the permeation properties. This is illustrated in Table 1.1.[26]

Table 1.1. The effect of side-chain and main-chain substitution on oxygen permeability.

Polymer		Tg (^oC)	P x 10^{-1} (molm^{-1} s^{-1} Pa^{-1}
A	$-CH_2CMe_2-$	-76	0.84
B	$-CH_2SiMe_2-$	-92	0.44
C	$-OSiMe_2-$	-123	437.0
D	 $-\mathrm{Si(Me)_2(CH_2)_8Si(Me)_2O}-$	-88	1.0
E	 $-\mathrm{Si(Ph)(Me)O}-$	-28	0.14

The Si-O backbone allows rapid chain segment motion to occur in the silicon rubber (Polymer C) and substitution of the Si-O linkage by Si-CH_2 (Polymer B) dramatically reduces the permeability to a value even less than that of butyl rubber (Polymer A). Insertion of $(CH_2)_n$ sequences into a siloxane backbone (Polymer D) also tends to a decrease in permeability. Similarly the Si-O backbone substitution of methyl by more bulky substituents decrease the permeability (Polymer E).

These decreases in permeability are mainly due to a decrease in permeant diffusivity caused by the increasing rigidity of the polymer backbone and the decreasing free volume available for the diffusion of permeant molecules. The substitution of bulky functional groups in the side chain appears to have a greater influence on decreasing the diffusivity than substitution of these groups in the polymer backbone.[27]

e) Crosslinking

Barrer and coworkers[28] have studied the diffusion of a series of alkanes through rubbers and reported that for low levels of crosslinking the diffusivity decreases linearly with increase in crosslink density. At higher levels of crosslink density rate of decrease of diffusivity levelled off.

In non-crystalline polymers, diffusion coefficients decrease approximately linearly with crosslink density at low to moderate levels of crosslinking.[29,30] For instance the diffusion coefficient of nitrogen in natural rubber is reduced ten fold on crosslinking the rubber with sulphur. Crosslinking reduces the mobility of the polymer segments and tend to make the diffusivity more dependent on the size and shape of the permeant molecules and on the permeant concentration.

The nature of crosslinks also can alter the transport properties. For the same polymer at the same crosslink density, diffusivity depends on the nature of the crosslinks.

Recently, Thomas and coworkers[31] have studied the effect of different types of vulcanising systems on the transport of aromatic solvents through natural rubber. They have found that peroxide vulcanization having -C-C- crosslinks shows lowest permeability and that conventional vulcanization which results in polysulphidic crosslinks has the highest permeability. The mixed system consisting of peroxide and sulphur showed intermediate behaviour.

f) Crystallinity and orientation

In crystalline polymers the crystalline areas act as impermeable barriers to permeating molecules and have the same effect as inert fillers. That is they force the permeant molecules to diffuse along longer path lengths.The thermal history of a crystallisable polymer can be profoundly affect the permeation properties, since this can affect the number and size of crystallites present. Alter[32] has presented decrease in permeability coefficient of nitrogen in polyethylene with increased crystallinity.

The reduction in diffusivity solubility and permeability coefficients with increasing crystalline content was first noted by Van Amerongen[33] with gutta percha. Lasosky and Cobbs[34] reasoned that the solution and diffusion occurred only in the amorphous region, the solubility and diffusion coefficients might be proportional to the volume fraction of amorphous polymer.

Orientation of the polymer may also influence permeation properties. However, the overall effect is highly dependent upon crystallinity. For example deformation of elastomers has little effect on permeability until crystallisation effects occur.[35] Orientation of amorphous polymers can result in a reduction in permeability around 10 to 15% whereas in crystalline polymers example poly(ethylene teraphthalate) reductions of over 50% have been observed.[36]

Stretching or drawing of polymer films increases the orientation of the polymer chains and hence a change in permeability is activated. The permeability may increase or decrease depending on the mode of deformation.

If the temperature is reduced so that the oriented chains will be frozen and will have lower diffusivity than the unoriented polymer.[37] But elastically deformed polymers are more permeable in the deformed state.[38] This may be attributed to an increase in the free volume accompanying deformation.

1.7 Effect of plasticizers

The addition of plasticizers to a polymer results in increased segmental mobility and hence enhanced penetrant transport. Barrer and coworkers[39] reported on the increase in diffusion and permeability coefficients of hydrogen and neon through poly(vinyl chloride) by the addition of tricresyl phosphate as plasticizer to the polymer. But it lowered the solubility coefficient and glass transition temperature.

1.8 Effect of penetrant properties

An increase in size in a series of chemically similar penetrants, generally leads to an increase in their solubility coefficients due to their increased boiling points, but will also lead to a decrease in their diffusion coefficients due to the increased activation energy needed for diffusion.[40]

Also the permeability depends on the shape of the permeant. For example flattened or elongated molecules have higher diffusion coefficient than spherical molecules of equal molecular volume.[41,42] Generally permeant size and shape effects are more pronounced in glassy than in rubbery polymers.

Kim et al.[43] have reported the decrease in equilibrium penetrant uptake with increasing penetrant chain length in the transport of alkanes from heptane to dodecane through crosslinked polystyrene. Aminabhavi and coworkers[44,45] studied the effects of nature of polymer and penetrant size on diffusion of organic solvents through polymers. They have reported lowering of diffusivity through natural rubber, SBR, etc. with increasing size of the penetrants from benzene to mesitylene.

1.9 Effect of fillers

The mechanical properties and durability of rubber can be improved by the use of reinforcing fillers, like carbon black and silica. A large number of studies have been reported in the literature about the effects of fillers on the sorption behaviour of elastomers.

The addition of inert fillers may either increase or decrease the permeability depending upon their degree of adhesion and compatibility with the polymer. Generally fillers are impermeable to the permeant molecules. If an inert filler is compatible with polymer matrix it will slower the permeation rate due to the reduced area for transport and the increased tortuosity of the permeation path.[46,47] The degree of tortuosity is dependent on the volume fraction of the filler and shape and orientation of the particles. When the filler is incompatible with the polymer, voids will occur at the interface resulting in an increased free volume of the system, which leads to an increase in permeability.

Kwei and Kumins[48] reported that the sorption of chloroform by an epoxy resin was lowered by about 70% when 5% filler was incorporated.

The equilibrium swelling data of natural rubber and a number of synthetic rubbers in a variety of solvents with and without filler is studied by Boonstra and Dannenberg.[49] They found that the solvent uptake of carbon black filled membrane depends on the volume loading of the filler. The non black fillers caused a reduction in rubber swelling which did not depend on the filler loading.

Coran et al.[50] studied the transport of solvents in unidirectional rubber-fibre composites and concluded that fibres restrict the solvent uptake. The rubber fibre adhesion in fibre filled composites can be tested by the technique of equilibrium swelling in solvents. Lowering of equilibrium swelling in fibre filled samples indicates fibre-rubber adhesion. Recently Thomas and coworkers[51] have used equilibrium swelling to study adhesion of short sisal fibre to natural rubber. They found that the equilibrium swelling of short sisal fibre - natural fibre composites containing the dry bonding system of hexa methylene diamine and resorcinol is lower than that without the bonding agent. This indicates that the bonding agent used was effective in rubber-fibre adhesion. They have also found from swelling studies that chemically treated fibres have got better adhesion to natural rubber than untreated fibres.

Unnikrishnan and Thomas[52] have reported that natural rubber compounds incorporated with high abrasion furnace (HAF) black take lesser amount of aromatic hydrocarbons compared to silica filled samples. This can be explained by the formation of bound rubber in carbon black filled samples which restricts segmental mobility and also to lower crosslink density of the silica filled samples due to the deactivation of the accelerator by the polar surface of silica.

Stickney and Muller[53] studied the kinetics of swelling of carbon black filled styrene-butadiene rubber vulcanizates in presence of isooctane. It was found that for rubber vulcanizates diffusivity increased with the concentration of the penetrant. Lawandy and Helay[54] investigated the diffusion of chloroform in neoprene rubber vulcanizates consisting of different carbon black types and loadings. In this work they found a decrease in penetration rate with the increase of particle size and a decrease in penetration rate at a higher degree of equilibrium volume swelling. These results were attributed to the wrinkles formed at the surface of rubber at these high equilibrium swelling. Horkay et al.[55] studied the effect of silica particles on the elastic and osmatic properties of chemically crosslinked polydimethyl siloxane networks swollen in toluene. The properties were compared with the corresponding unfilled gels. The elastic modulus of the filled samples was found to exceed considerably that of the unfilled samples, highlighting the reinforcing effect of silica particles which behave like additional crosslinks.

1.10 Scope of the work

Natural rubber has many engineering applications, owing to its high resilience and good abrasion resistance. It has many applications on the field of engineering and in industry. The hardness and tensile properties of natural rubber can be improved by using reinforcing fillers. Natural rubber (NR) is a historical choice for many applications. The typical applications include shock mounts, drive belts, bushings, etc. Although NR is not inherently oil resistant, there are many instances where NR containing products are coming in contact with oils and fuels. The data on solvent penetration through natural rubber and the effect of white fillers on solvent penetration of natural rubber are insufficient and therefore it is imperative to throw light on solvent transport through this polymer. In this study the solvents selected are petrol, mineral turpentine and diesel which are not yet come under the solvent transport studies. In fact these solvents are the most widely used aliphatic hydrocarbons mainly as fuels and solvents.

The objective of the present work is to investigate the mode of diffusion and the extent of interaction of petrol, diesel and mineral turpentine through crosslinked NR containing different types of silica filler such as ordinary precipitated silica, Hysil-210 and ultrasil VNO_3. The transport parameters are determined using a sorption gravimetric method. The effect of crosslink density on diffusion is studied using samples of the same curing system with various cure times. To study the effect of temperature on diffusion, experiments are conducted at three temperatures. From this activation energy for diffusion and permeation are calculated. Heat of sorption, entropy of sorption etc. are also evaluated, to know about the mode of permeation of the solvent and to understand the nature of the solvent molecules within the polymer matrix. The polymer – solvent interaction parameters are calculated using Flory-Rehner theory to compare the solvent interaction of the systems with different silica fillers. The number average molecular mass between crosslinks and degree of crosslinking have also been calculated. The effect of increase in solvent size in the transport behaviour has also been evaluated. Finally, the concentration dependence of diffusion coefficient D in the three solvent is also investigated.

Chapter 2

MATERIALS AND EXPERIMENTAL METHODS

MATERIALS AND EXPERIMENTAL METHODS

2.1 Materials

Natural rubber (NR) used was of ISNR-5 grade. The fillers selected were of (i) ordinary precipitated silica commercially available in the market (particle size 32 nm), ultrasil-VN_3 (particle size 15 nm) and Hysil-210 (particle size 22 nm). The solvents petrol, mineral turpentine and diesel used in the present study were distilled, before use. Some important physical properties of the solvents are given in Table 2.1. All other chemicals were of laboratory grade.

Table 2.1. Physical properties of penetrants used.

Penetrant	Density at 25°C g/cm^3	Molecular weight	B.P (≈)
Petrol	0.7144	100	95
Mineral turpentine	0.78	170	200
Diesel	0.8278	326	300

2.2 Preparation of the samples

The NR samples were vulcanized by conventional vulcanization technique using accelerated sulphur. The formulation of the mixes used is given in Table 2.2. The mixing was done in a two roll mixing mill (friction ratio 1:1.4 at 30^{o}C). The vulcanization behaviour of the samples were studied by a Monsanto rheometer R_{100}. The rheographs of the mixes are shown in Figure 2.1 and the main characteristics of cure graph are given in Table 2.3. In order to study the effect of cure time and the effect of different silica fillers, the three types of filled NR and the gum sample were cured to different cure times, i.e., t_{70}, t_{80}, t_{90} and one sample was over cured 5 minutes beyond t_{100}. It may be noted that t_{90} represents the optimum cure time at which the sample has been cured to 90% of the maximum torque. Similarly t_{70} and t_{80} samples were cured to 70% and 80% of the maximum torque respectively. The curing was done on a hydraulic press at 160^{o}C and under a pressure of 25 tonnes.

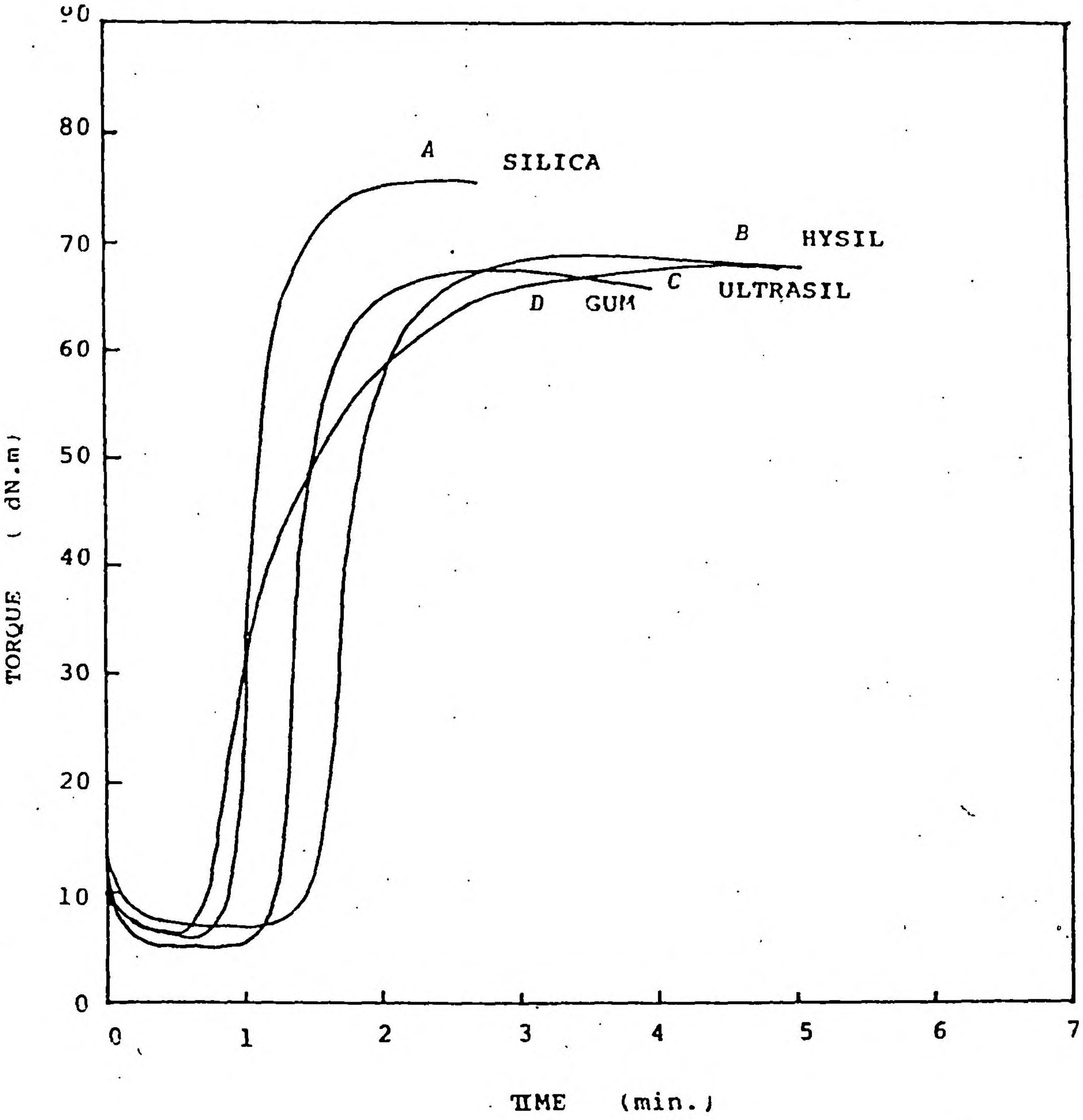


Figure 2.1 Rheographs of mixes A, B, C, and D

Table 2.2. Formulation of mixes.

	Ingredients	mixes			
		A	B	C	D
1.	Natural rubber	100	100	100	100
2.	Stearic acid	1.5	1.5	1.5	1.5
3.	Zinc oxide	5	5	5	5
4.	Ordinary precipitated silica	30	--	--	--
5.	Hysil-210	--	30	--	--
6.	Ultrasil	--	--	30	--
7.	CBS*	0.7	0.7	0.7	0.7
8.	TMTD**	0.075	0.075	0.075	0.075
9.	Sulphur	2.0	2.0	2.0	2.0

*Cyclohexyl benzothiozyl sulphenamide.
**Tetramethyl thiuram disulphide.

Table 2.3. Cure characteristics of the mixes A, B, C and D

Cure properties	A	B	C	D
Minimum Torque (dN.m)	5.9	7	7	5
Maximum Torque (dN.M)	75.5	68.8	69	67.2
Cure time (min) at 20 d N.m	0.96	1.619	0.857	1.33
Optimum cure time(min)	1.4	2.19	2.1	1.095

2.3 Diffusion experiments

The vulcanized samples with different fillers and the gum compound were cut into uniform size circular pieces (diameter 1.9 cm) using a steel die. The thickness of the samples was measured at several points using a micrometer. Dry weights of the cut samples were taken before immersion into different liquids taken in air tight bottles. After immersion of the samples into respective liquids, the bottles were placed in a thermostatically controlled oven.

The samples were removed from the test bottles at periodic intervals, the wet surfaces were dried between filter papers and weighed immediately. They were then placed back into test bottles. The samples should be put back into the air tight container after weighing within 40 seconds. Otherwise error may be occurred in the calculation. The process was continued until equilibrium swelling was achieved. The experiments were conducted 28, 50 and 60°C. The results of sorption experiments were expressed as moles of liquid sorbed by 100 g of NR sample, at different time intervals (Q_t). The curves are plotted with $\surd t$ vs Q_t where t is the time intervals in seconds at which the weight of swollen samples are taken.

Chapter 3

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

3.1 Effect of particle size of fillers

The sorption curves of gum (unfilled) and different types of silica filled samples were given in Figures 3.1, 3.2, 3.3 and 3.4. The Q_t increases linearly at the initial stage of sorption and then gradually levels off, as in the Fickian transport mechanism. It can also be seen from the figure that the loading of natural rubber samples with ultrasil-VN_3 and Hysil 210 reduces Q_t considerably. The lowering of Q_t is maximum for ultrasil, in mineral turpentine and petrol. In diesel Hysil shows the lowest Q_t value. It is surprising to note that there is no reduction of Q_t for the sample filled with the commercially available precipitated silica used in this experiment, and the Q_t values are even slightly higher than gum compound in diesel and in mineral turpentine.

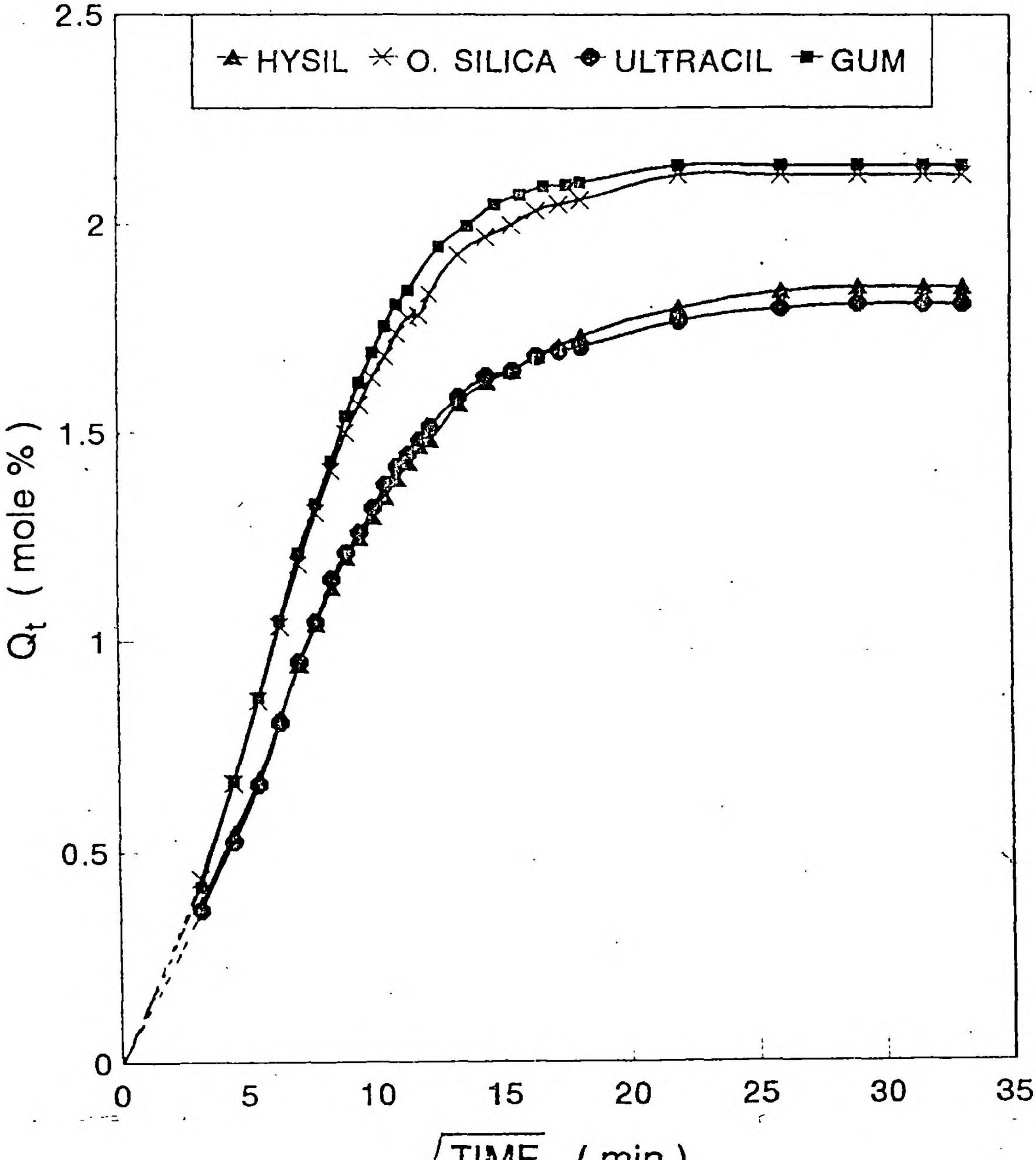


Figure 3.1 Effect of three silica fillers
(penetrant: petrol, cure time: t_{90})

②

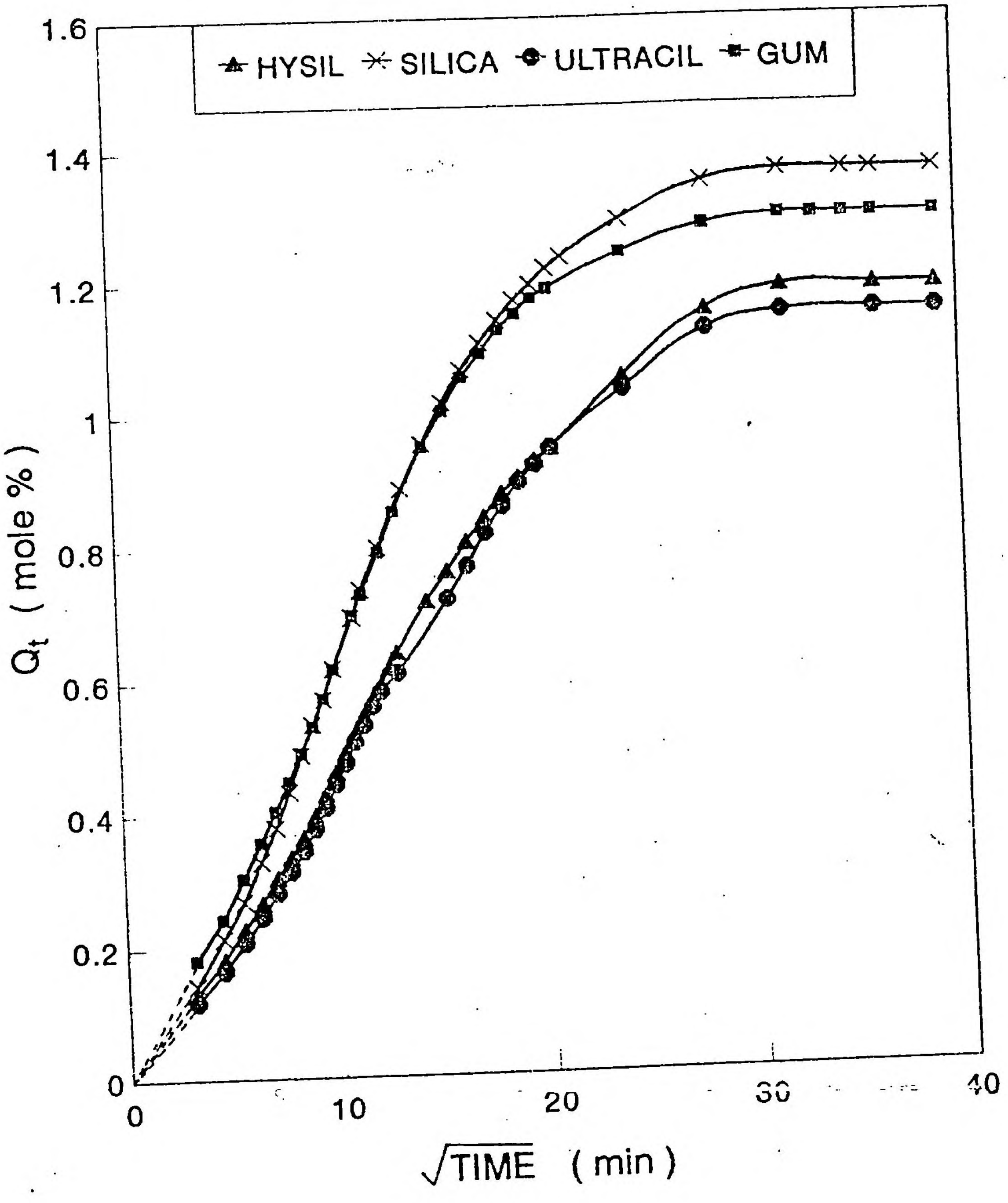


Figure 3. 2 Effect of three silica fillers
(penetrant: mineral turpentine, cure time: t_{90})

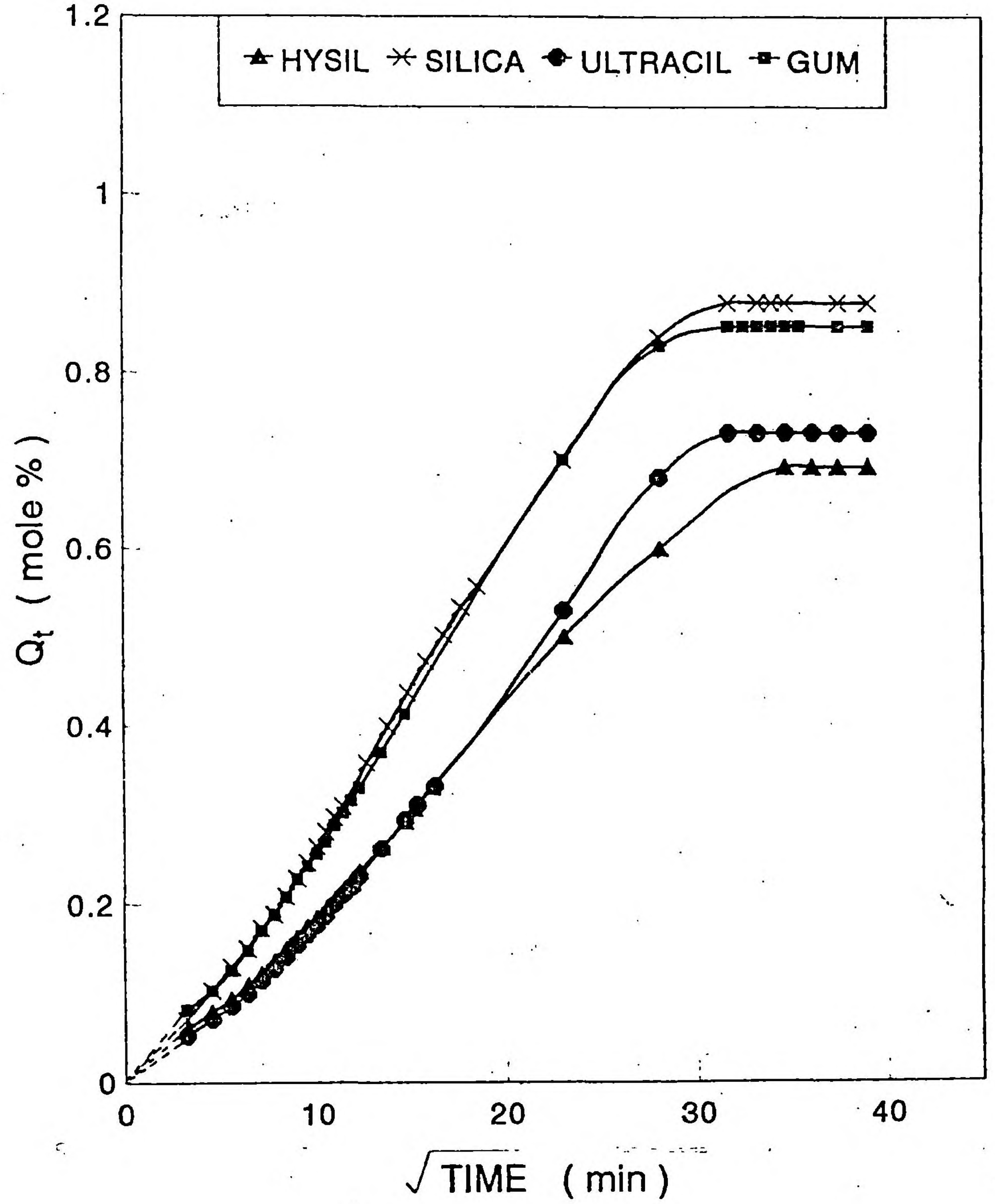


Figure 3.3 Effect of three silica fillers
(penetrant: diesel, cure time t_{90})

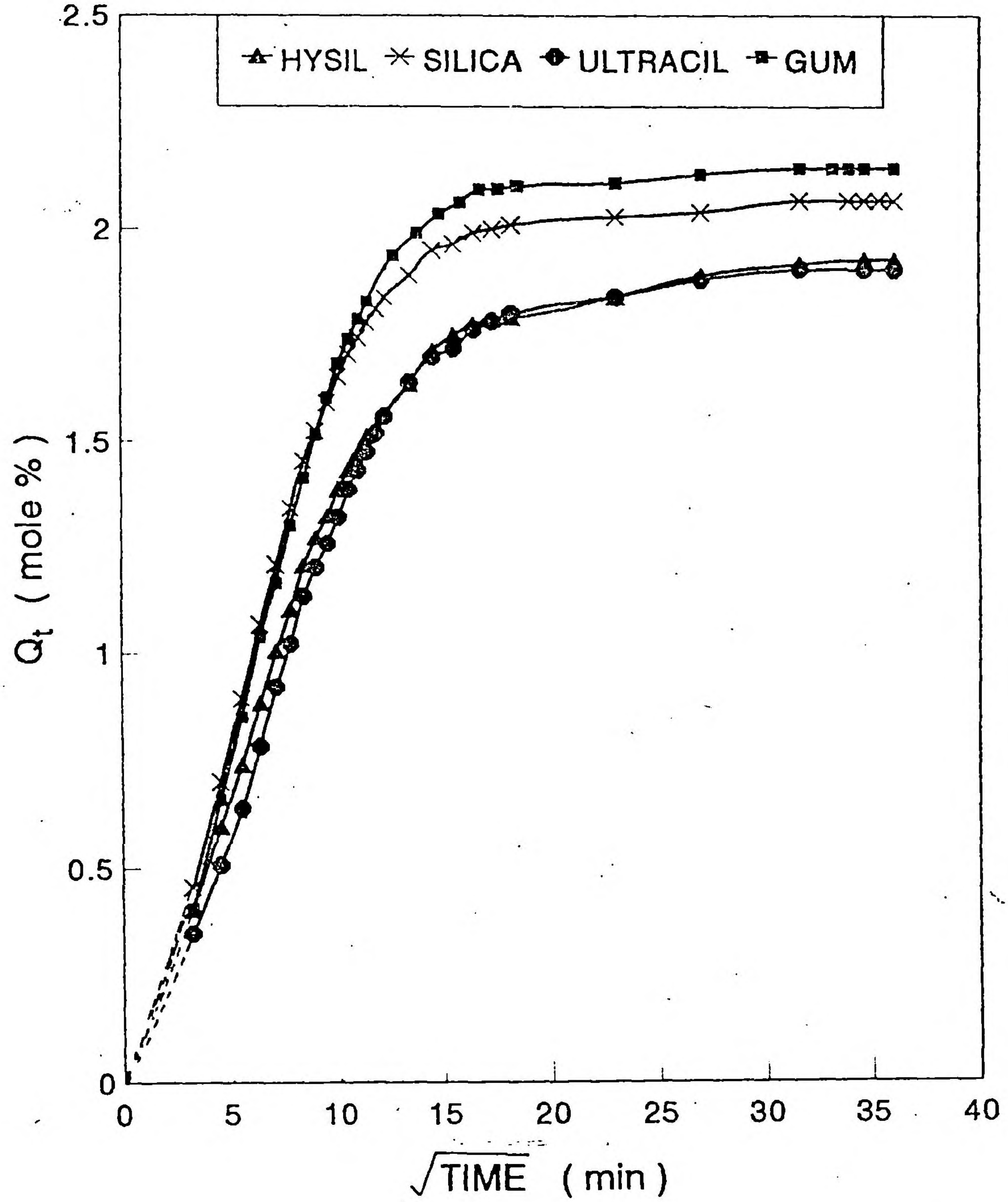


Figure 3. 4. Effect of three silica fillers

(penetrant: petrol, cure time t_{70})

⑤

Any way the Q_∞ values of ultrasil-VN_3 and Hysil-210 filled samples have comparably lower values than the gum sample, in the three solvents tried i.e., petrol, mineral turpentine and diesel. This is shown in Table 3.1. The lower value shown by ultrasil VN_3 and Hysil-210 can be explained by high crosslinking density and the bound rubber formation in these samples which effectively binds the individual polymer resins. The estimated bound rubber formed by the three types of filers are given below. [Ordinary precipitated silica - Nil, Ultrasil VN_3 - 8.43% and Hysil-210 - 7.61%].

Table 3.1. Values of Q_∞ in various solvents for the three vulcanizing systems cured to t_{90}.

Solvent	Filler used in the system		
	Ordinary precipitated silica	Hysil-210	Ultrasil-VN_3
Petrol	2.1153	2.018	1.8058
Mineral turpentine	1.3612	1.2765	1.1470
Diesel	0.8786	1.6918	0.7303

The bound rubber can reduce the free volume of the system and the solvent uptake will be reduced. The bound rubber content of commercially available precipitated silica used for the experiment is found to be negligible.

In order to confirm the extent of crosslinking in these samples we have estimated the molar mass M_c between crosslinks of NR samples using the Flory-Rehner theory.

$$M_c = \frac{-\rho_p \, V(\phi)^{1/3}}{\ln(1-\phi) + \phi + \chi \phi^2} \qquad (3.1)$$

where V is the molar volume of the solvent and ρ_p, the density of the polymer, χ and ϕ are the polymer-solvent interaction parameter and the volume fraction of rubber in the solvent swollen sample respectively. The volume fraction of the swollen polymer is calculated as

$$\phi = \frac{(d-fw)/\rho_r}{(d-fw)/\rho_r + A_0/\rho_s} \qquad (3.2)$$

where d is deswollen weight of polymer, f, insoluble components, w, initial weight of the sample, ρ_r, density of the polymer, ρ_s, density of the solvent and A_o, solvent weight at equilibrium. χ parameter has been calculated using the following equation.

$$\chi = \frac{d\phi}{dt} \, \frac{[(\phi/1-\phi) + N \ln(1-\phi) + N\phi]}{[2\phi \, (d\phi/dT) - \phi^2 N \, d\phi/dT - \phi^2/T]} \qquad (3.3)$$

$$\text{and} \quad N = \frac{(\phi)^{2/3} - 2/3}{\phi^{1/3} - 2\phi/3} \qquad (3.4)$$

The values of degree of crosslinking (ν), and the estimated χ values and the volume fraction of swollen rubber ϕ of samples with different fillers in mineral turpentine are given in Table 3.2 and 3.3.

Table 3.2. values are crosslink density of samples with different fillers in mineral turpentine.

	Ordinary precipitated silica	Hysil-210	Ultrasil VN_3
χ value	0.1888	0.4411	0.3157
M_c	6333.7	13100	8570
$\nu \times 10^5$	7.894	3.817	5.834

Table 3.3. Volume fraction of the samples with the three silica fillers for conventionally vulcanized natural rubber in mineral turpentines at various cure times.

	Samples with								
Temperature	Ordinary precipitated			Hysil-210			Ultrasil		
°C	t_{50}	t_{70}	t_{90}	t_{50}	t_{70}	t_{90}	t_{50}	t_{70}	t_{90}
28°	0.2276	0.2275	0.2207	0.2453	0.2487	0.2469	0.2210	0.2294	0,2497
50°	0.2216	0.2258	0.2146	0.2300	0.2310	0.2256	0.2127	0.2338	0.2498
60°	0.2213	0.2216	0.2158	0.2246	0.2260	0.2248	0.2044	0.2269	0.2459

It is seen from the table that the interaction parameter value (χ) for ordinary precipitated silica is minimum. This clearly suggests that highest degree of interaction of ordinary precipitated silica filled sample, with the hydrocarbons . The bound rubber content is also negligible and so the solvent uptake is highest for ordinary precipitated silica than Hysil-210 and ultrasil VN_3. The particle size of ordinary precipitated silica is higher than Hysil-210 and ultrasil VN_3.

3.2 Effect of cure time

The influence of cure time on the sorption behaviour of silica filled sample is shown in Figures 3.5, 3.6 and 3.7, respectively. In all the figures the Q_t values of ultrasil incorporated samples, cured to different cure times i.e., t_{50}, t_{70}, t_{90} and overcured samples in the three solvents are plotted against square root of time. The solvent used for sorption is mineral turpentine in Figure 3.5 and diesel in Figure 3.6. There is considerable difference in the maximum value of Q_t between samples cured for different cure times. The t_{90} sample shows the minimum Q_t value while the t_{50} sample shows highest. The over cured sample might have undergone devulcanization which reduces the number of crosslinks between the rubber chains. The increase in crosslink density with increase in cure time can be seen from the Table 3.4.

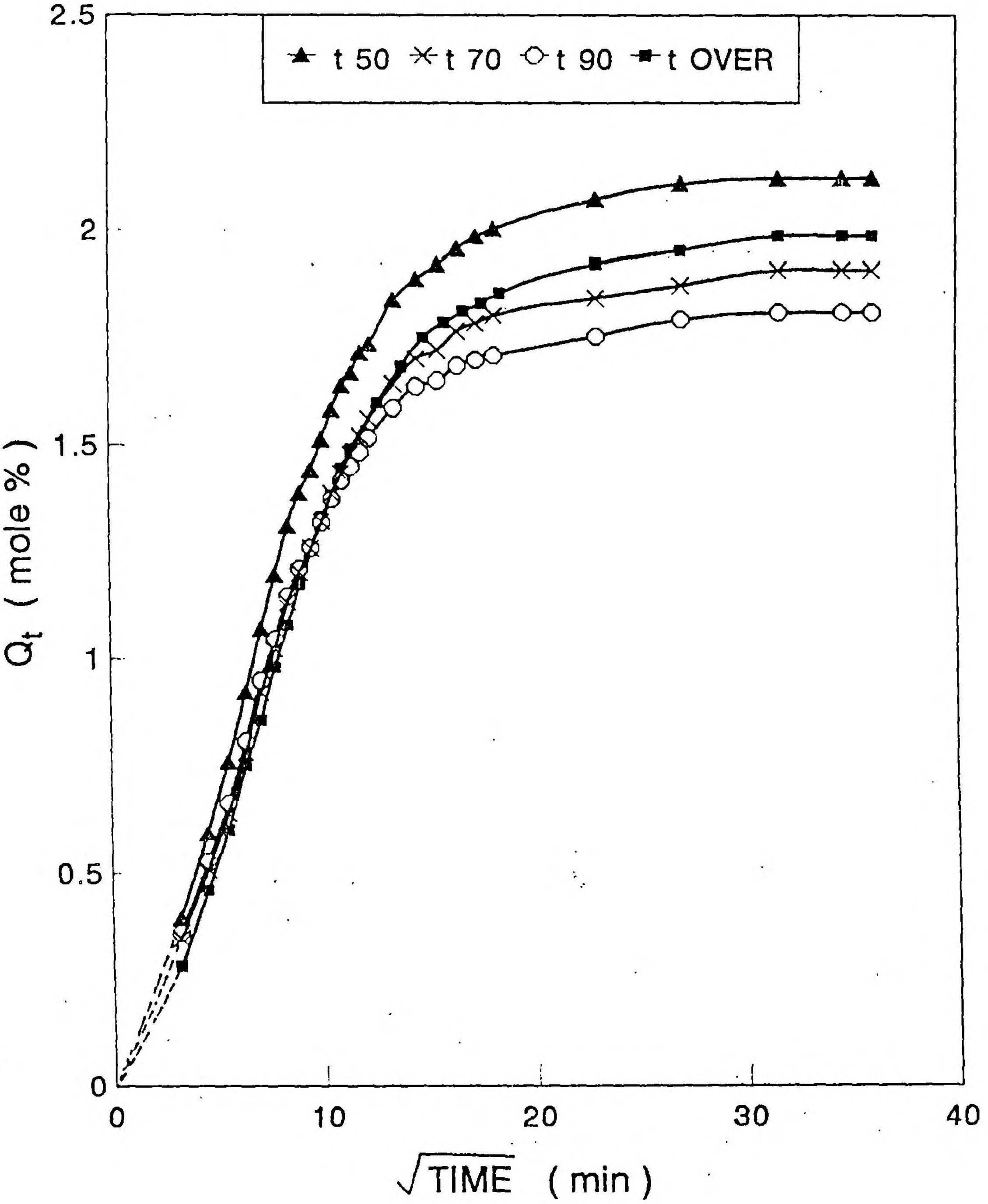


Figure 3.5 Effect of cure time
(Filler: ultrasil, penetrant: petrol)

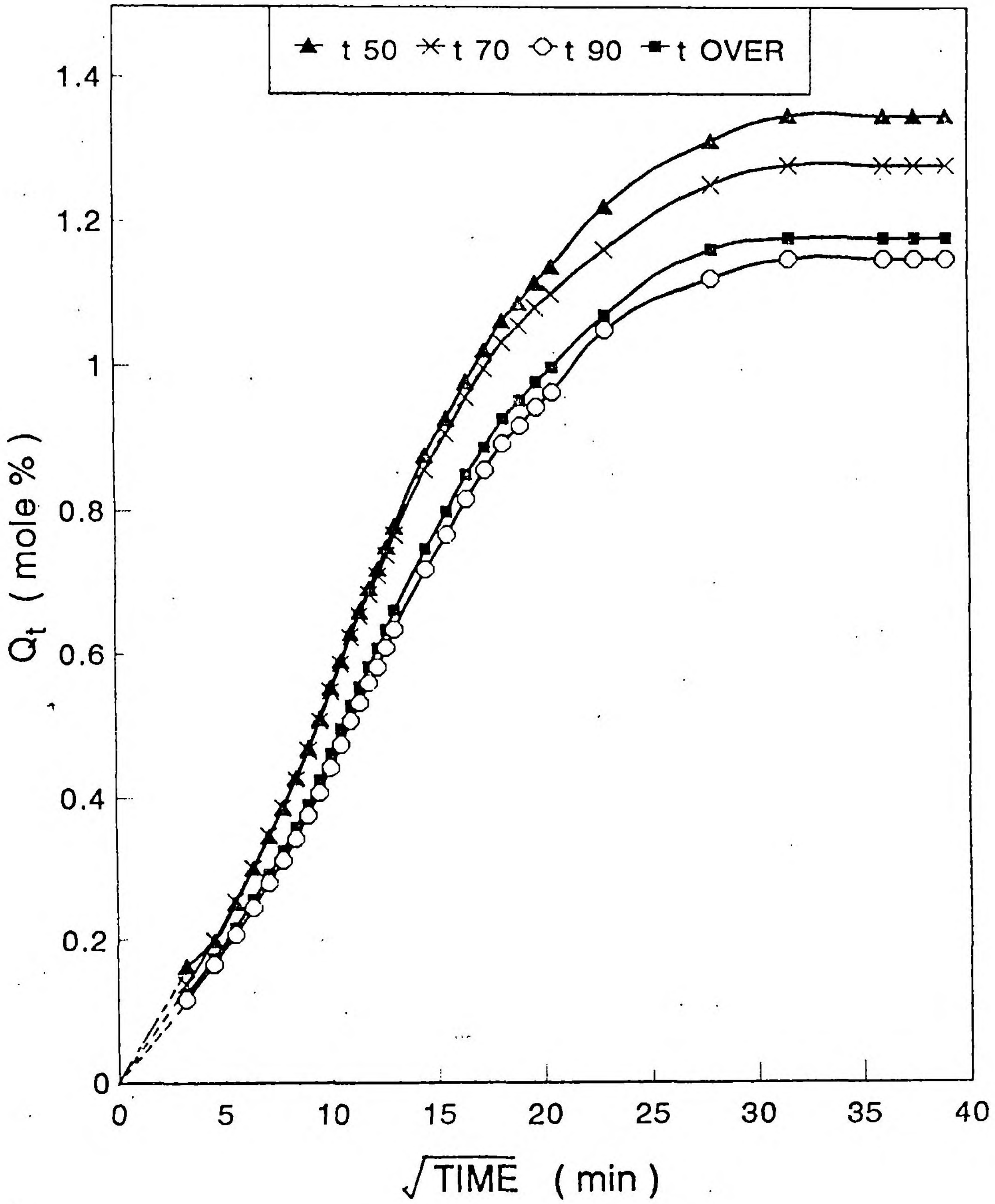


Figure 3. 6 Effect of cure time
(Filler: ultrasil, penetrant: mineral turpentine)

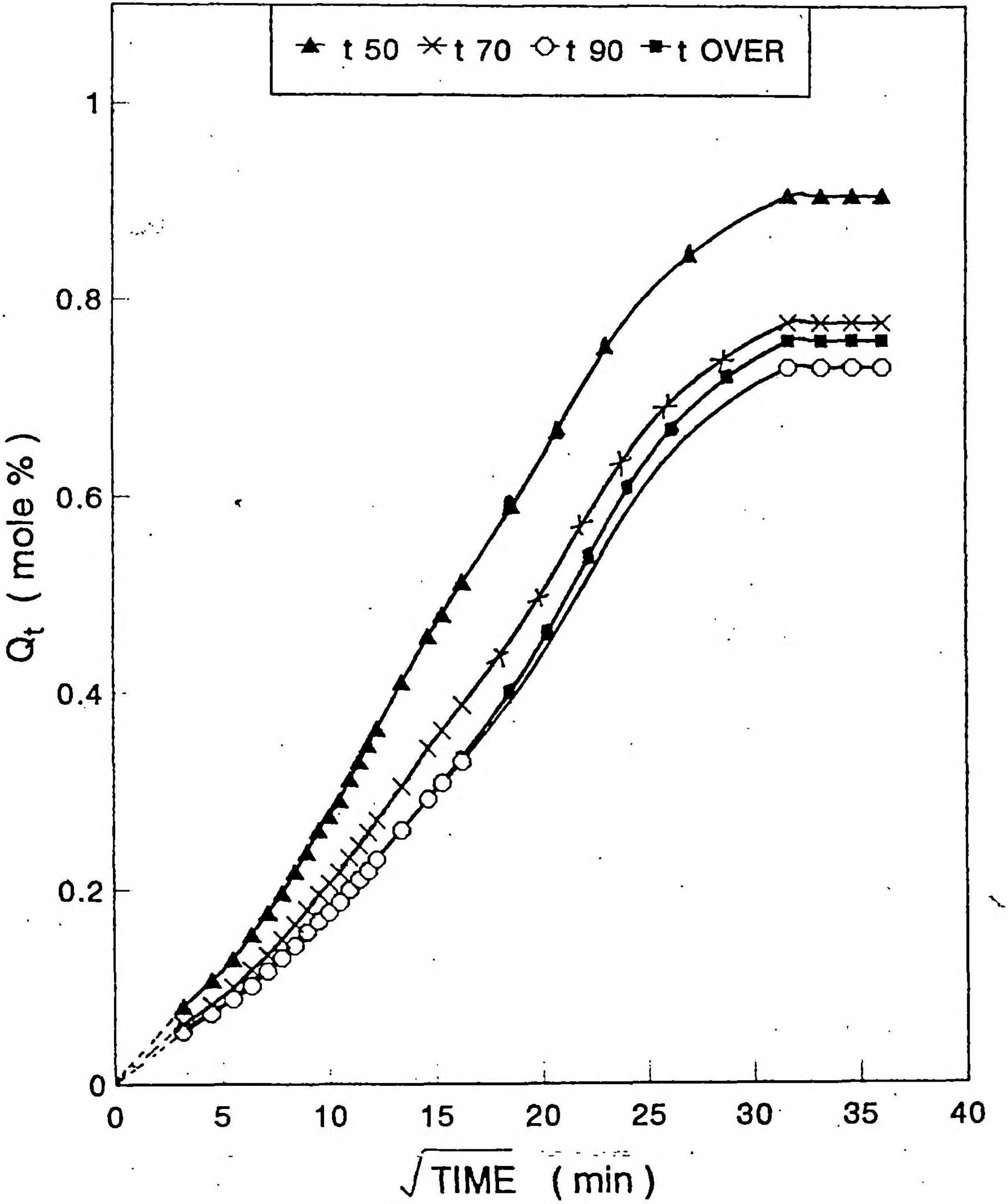


Figure 3. 7. Effect of cure time
(Filler: ultrasil, penetrant: diesel)

8

Table 3.4. Effect of cure time on crosslink density of the samples filled with the three silica fillers. Solvent used is mineral turpentine.

Filler	t_{50}	t_{70}	t_{90}
Ultrasil	4.04	5.83	11.05
Ordinary precipitated silica	7.13	7.85	7.89
Hysil-210	3.82	3.91	4.94

3.3 Effect of penetrant size

In Figure 3.8 the sorption curves of petrol, mineral turpentine and diesel on natural rubber samples filled with Hysil-210 and cured to t_{90} are presented. There is a systematic trend in the sorption behaviour of these aliphatic hydrocarbons. With an increase in molecular weight of the penetrant there is a decrease in the Q_t values. Here petrol shows highest solvent uptake while diesel shows lowest. The same trend is shown by the other two samples filled with the other types of silica. The fact is clear from Table 3.1. The decrease in Q_t values with increase in penetrant size might be due to the greater activation energy needed for activating the diffusion process. The decrease in the values of interaction parameters with increase in the molecular weight of the penetrant can be seen from Table 3.5. It is due to the differences in the values of solubility parameters of the fillers in the solvent.

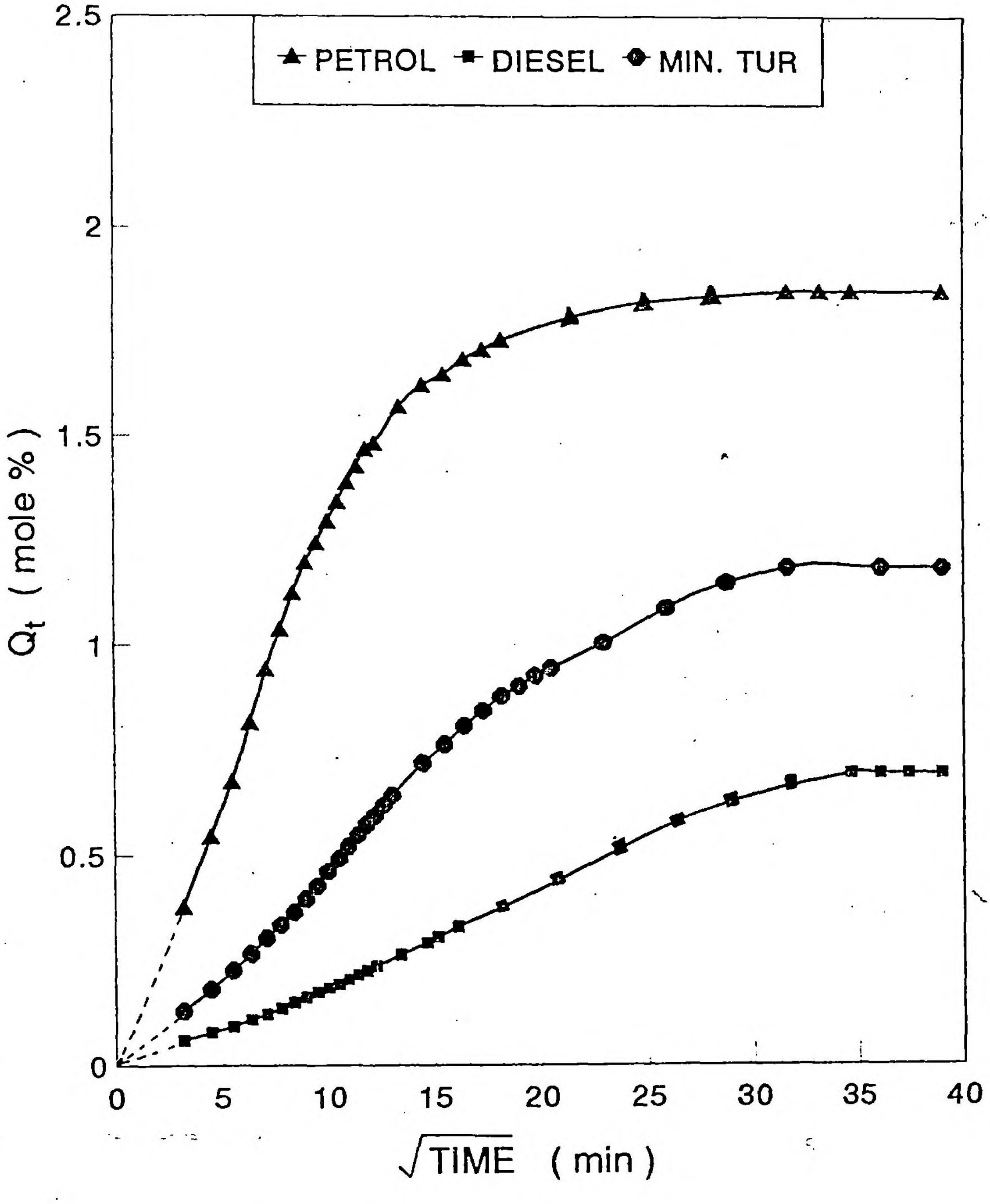


Figure 3.8 Effect of penetrant

(Filler: hysil 210, cure time t_{90})

a

Table 3.5. values and crosslink density values of the sample filled with Hysil-210 in the three solvents.

Solvents	χ	M_c	$\nu \times 10^5$
Petrol	0.3057	4996.9	10.00
Mineral turpentine	0.4412	13112	3.8
Diesel	0.4415	4352	11.488

3.4 Mechanism of transport

Mechanism of sorption can be analysed using the empirical equation.

$$\log Q_t/Q\infty = \log k + n \log t \qquad (3.5)$$

where Q_t and $Q\infty$ are the mole percentage sorption at time t and at equilibrium respectively. k is a constant which depends on the structural features of the polymer material and gives some idea regarding the interaction between the polymer and the solvents. The value of n gives an idea abut the mechanism of sorption.

If $n = \frac{1}{2}$ the mechanism of sorption is said to be regular Fickian. In Fickian type sorption the rate of diffusion of permeant molecules is much less than the polymer segment mobility. If n = 1 the mechanism of sorption is said to be non-Fickian. This arises when the rate of diffusion of permeant molecules is much greater than the polymer segment mobility.

If n lies between 0.5 and 1 then mechanism of sorption follows an anomalous trend. Here the mobility of permeant molecule and polymer segment relaxation rate are similar. From the sorption data of the experiment the values of n and k at different cure times are calculated by regression analysis and placed in Table 3.6. The values of n ranges from 0.4394-0.689. This suggests that our systems under study slightly deviates from normal Fickian mode. There is a regular trend in the values of k i.e., with an increase in molecular weight of the solvent there is a decrease in the value of k. Higher values of k indicates good interaction between polymer and solvent. The values of n and k at higher temperature are given in Table 3.7. However no systematic trend could be seen at higher temperature.

Table 3.6. Analysis of sorption data of aliphatic hydrocarbons on natural rubber membrane

		n			$k \times 10^2$ g/g $\min^n$		
		Solvent					
System	State of cure	Petrol	Mineral turpentine	Diesel	Petrol	Mineral	Diesel
Ordinary silica A	t_{50}	0.6236	0.5919	0.5879	5.724	2.810	2.161
	t_{70}	0.6082	0.5767	0.5751	5.452	2.853	1.935
	t_{90}	0.6219	0.6012	0.5456	4.908	2.608	2.323
	t_{over}	0.5854	0.6002	0.5199	5.248	2.435	2.289
Hysil-210	t_{50}	0.5607	0.5329	0.4493	6.500	3.118	3.255
	t_{70}	0.5644	0.5181	0.4385	5.688	3.170	3.356
	t_{90}	0.5612	0.5240	0.4394	5.559	3.250	3.143
	t_{over}	0.5661	0.5028	0.4385	7.276	3.819	3.309
Ultrasil	t_{50}	0.6166	0.4733	0.4894	5.246	3.867	2.772
	t_{70}	0.5978	0.5725	0.4831	4.522	2.862	2.434
	t_{90}	0.5936	0.5433	0.4718	5.004	2.883	2.324
	t_{over}	0.6890	0.5250	0.4554	2.935	3.145	2.552

Table 3.7. Effect of temperature on the values of n, k, P, S, D, K_s, ν, ϕ of Hysil-210 in petrol (Cure time: t_{90}).

Solvent	Temp.°C	n	$k\times10^2$	S	$P\times10^7$	$D\times10^7$	$K_s\times10^2$	ϕ	ν
Petrol	28	0.5448	5.817	1.85	12.58	6.80	1.850	0.2390	1.001
	50	0.6337	4.613	1.93	18.48	9.56	1.930	0.2360	0.972
	60	0.4745	8.880	2.03	13.97	6.89	2.020	0.2280	0.899
Mineral	28	0.5138	3.340	2.01	3.34	1.66	1.185	0.2460	0.381
	50	0.6861	2.004	2.20	4.40	1.91	1.300	0.2256	0.306
	60	0.5321	3.400	2.25	5.05	2.20	1.325	0.2248	0.304
Diesel	28	0.4264	3.250	1.56	1.04	0.66	0.692	0.4145	1.149
	50	0.3214	4.880	1.89	1.63	0.93	0.838	0.4037	1.072
	60	0.4102	5.230	1.98	2.46	1.24	0.880	0.3929	1.008

3.5 Diffusion, sorptivity and permeability

The solvent diffusivity D into natural rubber samples was calculated using the equation

$$D = \pi \left[\frac{h\theta}{4Q_\infty} \right]^2 \qquad (3.6)$$

where h is the initial sample thickness, θ the slope of the linear portion of sorption curve before attainment of 50% equilibrium and Q_∞ has the same meaning as before. Diffusivity is a kinetic parameter which depends on the polymer segmental mobility. From Figure 3.9 it is clear that diffusivity varies inversely with molecular weight of the penetrant.

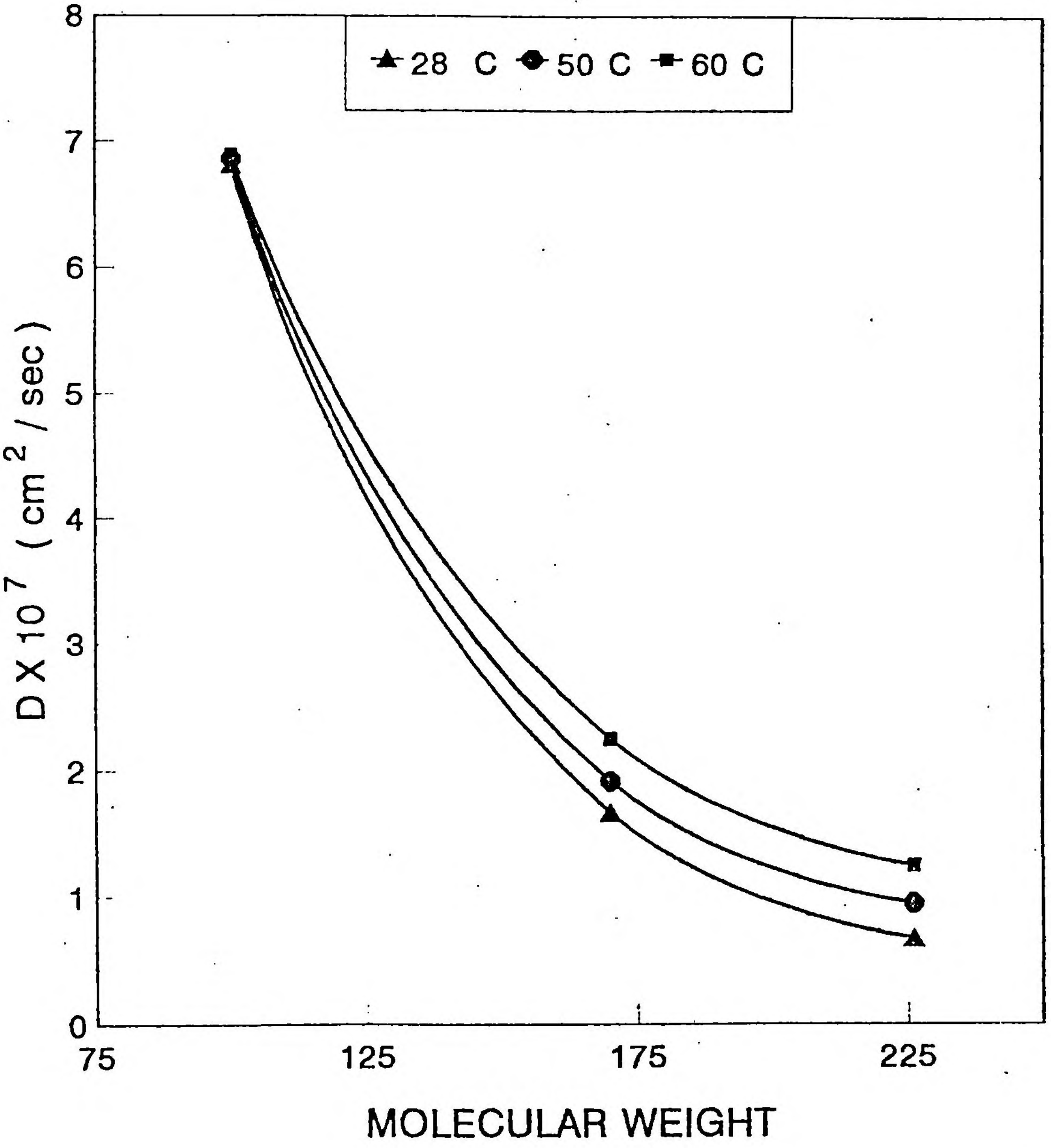


Figure 3.9 Effect of molecular weight of penetrants on diffusion coefficient

Sorption describes the initial penetration and dispersal of permeant molecules into the polymer matrix. Sorption coefficient is calculated from the equilibrium swelling using the relation.

$$S = M_\infty/M_0 \qquad (3.7)$$

where M_∞ is the mass of solvent taken up at equilibrium and M_0 is the initial mass of polymer sample. Sorption coefficient is a thermodynamic parameter which depends on the strength of the interactions in the polymer/penetrant mixture. Permeation is a combined process of diffusion and sorption and hence the permeability of solvent molecules into polymer membrane depends upon both diffusivity and sorptivity. Hence the permeation coefficient P can be defined as

$$P = D \times S \qquad (3.8)$$

where D is the diffusion coefficient and S, the sorption coefficient. Table 3.7 shows the values of S and P.

The sorption coefficients unlike diffusion coefficients show a regular trend in all the solvents. Sorption coefficient values are found to increase with increasing temperature.

The permeation coefficient values are also found to decrease with increasing penetrant size (Table 3.7). It is minimum for diesel solvent and maximum for petrol solvent. But there is no systematic trend with increasing temperature.

3.6 Concentration dependence of diffusion coefficient

The concentration dependence of the diffusion coefficient D can be seen from the Figure 3.10. The diffusion coefficient first increases and then remains constant over a wide range of concentration for mineral turpentine, and for petrol it increases to maximum and then decreases. For diesel, D remains constant for a range of concentration initially and then increases to maximum and gradually decreases.

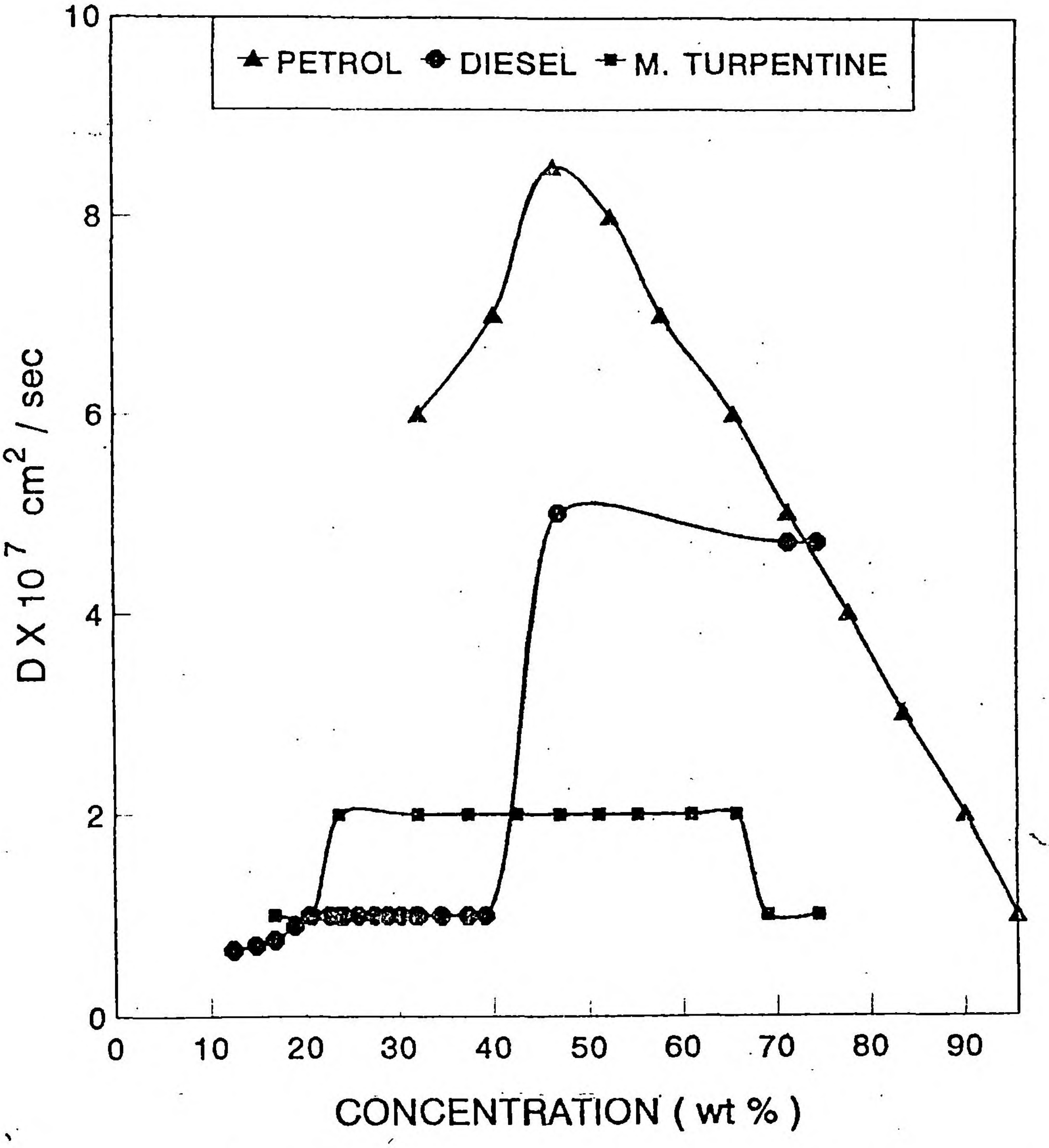


Figure 3. 10 Concentration dependence of diffusion coefficient

11

3.7 Thermodynamic analysis

For the further study of the variation of interaction of solvents with the polymer samples filled with different types of silica the experiments were conducted at 50 and 60 in addition to 28°C. The sorption curves of sample filled with Hysil-210 at 28, 50 and 60°C are given in Figure 3.11. The solvent used is petrol. From the figure it is clear that as the temperature increases the rate of diffusion also increases, that is, temperature activates diffusion process. The slope of the linear portion increases with temperature indicating that the transport process is temperature activated. Even at 60°C the shape of the curves remains the same as that at 27°C. This indicates that solvent transport process occurs by the same mechanism in the temperature range studied. The Q_∞ values increase with temperature indicating that the temperature activates the solvent uptake. The values of constant k and the exponent n in the equation is obtained by power regression analysis of the equation using values of Q_t/Q_∞ and t for the linear part of the respective plots. The values of n and k are given in Table 3.7. The values of n did not show any significant variation with change in temperature. So the mode of transport is same in the temperature range studied.

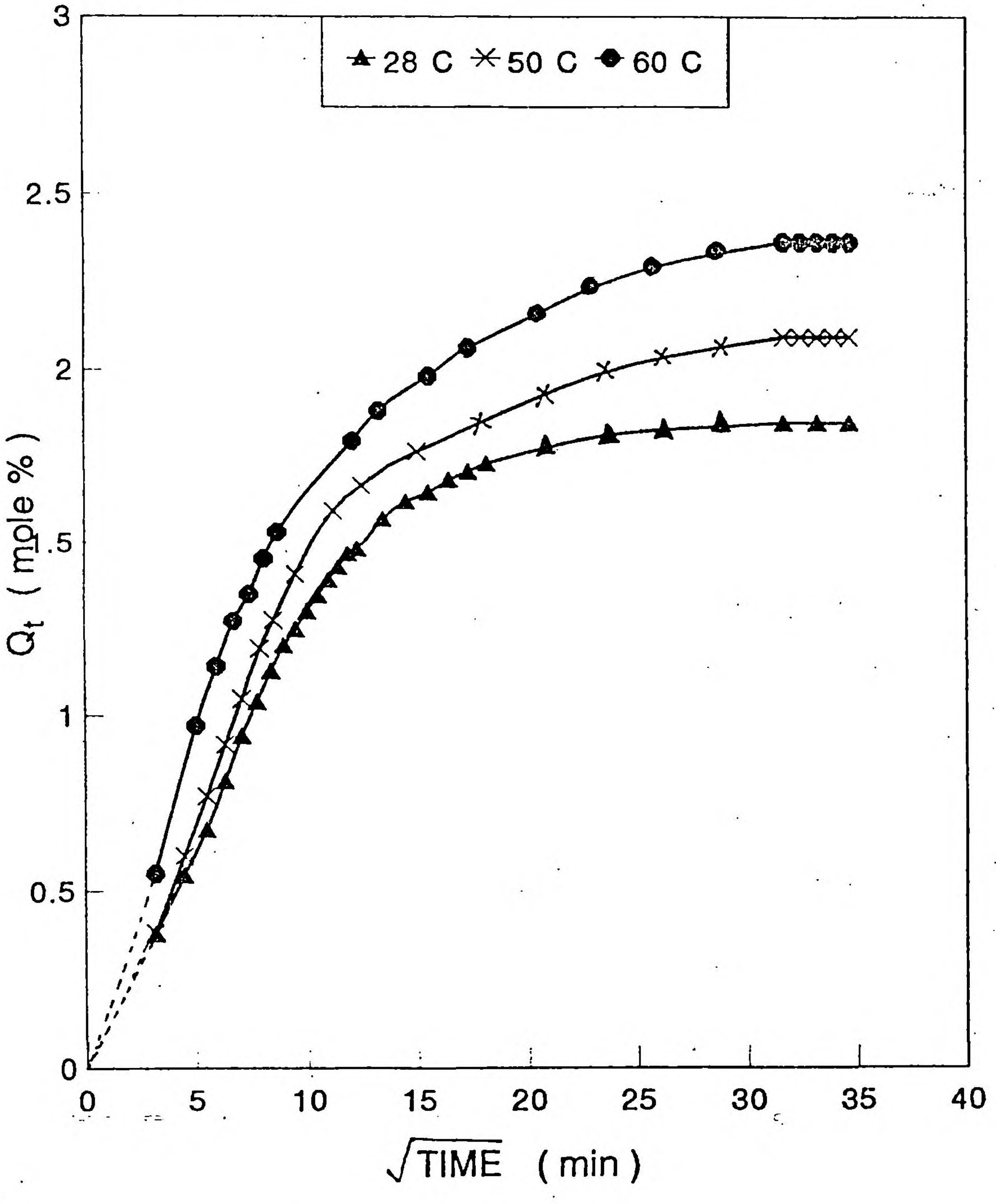


Figure 3.11 Effect of temperature

(Filler: hysil 210, solvent: petrol, cure time t_{90}))

The changes of values of D, S, P and K_S with increasing temperature are tabulated in the Table 3.7.

The apparent activation energy for diffusion, E_D, and that for permeation, E_P, can be found out by using Arrhenius relationship. The equation for the same is given in earlier (equation 1.15). Figures 3.12 and 3.13 are the Arrhenius plots. The plots are made for Hysil-210 filled system using three solvents. Figure3.12 is plot of ln D vs 1/T and Figure3.13 is ln PVS 1/T. The slopes of the above linear plots are obtained by least square analysis. The values of E_D and E_P were calculated from the slopes of plots in Figures 12 and 13 respectively. The results are shown in Table 3.8. From the results it is clear that both E_P and E_D vary with size of the penetrant molecules. For instance E_D for Hysil filled systems in petrol is 0.133 kJ/mole and that in mineral turpentine is 3.219 kJ/mole and in diesel it is found to be 6.824 kJ/mole. But the increase in the activation energy is not uniform with increase in the penetrant size. This may be due to the following reason; the smaller molecules may be fit into the holes or free space already available in the polymer matrix. But larger molecules do not fit into the holes or free space already available in the polymer matrix. They require more energy to create additional space which are known as Eyring holes within the polymer matrix.

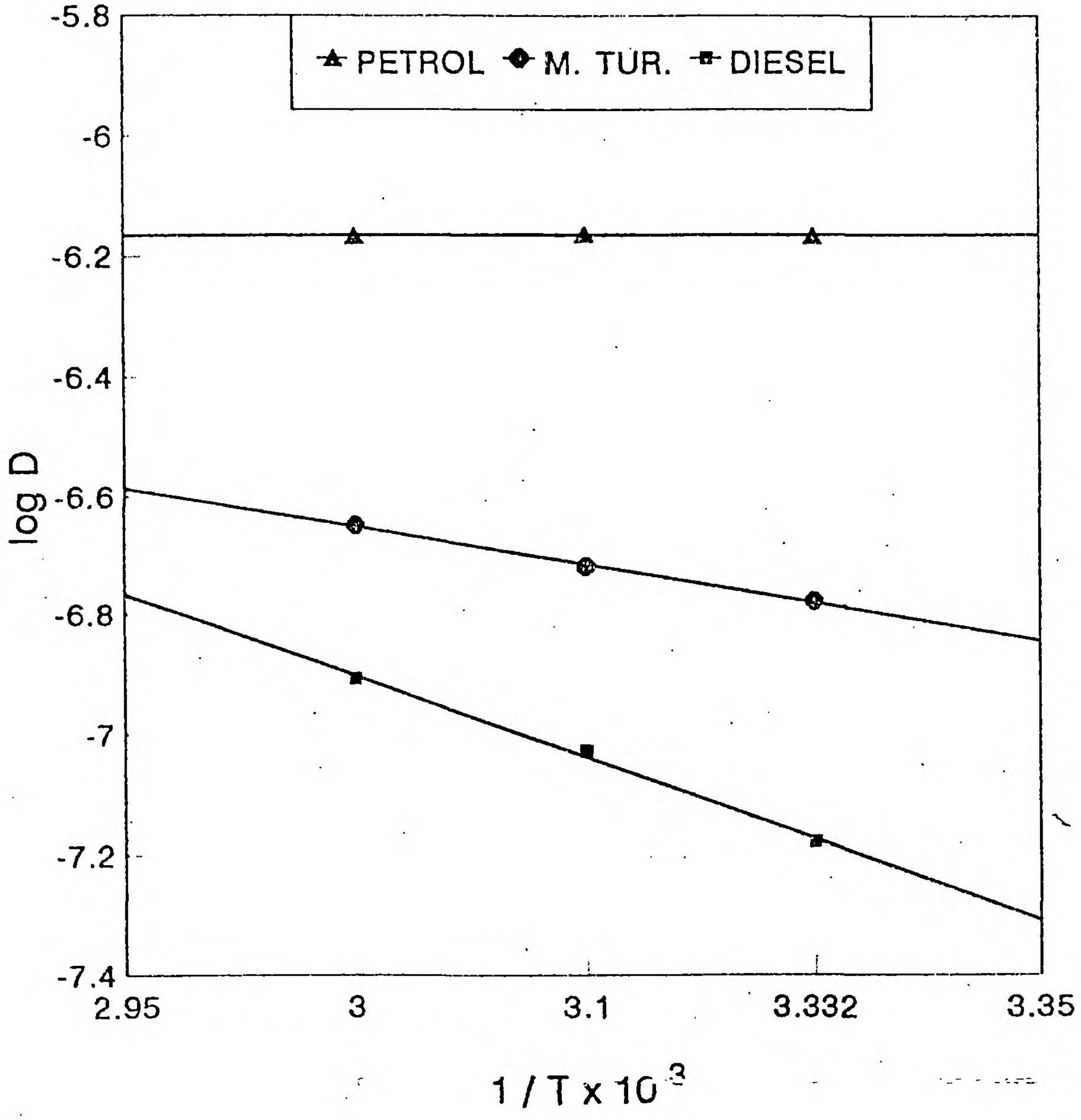


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Figure 3. 12 Arrhenius plots of log D vs 1/T

Table 3.8. Activation parameters for NR samples filled with Hysil-210 in the three aliphatic hydrocarbons solvents.

Solvent	E_D (kJ mol^{-1})	E_P (kJ mol^{-1})	$\Delta H_s = E_P - E_D$ (kJ mol^{-1})
Petrol	0.133	1.181	1.048
Mineral turpentine	3.219	4.6425	1.424
Diesel	6.824	9.318	2.494

9

The heat of sorption ΔHs, was calculated as

$$\Delta Hs = E_P - E_D \tag{3.9}$$

This gives additional information about molecular transport through polymer matrix. Table 3.9 shows the values of E_D, E_P and ΔH_s of the systems with different fillers in mineral turpentine.

Table 3.9. Activation parameters of NR samples conventionally vulcanized with different types of fillers. (Cure time: t_{90}, Solvent used is mineral turpentine).

Fillers used in the sample	E_D (kJ mol^{-1})	E_P (kJ mol^{-1})	$\Delta H_s = E_P - E_D$ (kJ mol^{-1})
Ordinary precipitated silica	9.267	9.328	0.061
Hysil-210	3.219	4.648	1.429
Ultrasil	12.382	12.690	0.308

All the values are positive and the highest values is for diesel. This indicates the lower permeability of diesel solvent through the system. ΔH_s is a composite parameter involving Henry's law type Langmuir type sorption mechanisms. In Henry's law model site formation within the polymer matrix occurs followed by the dissolution of penetrant into that site. The site formation by segmental motion of polymer chain makes an endothermic contribution. In Langmuir mode the site already exists within the polymer matrix and only sorption by hole fitting which is exothermic occurs. The positive value of ΔHs suggests that sorption of petrol, mineral turpentine and diesel in the system is by Henry's law type.

The equilibrium sorption constant, K_s, calculated from the equilibrium swelling is considered as the thermodynamic sorption constant K_s defined by the following equation.

$$K_s = \frac{\text{No. of moles of the penetrant sorbed at equilibrium}}{\text{Mass of the polymer sample}} \tag{3.10}$$

K_s for the samples with three types system at room temperature and for the Hysil-210 containing system at 28, 50 and 60^{o}C are included in the Table 3.7. The values of

K_s are substituted in the following Van't Hoff's equation to obtain the values of ΔS^o and ΔH^o.

$$\ln K_s = \Delta S^o/R - \Delta H^o/RT \tag{3.11}$$

In this equation, ΔS^o is the standard entropy of sorption and ΔH^o is the standard heat of sorption. The plots of $\ln K_s$ vs $1/T$ shown in Figure 3.14 are linear. From the intercept of linear plot on the y-axis ΔS^o is calculated and ΔH^o is obtained from slope. The estimated values are given in Table 3.10. The thermodynamic functions for natural rubber vulcanised with the three fillers (optimum cured) on mineral turpentine is also estimated and reported on Table 3.11. The ΔH^o values more or less are in agreement with the values obtained from $E_P - E_D$.

Table 3.10. Thermodynamic functions for natural rubber conventionally vulcanized with Hysil-210 filler (Optimum cured) in the three aliphatic hydrocarbon solvents.

Solvent	ΔH^o (kJ mol^{-1})	$-\Delta S^o$ (J mol^{-1})	ΔG (kJ mol^{-1})
Petrol	2.31	25.53	10.003
Mineral turpentine	2.99	26.90	11.096
Diesel	6.408	28.40	12.439

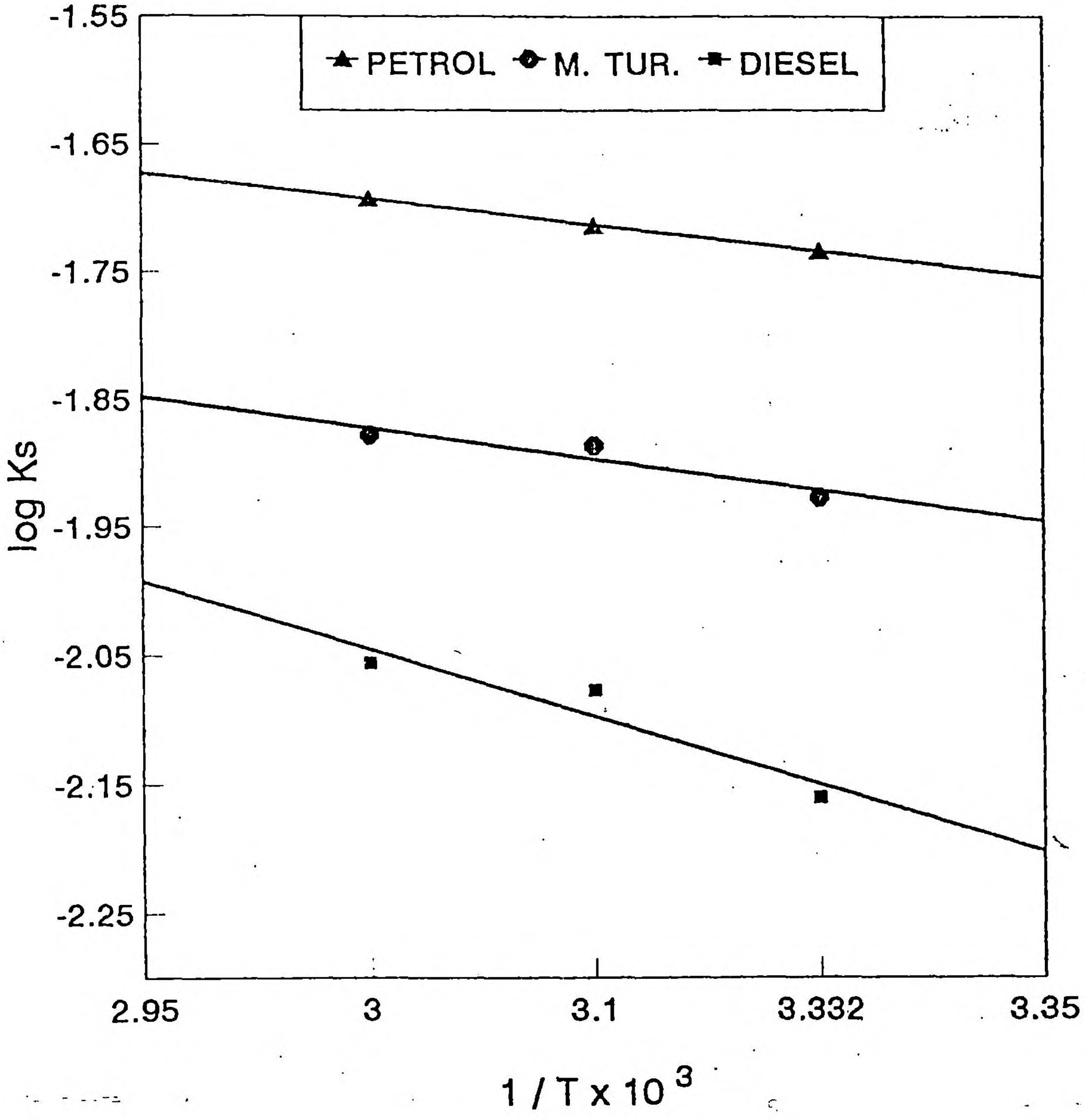

Figure 3.14 log Ks vs 1/T

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Table 3.11. Thermodynamic functions for natural rubber conventionally vulcanized with the three silica fillers. (Optimum cured) Solvent used is mineral turpentine.

Solvent	ΔH^o (kJ mol^{-1})	$-\Delta S^o$ (J mol^{-1})	ΔG (kJ mol^{-1})	ΔH (E_P-E_D)
Ordinary precipitated silica	0.0972	25.44	10.77	0.061
Hysil-210	3.000	26.89	11.096	1.429
Ultrasil	0.735	34.72	11.186	0.308

The ΔS^o values are all found to be negative indicating that vapourisation of the solvent molecules inside the polymer matrix has not taken place and disordered movement of the liquid molecules is restricted within the polymer matrix.

The standard free energy of the process was determined from the values of ΔH^o and ΔS^o by using the relation.

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (3.12)$$

The ΔG^o values are also given in Tables 3.10 and 3.11. The free energy values are found to be positive and magnitudes are small. Standard free energy increases with increasing penetrant size for each system. From the free energy values it can be concluded that the sorption process is more spontaneous for ordinary precipitated silica filled samples than Hysil and ultrasil.

Chapter 4

SUMMARY AND CONCLUSION

SUMMARY AND CONCLUSION

The effects of silica fillers (ordinary silica, Hysil and ultrasil) the sorption and diffusion of aliphatic hydrocarbons through natural rubber have been studied. It is found that the diffusion follows Fickian trend up to more than 50% equilibrium solvent uptake. The equilibrium solvent uptake was reduced considerably by the incorporation of Hysil-210 and Ultrasil-VN_3. However, addition of precipitated silica slightly increases solvent uptake as compared to gum sample in mineral turpentine and diesel solvents. A similar trend was shown by sorption coefficients and permeability coefficients. The difference in the solvent uptake with different fillers used, is explained on the basis of the difference in the bound rubber formation with different fillers, and the volume fraction (ϕ) and solvent interaction parameter (χ) of the particular systems.

The sorption experiments were done with polymer samples prepared at different cure times (t_{50}, t_{70}, t_{90} and t_{100}). It is found that the solvent uptake decreases with increase in cure time up to complete cure and then increases for over cured samples. This has been explained on the basis of crosslink density of the samples.

It has been observed that the diffusions coefficients decrease regularly from petrol to diesel. It is clear that as the size of the molecules increases, solvent uptake decreases.

The gravimetric method used is helpful in obtaining the thermodynamic data from sorption experiments. Studies of samples in the temperature range 28^{o}-60^{o}C suggest that diffusion in these systems is temperature activated.

The variation of diffusion coefficient and permeability coefficient with temperature, in the temperature range studied was found to obey standard Arrhenius relationship. From this the energy of activation for diffusion and permeation and heat of sorption were estimated. The ΔH_s is found to be highest for Hysil-210 filled system and lowest for commercially available precipitated silica. The variation of equilibrium sorption coefficient with temperature was fitted into the Van't Hoff equation and the enthalpy of sorption and entropy of sorption were estimated for the three silica filled systems, and for the three different solvents used. These values also support the earlier observation of increase in permeability through ordinary precipitated silica filled samples. The values of ΔH_s were found to be positive for all the three systems suggesting predominance of Henry's law mode of transport for the systems studied.

The Henry's law mode requires both the formation of a site in the polymer matrix and the dissolution of a species into that site. The formation of a site involves an endothermic contribution to this process.

Using Flory-Rehner theory the solvent interaction parameter, χ , the number average molecular weight between crosslinks, M_c, and the crosslink density, ν , were estimated.

The concentration dependence of solvent for diffusion coefficient is examined and found that diffusion coefficient increases initially with concentration remains steady for a range of concentration and then decreases for mineral turpentine. For petrol the diffusion coefficient increases first to maximum and then decreases sharply with increase in concentration. For diesel, initially the diffusion coefficient remains constant for a range of concentration and then increases to maximum and decreases gradually.

Finally it is important to mention that gravimetric sorption method is highly useful for the transport studies of liquids through crosslinked rubber membranes. Using this technique it is possible to evaluate successfully the thermodynamic data.

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