STUDIES ON MOLECULAR TRANSPORT CHARACTERISTICS OF ETHYLENE PROPYLENE DIENE MONOMER/POLYVINYL CHLORIDE SYSTEMS

THESIS

SUBMITTED BY

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CERTIFICATE

This is to certify that the thesis entitled **STUDIES ON MOLECULAR TRANSPORT CHARACTERISTICS OF ETHYLENE PROPYLENE DIENE MONOMER/POLYVINYL CHLORIDE SYSTEMS** is a bonafide record of the research work carried out by **Mr. Mohamed Kutty C.P.** in the Department of Chemistry, Farook College, Calicut, University of Calicut, Kerala, India, under my direct supervision and guidance in partial fulfillment of the requirements for the award of the degree of **Doctor of Philosophy in Chemistry**. The work reported in this thesis has not been submitted for any other degree or diploma earlier. It is also certified that Mr. Mohamed Kutty C. P. has successfully completed the qualifying examination, for the award of the Ph.D. degree of the University.

12th February 2012.

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DECLARATION

I hereby declare that the thesis entitled "Studies on molecular transport characteristics of ethylene propylene diene monomer/polyvinyl chloride systems" is an authentic record of my own research work carried out under the supervision of ***Dr M. Jahfar****, Associate Professor, Department of Chemistry, Farook College, Calicut, University of Calicut, Kerala, and that, to the best\ of my knowledge and belief, it does not contain any material previously written or published by any other person or material which has been accepted for the award of any degree or diploma of University of Calicut or any other University/Institute of higher learning, except where due acknowledgement has been given in the text.*

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LIST OF SYMBOLS

Activation energy - E

Activation energy of diffusion - E_D

Activation energy of permeation - E_P

Average size of the free volume holes - V_f

Crosslink density - ν

Cure rate - R_H

Concentration of the diffusing molecule c

Concentration of the penetrant at the downstream polymer- membrane face - c_1

Concentration of the penetrant at the upstream polymer-membrane face - c_2

Density of blend - ρ_p

Density of solvent - ρ_s

Diffusion coefficient - D

Diffusive flux - J

Enthalpy of mixing - ΔH_m

Entropy of mixing - ΔS_m

Final decomposition temperature - T_f

Glass transition temperature - T_g

Initial polymer mass - M_p

Initial thickness of sample - h

Initial weight of sample - w_1

Intrinsic diffusion coefficient - $D*$

Mass of solvent uptake at equilibrium - M_∞

Maximum change in torque during vulcanization - ΔM_{max}

Maximum rheometric torque - M_H

Melting temperature - T_m

Minimum rheometric torque - M_L

Molar mass between crosslinks - M_c

Molar volume of solvent - V_s

Moles of solvent sorbed by 0.1 kg of polymer blend at equilibrium - Q_∞

Moles of solvent sorbed by 0.1 kg of polymer blend at time ‘t’ - Q_t

Optimum cure time - t_{90}

Permeating area of the membrane - A

Permeation coefficient - P

Polymer-solvent interaction parameter - χ

Pressure - p

Rheometric torque corresponding to optimum cure time - M_{90}

Rheometric torque corresponding to scorch time - M_2

Scorch time - t_2

Slope of the initial portion of the *Qt* versus time relationship - θ

Sorption coefficient - S

Swelling coefficient - α

Temperature - T

Tensile strength after swelling - TS_{after}

Tensile strength before swelling - TS_{befor}

Time - t

Universal gas constant - R

Volume fraction of blend in fully swollen filled sample - V_{rF}

Volume fraction of blend in fully swollen unfilled sample - V_r

Volume fraction of component 1 - φ_1

Volume fraction of component 2 - φ_2

Volume fraction of gum rubber - φ

Weight fraction of component 1 - W_1

Weight fraction of component 2 - W_2

Weight of sample at equilibrium swelling - w_2

LIST OF ABBREVIATIONS

ABS – Acrylonitrile butadiene styrene copolymer
ACM – Acrylate rubber
BR – Butadiene rubber
CPE – Chlorinated polyethylene
CR – Chloroprene rubber
CRI – Cure rate index
DCP – Dicumyl peroxide
DOP – Dioctyl phthalate
DSC – Differential scanning calorimetry
ENB – Ethylidene norbornene
ENR – Epoxidized natural rubber
EPDM – Ethylene propylene diene monomer
EPR – Ethylene propylene rubber
EPR-g-MA – Maleic anhydride grafted – ethylene propylene rubber
EPDMMA – Maleic anhydride modified ethylene propylene diene rubber
EVA – Poly (ethylene-co-vinyl acetate)
FTIR – Fourier transform infrared spectroscopy
HDPE – High density polyethylene
LDPE – Low density polyethylene
MBTS – Mercapto benzothiazyl disulphide
NBR – Acrylonitrile butadiene rubber
NR – Natural rubber
N6 – Nylon-6
PBMA – Poly (butyl methacrylate)

PE – Polyethylene
PET – Poly (ethylene terephthalate)
PMMA – Poly (methyl methacrylate)
PP – Polypropylene
PP-g-MA – Polypropylene graft maleic anhydride
PP-g-PS – Polypropylene graft polystyrene
PS – Polystyrene
P U – Polyurethane
PVC – Poly (vinyl chloride)
S-D-RS-RD – Sorption-desorption-resorption-redesorption
SAN – Styrene acrylonitrile copolymer
SBR – Styrene-co-butadiene rubber
SEM – Scanning electron microscopy
TG – Thermogravimetry
TGA – Thermogravimetric analysis
TMTD – Tetramethyl thiuram disulphide
TPE – Thermoplastic elastomer
TPV – Thermoplastic vulcanizate
UV – Ultraviolet
VA – Vinyl acetate
XRD – X-ray diffraction

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PREFACE

Over the years, economic, technological, and other regulatory pressures have gradually narrowed the further development of new varieties of polymers. Thus mixing of easily available polymers has emerged as a simple and efficient method for designing and controlling the performance of macromolecular systems. A blend /composite can offer a set of properties those may give it the potential of entering application areas not possible with either of the constituent polymer comprising it. Physical properties of the polymers are structure sensitive; thus modification of the properties could be effected by the changes in the structure of the composite including changes in crystallinity, crosslinking and the use of additives, reinforcement etc. Ethylene propylene diene monomer (EPDM) is a synthetic amorphous polymer. The high filler loading capacity, excellent weather resistance and high water resistance of EPDM make it useful for several engineering and industrial applications. However, its performance is inferior in the presence of organic solvents and oils. Polyvinyl chloride (PVC), owing to its rigid nature and polarity, can be considered as an ideal partner for alleviating the inherent drawbacks of EPDM and to enhance the barrier property. The aim of the present work is to develop composite systems based on EPDM and PVC, with different crosslinking systems, crosslinking techniques and to characterize them in terms of sorption, mechanical and thermal properties. The contents of this thesis have been presented in eight chapters. In the introductory chapter (Chapter 1) the importance of composites, classification of composites, different strategies for strengthening the system and a related literature review have been given. This chapter also highlights the scope and objectives of the present investigation. The details of the materials used and the experimental techniques adopted are given in Chapter 2.Chapter 3 deals with the mechanical, electrical, morphological and thermal properties of EPDM/PVC composites. The properties have been examined with special reference to the effect of PVC loading and the three different vulcanizing systems used. Vapour permeation study of EPDM/PVC composites using aromatic solvents like benzene, toluene and xylene and also n-propanol have been presented in Chapter 4 .The molecular transport property of chloromethanes have been discussed with special reference to amount of PVC, nature of crosslinking agents ,temperature and type of vulcanization in Chapter 5. The mechanism of solvent transport has been analysed. Chapter 6 covers a systematic study on the interaction of three liquid fuels viz; petrol, diesel and kerosene with EPDM/PVC composites. Chapter 7 deals with the ageing characteristics of, ethylene propylene diene monomer and EPDM/PVC composites after exposing them to various degrading agents such as temperature, organic solvents acids and alkalies. The important conclusions and future outlook of the investigation are presented in Chapter 8.

Chapter 1

Introduction

Summary

Composites are heterogeneous structural materials, which consist of two or more components. Mixing of two or more materials results in a new material that may be better for a particular application than either of the original components. This chapter gives an account of the fundamental principles involved in the development and characterization of polymer blends and composites and also the transport properties of polymer composites and the strategies for improving the properties. A review of the earlier reports on the investigation of barrier properties of polymer systems has been given. The scope and objectives of the present investigation are also highlighted.

1.1 Polymers

A large group of engineering materials of steadily increasing importance in industrial applications is composed of natural and synthetic organic polymers. Natural polymers have been utilized throughout the ages. Since his beginning, man has been dependent on animal and vegetable matter for substances, shelter, warmth and other requirements and desires. Natural resins and gums have been used for thousands of years Polymers play a very important role in human life. In fact, our body is made of lot of polymers, e.g. Proteins, enzymes, etc. Other naturally occurring polymers like wood, rubber, leather and silk are serving the humankind for many centuries now. Modern scientific tools revolutionized the processing of polymers thus available synthetic polymers like useful plastics, rubbers and fiber materials. As with other engineering materials (metals and ceramics), the properties of polymers are related their constituent structural elements and their arrangement. The suffix in polymer ‘mer’ is originated from Greek word meros – which means part. The word polymer is thus coined to mean material consisting of many parts/mers. Most of the polymers are basically organic compounds, however they can be inorganic (e.g. silicones based on Si-O network).

Depending on its ultimate form and use, a polymer can be classified as plastic, elastomer, fibre or liquid resin. When for instance, a polymer is shaped into hard and tough utility articles by the application of heat and pressure, it is used as a plastic. When vulcanized into rubbery products exhibiting good strength and elongation, polymers are used as elastomers.If drawn into long filament-like materials, whose length is at least 100 times its diameter, polymers are said to have been converted into fibers.

1.1.1. Elastomers

Elastomers (rubbers) are an amorphous class of polymers, characterized by their ability to display large extensions, which are reversible. The American Society for Testing and Materials (ASTM) defines as elastomer as “a polymeric material, which at room temperature can be stretched to at least twice its original length and upon immediate release of the stress will return quickly to approximately its original length”. They are usually above their glass transition temperature, *Tg*, at ambient temperature but they have to be crosslinked by vulcanization to prevent flow. Due to their crosslinked nature, permanent chain slippage is largely avoided during deformation of elastomers and almost all polymer chains return to their original location upon release of the strain, thus, they exhibit elastic behavior. This elastic nature associated with high deformation renders elastomers very suitable for many sealing applications.

The major parameters affecting performance of an elastomeric seal can be controlled at the compounding stage with the proper choices of chemistry of base polymer, vulcanization agents, curing chemicals, type of fillers, antidegradants and softeners during processing. Both mechanical properties and chemical resistance of elastomers mainly rely on their formulation developed to provide the cured rubber with the desired properties [1].

Characteristics of rubbers

- They are in general noncrystalline in structure.
- They are non-conductors of electricity and are relatively low heat conductors.
- They are high in resistance to chemical and corrosive environments.
- They have relatively low softening temperatures.
- They exhibit viscoelastic behavior generally largely than plastics.

They oxidize or age, causing deterioration and changes in properties, more than plastics.

However, in recent years, economic, technological and other regulatory pressures have gradually narrowed the further development of new chemical varieties of polymers. Mixing of two or more existing polymers or copolymers is now a days a widely accepted method in order to respond to the demand for new materials. Two polymers in a blend or composite usually give rise to a new material having better balance of properties than obtainable with a single polymer [2-7].

Thermoplastic elastomers

There are two general types of rubbers or elastomers, i.e., crosslinked elastomer and thermoplastic elastomer (TPE). Most of the commonly used rubbers are crosslinked ones with their chains chemically bonded during the curing process. Once formed, this type of rubber cannot be reprocessed, softened, melted or reshaped by following reheating. Thermoplastic elastomers, on the other hand, are rubbers which act in a way similar to crosslinked materials but are copolymers or physical mix of thermoplastics and rubbers with both thermoplastic and elastomeric properties. These elastomers are usually hydrocarbon-based polymers mainly consisting of carbon and hydrogen atoms.

Thermoplastic elastomers (TPEs**)** combine the elastic and mechanical properties of thermoset cross linked rubbers due to the melt processability of thermoplastics.Today,TPEs comprise the fastest growing rubber market.TPEs can be processed by a variety of techniques, such as extrusion blow moulding,injection moulding,vacuum forming and calendaring. Thermoplastic vulcanisates(TPVs) are a particular family of TPEs,which are produced via dynamic vulcanization of non-miscible blends of a rubber and a thermoplastic. ie., the selective cross linking of the rubber while simultaneous melt mixing with thermoplastic. In recent years, TPEs and TPVs have replaced conventional rubbers in a variety of applications including appliance, automotive, medical, engineering etc. TPEs are made by copolymerization and by blending thermoplastics with a rubbery component. TPVs, on the other hand, are made by dynamically vulcanizing the rubber component in a rubber/thermoplastic blend during mixing. Thermoplastic elastomers exhibit the functional properties of conventional elastomeric material and can be processed with thermoplastic processing machine.

TPEs combine the elastic and mechanical properties of thermoset crosslinked rubbers due to the melt processability of thermoplastics. Today, TPEs comprise the fastest growing rubber market. TPEs can be processed by a variety of techniques, such as extrusion blow moulding, injection moulding, vacuum forming and calendaring.

1.1.2 Polymer Blends and Composites

In recent years, significant progress has been made in many areas of polymer blend and polymer matrix composite science and technology. The term polymer blend refers to intimate mixture of two or more polymers. The blends may be homogeneous or heterogeneouss on a microscopic scale, but should not exhibit in homogeneity on a macroscopic scale. The number of polymeric components which comprises a blend is often designated by an adjective, viz., binary, ternary and quaternary.

Composites are engineering materials made from two or more constituents with significantly different physical or chemical properties which remain separate and distinct on a macroscopic level within the finished structure [8]. i.e., a composite is commonly defined as a combination of two or more distinct materials, each of which retains its own distinctive properties, to create a new material with properties that cannot be achieved by any of the components acting alone.

1.1.3 Preparation of Blends/composites

The manner by which two polymers are mixed together is of vital importance in controlling the properties of their blends. The methods of preparation of polymer-polymer systems can be classified as: (i) melt mixing, (ii) solvent casting, (iii) co-precipitation, (iv) latex blending, and (v) interpenetrating polymer networks' technology.

i. **Melt mixing** involves the mixing of two polymers in the molten state under shear and is usually achieved with the help of either a Brabender Plasticoder type batch mixer or an extruder (single or double screw).

ii. **Solvent casting** involves dissolving the polymers in a common solvent and casting a film from the solution.

iii. **Co-precipitation** involves the dissolution of the polymers in a common solvent and the subsequent removal of solvent.

iv. **Latex-blending** involves the mixing of lattices of polymers and spraying the mixture followed by drying.

v. **Interpenetrating polymer networks' (IPN)** technology involves the polymerization of one monomer usually dissolved in a solvent containing a polymer.

1.1.4 Components of composites

The composite materials are mainly composed by two phases. The first phase is termed as matrix which is generally continuous into which the other phase is embedded; often called the reinforcement or dispersed phase. The region between these two components is known as interface. Figure 1.1 is a schematic representation of a composite system.

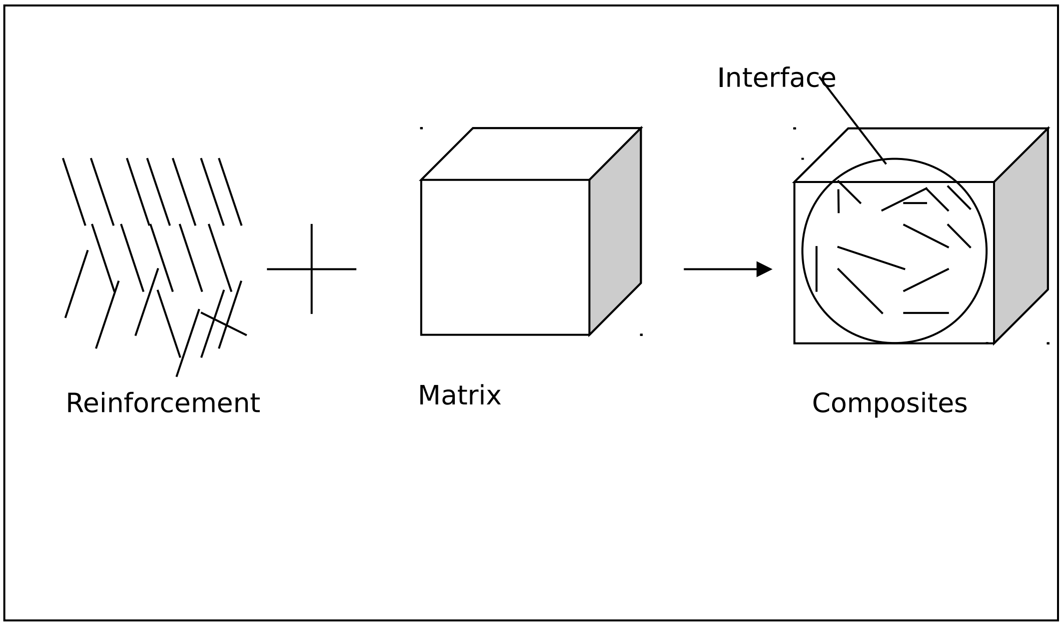


Figure 1.1 Schematic representation of a composite

1.1.4.1 Matrix

Matrix is generally continuous which provides the composite system with toughness and ductility. The main role of the matrix is to transmit and distribute stresses along the reinforcement phase. They maintain the reinforcement phase separately in the desired orientation and thereby contribute to the cohesion of the product. They protect the reinforcing phase from abrasion and degradation by the influence of different environmental conditions. They also bind the dispersion phase together and cause them to act as a team in resisting failure or deformation under an applied load.

The matrix may be metallic, ceramic or polymeric in origin. It gives the composites their shape, surface appearance, environmental tolerance and overall durability while the fibrous reinforcement carries most of the structural loads thus giving macroscopic stiffness and strength

A composite material can provide superior and unique mechanical and physical properties because it combines the most desirable properties of its constituents while suppressing their least desirable properties. At present composite materials play a key role in aerospace industry, automobile industry and other engineering applications as they exhibit outstanding strength to weight and modulus to weight ratio. High performance rigid composites made from glass, graphite, kevlar, boron or silicon carbide fibers in polymeric matrices have been studied extensively because of their application in aerospace and space vehicle technology.

a) Metal matrix composites (MMCs)

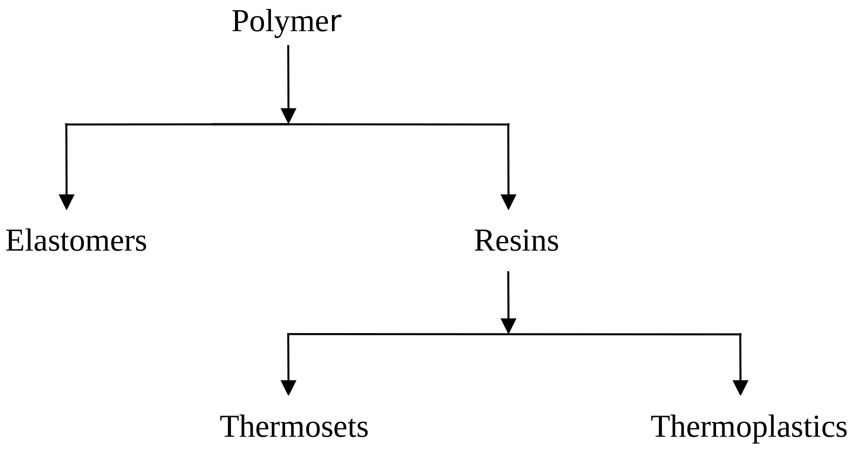
The metals which have been extensively used for making composites are aluminum, magnesium and those with special electrical properties, like lead and copper. Titanium and nickel attract interest because of their higher strength. Metal matrices are used generally by reinforcing with high modulus fibres which are also light. The reinforcement phases in metal matrix composite systems are either metallic or non-oxide ceramic (silicon carbide, carbon and boron) or oxide ceramic (alumina and glass). MMCs have higher temperature resistance than other composite systems and are preferred for service temperatures above 150^0C. An interesting possibility for MMCs is the chemical interaction between the fibre and matrix, leading to enhanced physical properties particularly at elevated temperatures. Due to the high modulus of metal matrices, they transmit the load between the fibres better than in the case with polymer matrices and are thus the right matrix material for whisker based composite products.

b) Ceramic matrix composites (CMCs)

The development of composite materials based on ceramic matrices has received a considerable boost in the recent past, particularly with ceramic fibres since they can be operated at very high temperatures of about 1800^0C. Ceramics are strongly bonded materials with ionic and covalent character, which results in high strength and hardness. However, a consequence of this is that there is little dislocation movement and the material is brittle. The strength of many polycrystalline ceramics is much lower than the theoretical values because of the flaws in them. Recently, CMCs such as glass, glass-ceramic and oxide ceramic matrices have gained importance. One of the most promising applications for CMCs is in the area of cutting tools and in heat engines where the components require resistance to aggressive environments.

c) Polymer matrix composites (PMCs)

Polymers constitute the most important matrix materials and are used in more than 95% of the composite products in use today. The polymeric matrices are mainly classified as shown in Scheme 1.1



Scheme 1.1 Classification of polymer matrices

i) Thermoplastic polymer matrices

The thermoplastics are incorporated in the composite system by melting and then solidifying by cooling; the physical reaction being reversible in nature. In general, thermoplastics have low creep resistance and low thermal stability compared to thermosetting resins. When thermoplastics form the matrix, the composite products can be manufactured by high speed processes. However, because of the low strength and modulus of polymers in general and thermoplastics in particular, the loads are not transferred very efficiently from one fibre to the other, in fibrous composite systems. When discontinuous fibres form the reinforcing phase, the fibre length must be as long as possible and the shear modulus be large so that the load transfer is effectively achieved and the fibre contributes its share to the mechanical properties of the composites. The range of thermoplastics used for composite fabrication includes polyether ether ketone, polyethylene, polypropylene, polyethylene terephthalate, polyamides, polyvinyl chloride, polyimides, polycarbonate etc.

ii) Thermoset polymer matrices

The thermosetting resins are more common for the development of composite systems and in them solidification from the liquid phase takes place by the action of an irreversible chemical cross-linking reaction, generally in the presence of heat and pressure. In thermosetting polymers, the liquid resins are converted into hard brittle solids by chemical cross-linking which leads to the formation of a tightly bound three-dimensional network of polymer chains. The low viscosity of the thermosetting resins allows the ready impregnation of them into the fibres. Among thermosetting matrices polyester resins, epoxy resins, vinyl esters resins, phenolics, silicones and urethanes are noteworthy.

iii) Elastomer based matrices

The greater extensibility and high-energy storing capacity make the elastomers as a suitable continuous phase for composite materials. Unlike plastics, a wide variety of flexible products can be made by using elastomers as the matrix phase . They offer elastic strain higher than that of metals and can be stretched rapidly, even under small loads, to about 100% elongation. On releasing the applied forces, rubbers retract rapidly almost fully.

1.1.4.2 Reinforcement

Based on the form of reinforcement, common composite materials can be classified as follows:

i) Structural composites and
ii) Particle reinforced composites
iii) Fibre reinforced composites
iv) Hybrid composites

i. Structural composites

The performance of structural composites depends not only on the properties of the constituent materials but also on the geometrical design of the various structural elements. Two most common structural composites are: (a) laminar composites and (b) sandwich panels. A laminar composite is composed of two-dimensional sheets or panels which have a preferred high-strength direction such as found in wood and continuous and aligned fibre-reinforced plastics

ii. Particulate reinforced composites

A composite whose reinforcement is a particle with all the dimensions roughly equal are called particulate reinforced composites. Particulate fillers are employed to improve high temperature performance, reduce friction, increase wear resistance and to reduce shrinkage [9]. The particles will also share the load with the matrix, but to a lesser extent than a fiber. A particulate reinforcement will therefore improve stiffness but will not generally strengthen. Particle filled polymer composites have become important engineering materials because of their wide applications and low cost .There is considerable interest in polymer blends and composites due to the difficulty in developing new polymeric materials from monomers.

Advances in our understanding of the relation between the molecular structure of polymers and their chemical and physical properties make it possible to design and produce various polymeric materials of required characteristics for specific engineering applications [10]. Many of our useful plastics, rubber and fibre materials are synthetic polymers. The synthetics can be produced inexpensively and their properties may be managed to the degrees that are superior to their natural counterparts. Polymer blending is a cost-effective way to produce composites with desirable properties [11, 12].

As mentioned earlier, mixing of two or more polymers in proper proportion produces material with better properties than that obtained with a single polymer. For example, a high melting crystalline plastic can be combined with an elastomer with low brittleness temperature to produce a TPE with a very good range of end use temperatures. Alternatively the high melting crystalline plastic can be combined with an oil resistant elastomer of good thermal-oxidative stability to give a TPE suited for applications in high aggressive environment**.** Typically, natural rubber (NR) is selectively blended with synthetic rubbers to improve its properties [13, 14]; Natural rubber/Nitrile rubber for application requiring resistance to swelling by oils combined with good physical properties, NR/Ethylene propylene diene monomer for combination of good resistance to ozone and good strength and NR/Acrylonitrile Butadiene Rubber_for combination of good physical properties and low dependance of dynamic properties on temperature are other examples.

Composites were developed because no single, homogeneous structural material could be found that had all of the desired characteristics for a given application. It is well known that composites can be produced exhibiting enhanced properties that the constituent materials may not exhibit fiber-reinforced composites were first developed to replace aluminum alloys, which provide high strength and fairly high stiffness at low weight but are subject to corrosion and fatigue If the composite is designed and fabricated correctly, it combines the strength of the reinforcement with the toughness of the matrix to achieve a combination of desirable properties not available in any single conventional material. Some composites also offer the advantage of being tailorable so that properties, such as strength and stiffness, can easily be changed by changing amount or orientation of the reinforcement material. The properties depend on amount and distribution of each type of material [15]. Collective properties are more desirable than possible with any individual material.

Based on the constituents, polymer blends/composites may be classified into rubber-rubber, rubber-plastic and plastic-plastic

Some of the common classifications of composites are:

- Reinforced plastics
- Metal-matrix composites
- Ceramic-matrix composites
- Sandwich structures
- Concrete

Composite materials can take many forms but they can be separated into three categories based on the strengthening mechanism. These categories are dispersion strengthened, particle reinforced and fiber reinforced. Dispersion strengthened composites have a fine distribution of secondary particles in the matrix of the material. These particles impede the mechanisms that allow a material to deform. (These mechanisms include dislocation movement and slip, which will be discussed later). Many metal-matrix composites would fall into the dispersion strengthened composite category. Particle reinforced composites have a large volume fraction of particle dispersed in the matrix and the load is shared by the particles and the matrix. Most commercial ceramics and many filled polymers are particle-reinforced composites. In fiber-reinforced composites, the fiber is the primary load-bearing component. Fiberglass and carbon fiber composites are examples of fiber-reinforced composites. Composite materials incorporated with two or more different types of fillers especially fibres in a single matrix are commonly known as hybrid composites.

Composites are made up of individual materials referred to as constituent materials. There are two categories of constituent materials: matrix and reinforcement. At least one portion of each type is required. The matrix material surrounds and supports the reinforcement materials by maintaining their relative positions. The discontinuous filler phase in a composite is usually stiffer or stronger than the binder phase.

The reinforcements impart their special mechanical and physical properties to enhance the matrix properties. A synergism produces material properties unavailable from the individual constituent materials, while the wide variety of matrix and strengthening materials allows the designer of the product or structure to choose an optimum combination.

Particle composites consist of particles of one material dispersed in a matrix of a second material. Particles may have any shape or size, but are generally spherical, ellipsoidal, polyhedral, or irregular in shape. They may be added to a liquid matrix that later solidifies; grown in place by a reaction such as age hardening; or they may be pressed together and then inter-diffused via a powder process. The particles may be treated to be made compatible with the matrix, or they may be incorporated without such treatment. Particles are most often used to extend the strength or other properties of inexpensive materials by the addition of other materials. High performance composites are composites that have better performance than conventional structural materials such as steel and aluminum alloys. They are almost all continuous fiber-reinforced composites, with organic (resin) matrices.

iii. Fibre reinforced rubber composites

Fibre reinforced rubber composites are of immense importance both in the industrial field and in the area of research and development. Reinforcement of rubber with short fibre combines the elasticity of rubber with strength and stiffness of the fibre. The additional benefit is that the fibre is incorporated into the compound as one of the ingredient of the recipe. The properties and performance of short fibre reinforced rubber composites depend on several factors such as nature and concentration of the fibre, its aspect ratio, orientation and degree of adhesion of fibre to the rubber matrix. Various synthetic and natural fibres such as glass, nylon, aramid and cellulose (synthetic) and sisal, coir etc. (natural) have been studied as reinforcement in both natural and synthetic rubber matrices. Fibre reinforced rubbers have become popular recently because they offer low weight corrosion resistance, high fatigue strength and fast assembly. They are used in aircraft structures, electronic packaging, medical equipment, space vehicles and building industry several researchers have attempted to fabricate V-belts, hoses, tyres and various articles of complex shape using short fibres [16].

The reinforcing efficiency of the fibres can be increased by having a high aspect ratio and by ensuring good dispersion. It is found that the properties of the composites mainly depend upon the type, value loading, aspect ratio orientation and dispersion of fibres and fibre – matrix adhesion. It is also reported that the lower reinforcing ability of glass fibres could be attributed to the severe reduction in their length compared to cellulosic fibres during mixing, Coran et al. [17] investigated the effects of glass rayon and polyamide fibres on both natural and synthetic rubbers and fibre orientation has a pronounced effect on the mode of fracture of composites. Resins and rubbers reinforced with natural fibres attract interest primarily because of a desire to cut the cost of raw materials while achieving high strength and retaining simple manufacturing principles. Sreeja and Kutty [18] studied the cure characteristic and mechanical properties of short polyamide fibre reinforced natural rubber they found that rheometric torque and cure rate increased with fibre concentration. The mechanical properties of short jute fibre reinforced SBR have been studied by Murthy and De [19]. They found that jute fibres offer good reinforcement to SBR compared to glass fibres.

1.2 Strengthening of immiscible polymer mixtures

Most polymer pairs in blends are thermodynamically incompatible; the incompatible blends often give poor mechanical properties for most end uses due to the lack of physical or chemical interactions between different phases and poor interfacial adhesion and to promote the development of a fine morphology. Miscibility between the two polymers is best accomplished either by reducing the heat of mixing or by making it negative. Compatibility refers to the degree of intimacy of blends. From a practical view point, it is most useful to consider polymer blend as compatible when it does not exhibit gross symptoms of polymer segregation. A blend that is in homogenous on a macroscopic level should thus be considered as incompatible. Compatibilization may be described as a process that reduces the enthalpy of mixing or making it negative. A typical method to improve the performance and stabilize the morphology is by dynamic vulcanization. Addition of suitable compatibiizers can also strengthen the interface resulting in enhanced properties. The role of compatibilization is to:

A. Reduce the interfacial energy and improve adhesion between phases.
B. Achieve finer dispersion during mixing.
C. Stabilize the fine dispersion against agglomeration during processing and throughout the service life.

Specific compounds can be used to bring together otherwise incompatible polymers into a stable blend through intermolecular bonding, and thus act as “compatibilizer” for these systems. Compatibilizers are generally polymers themselves, but there are exceptions, like monomeric silanes and organic peroxides. Compatibilizers act through reactive processing. i.e., through various grafting techniques or through hydrogen bonding based on polarity of the materials. In addition, a compatibilizer may function just as a surfactant can stabilize oil-water mixtures-by being soluble in one or both major components of the blend. A compatibilizer often works by a combination of these mechanisms, e.g., by attaching themselves to one blend component through chemical grafting and leaving a polymeric "tail" that is soluble in the other component, The ultimate objective is to develop a stable morphology that will facilitate smooth stress transfer from one phase to the other and allow the product to resist failure under multiple stresses. The combination of the two techniques discussed has opened the door to many new product opportunities.

The tensile strength of many filled polymers can be improved using adhesion promoters (compatibilizers), which improve the adhesion and the nature of the filler/matrix interface. Fillers with higher stiffness than the matrix can increase the modulus of the composites, but generally fillers cause a dramatic decrease in the elongation at break. Almost all of the elongation occurs in the matrix if the filler is rigid .If there is good adhesion between the filler and the matrix, a decrease of the elongation at break, even with small amounts of filler, can be expected. If the adhesion is poor, the elongation at break may decrease more gradually. This seems to agree with the results obtained by earlier study [20].

1.2.1 Dynamic vulcanization

Vulcanization brings about the formation of crosslinks between the long polymer chains. The three dimensional structure so produced restricts the free mobility of the molecules and gives a product having reduced tendency to crystallize, improved elasticity and substantially constant modulus and hardness characteristics over a wide temperature range. In fact, vulcanization enables useful materials and products to be produced from the rubbery polymer.

Dynamic vulcanization is the process of vulcanizing the elastomer, during the melt-mixing process, with a nonvulcanizable molten thermoplastic.

This process results in a most useful elastomeric alloy material with the properties of a conventional thermoset rubber, but which can be processed as a conventional thermoplastic. The temperature reached during the mixing must be sufficiently high to melt the thermoplastic resin and affect the chemistry of the cross linking reaction.

Dynamic vulcanization is a route to new thermoplastic elastomers which have properties as good or as even in some cases, better than those of block copolymers. Yet the new materials are prepared from mixtures of existing polymers. Thus, new, improved thermoplastic elastomers can be prepared from “old” polymers. Entirely, new process and materials can be avoided.

Examples of improvement of blends and composites are;

- Reduced permanent set
- Improved ultimate mechanical properties
- Improved fatigue resistance
- Improved high temperature utility, greater stability of phase morphology in the melt
- Greater melt strength and a more reliable thermoplastic fabricability.

In short, dynamic vulcanization can provide compositions which are very elastomeric in their performance characteristics. However, these same thermoplastic vulcanizate compositions can be rapidly fabricated into finished parts in thermoplastic processing equipment.

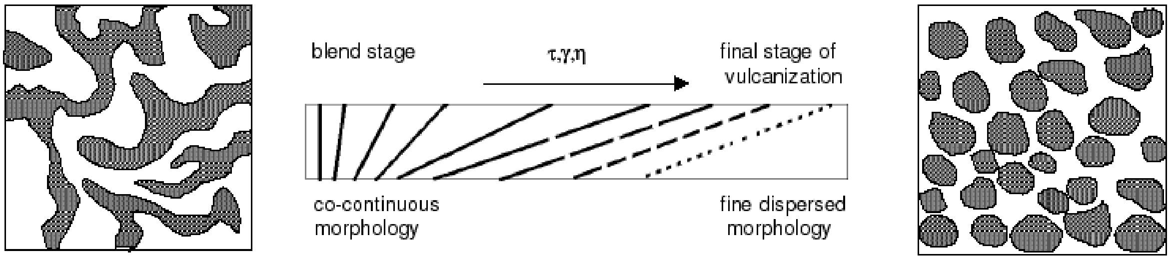


Figure 1.2 Scheme of morphology development of dynamic vulcanizates during the cross linking. The dynamic vulcanization process has been applied to many elastomer-plastic combinations. It can be described as follows: Elastomer and plastic is first melt mixed. After sufficient melt mixing in the internal mixer to form a well mixed blend, vulcanizing agents (curatives and cross linkers) are added. Vulcanization then occurs while mixing continues. The more rapid the rate of vulcanization, the more rapid the mixing must be to ensure good fabricability of the blend composition. It is convenient to follow the progress of vulcanization by monitoring mixing torque or mixing energy requirement during mixing. After the mixing, torque or energy curve goes through a maximum, mixing can be continued somewhat longer to improve the fabricability of the blend. After discharge from the mixer, the blend can be chopped, extruded, pelletized, injection molded etc. The effect of dynamic vulcanization on the properties of polymer blends and composites has been investigated by several researchers [21-25].

1.2.2 Compatibilization

A polymer-polymer system is a mixture of at least two macromolecular substances. They may be miscible or immiscible; the former defined as homogenous down to the molecular level, having negative free energy of mixing and the latter called heterogeneous. For two polymers to be completely miscible, optimum requirement are: similar polarity, low molecular weight, and hydrogen-bonding or other strong intermolecular attraction [26].

A polymer alloy is an immiscible, compatibilised polymer blend with modified interface and morphology. Compatibilization is a process of modification of the interfacial properties in immiscible polymer systems, resulting in reduction of the interfacial tension coefficient, formation and stabilization of the desired morphology. Thus, the compatibilization is an essential process that converts a mixture of polymers into an alloy that has the desired set of performance characteristics [27, 28].

There are several ways to improve the compatibility among different polymers, like addition of compatibilizer, typically block or grafted copolymer or inducing chemical reaction between polymers leading to a modification of interfaces in two phase blends, and thereby tailoring of phase structure and properties [[29] and copolymer, which is miscible with each homopolymer and the application of ultrasound to polymer systems [30]. Generally, adding compatibilizers also results in finer dispersion, as well as more regular and stable morphologies.

Adding compatibilizers (typically at 5 – 7 wt %) generally increases mechanical performance and surface properties. The coalescence of droplets in a blend is also influenced by compatibilization. Experimental studies have shown that the addition of surface active species causes a dramatic decrease in the rate of coalescence [31]. Dispersion of additives such as fillers and reinforcing agents (including cellulose, clay, glass fibers, and powdered metals) in a polymer matrix is enhanced by a compatibilizing agent at the additive-polymer interface; interfacial interaction promotes adhesion of solid polymers to polymeric or inorganic substrates [32]. Reactive compatibilization of immiscible polymer blends is a method which is very often used to obtain well dispersed and stabilized phase morphologies. The technique of reactive compatibilization is based on the in-situ formation of a block- or graft copolymer at the interface between the phases of polymer blend during melt-mixing. In some cases, a third polymer, which is miscible with one of the blend components and reactive with the other, can be used for the formation of a compatibilizing copolymer at the interface [33].

1.3 Properties of elastomer blends and composites

Considering the nature of elastomers, in particular their extensibility and viscoelastic behavior, some important properties are discussed

1.3.1 Cure Characteristics

In general, the study of the curing behaviour of blends/ composites is an evaluation of the functionality of both the unvulcanized polymer mix and the curative in forming crosslinks in the matrix. The number of crosslinks formed significantly depends upon the amount of curing agent used, its activity, its interaction with the matrix and reaction time. Technically, it is known as the degree of vulcanization or crosslink density. For a given system, there can be many stages of vulcanization, depending upon the blending components, their weight or volume ratio, curative type and its dosage. The cure stages attained by can be grouped into four types; viz., pre-vulcanization, under vulcanization, optimum vulcanization, and over-vulcanization. The cure characteristics of composites are generally examined by using rheometers .The most commonly used are torque, rotational and capillary rheometers. Torque rheometry is used extensively for measuring rheological properties as well as for determining melt flow values, thermal stability and degradation. The oscillating disc rheometer (ODR) is used in many rubber laboratories. A typical torque-time graph obtained from a rheometer is given in Figure 1.3.A rheograph conveys very vital informations regarding the characteristics of the samples being examined. The curve generally shows an immediate initial rise in torque due to the low chance to absorb heat from its surroundings. As it absorbs heat from the instrument, the compound softens and shows a minimum torque (ML). The torque then begins to increase, indicating the beginning of the curing process (vulcanization or crosslinking). The time required for the torque to increase by 2 units above ML is called scorch time (t_2). It is a measure of the pre-mature vulcanization of a material. It indicates the storage safety of a material. A short scorch time represents a short shelf life of a master batch. It also follows, from the Figure that the torque continues to increase with time, until there is no more significant rise. At this point the compound is fully vulcanized, and this maximum torque value is designated by the symbol M_H. The last major piece of information extracted is the time it takes to complete the cure, known as the cure time. This is the time required to reach 90% of the maximum cure. It is represented by the symbol t_{90}. In a cure graph, the width of the plateau is a preliminary measure of the stability of the blend, since it indicates the influence of the heat of vulcanization.

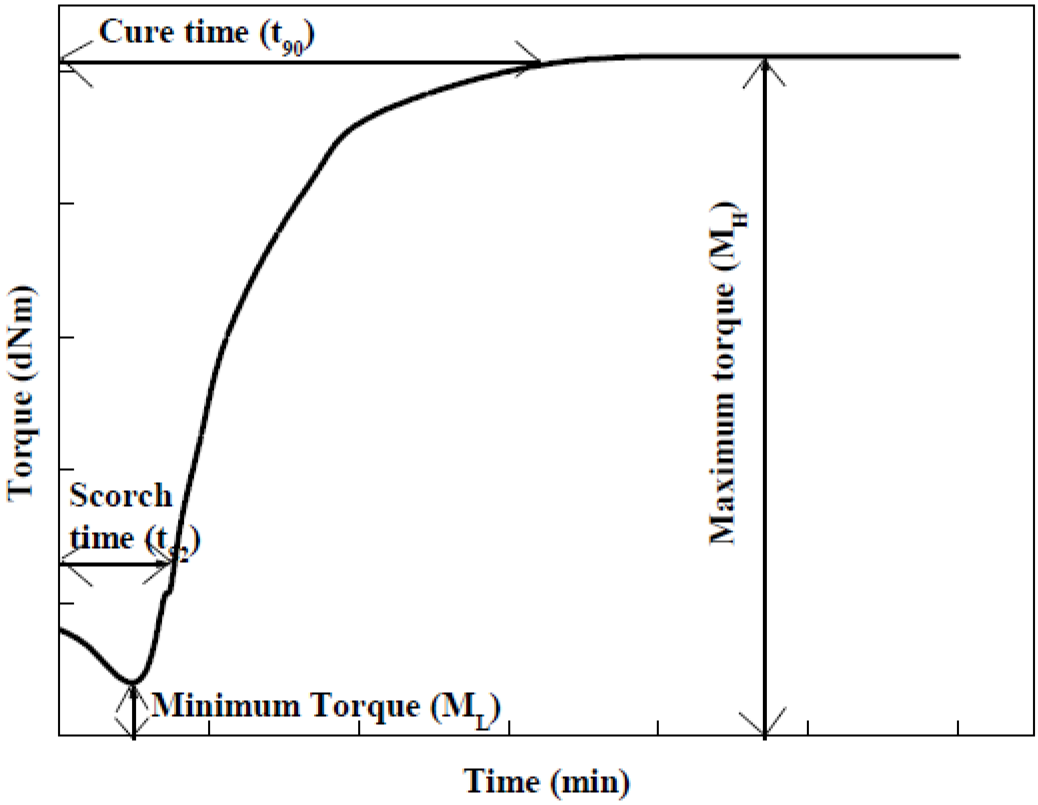


Figure 1.3 Typical curve for torque v/s time obtained by oscilatory disk rheometry

1.3.2. Morphological properties

The shape made by the two phases, and the arrangement of the two phases is called morphology. The biggest thing one can do to affect the morphology of an immiscible blend is to control the relative amounts of the two polymers one is using. Let's say we are trying to make an immiscible blend from two polymers, polymer A and polymer B. If we have a lot more of polymer A than polymer B, polymer B separate into little spherical globs. The spheres of polymer B will be separated from each other by a sea of polymer A, like we see in the picture below. In such a case we call polymer A the major component and polymer B the minor component. But if we put more polymer B into the immiscible blend, the spheres will get bigger and bigger, until they get so big that they become joined together. Now they aren't isolated spheres anymore, but a continuous phase. The immiscible blend now looks like the middle picture above. The domains of polymer B are now joined together, but so are the domains of polymer A. When this happens, we say that the polymer A phase and the polymer B phase are co-continuous. But if one keep adding more polymer B, eventually there will be so much more polymer B in the immiscible blend that polymer A will become nothing but isolated spheres surrounded by a continuous phase of polymer just like the picture above on the right. Polymer B is now the major component and polymer A is the minor component, and the situation is reversed from what we had at first.

Figure 1.4 Relative amount of polymer B in the immiscible polymer-polymer system of A and B**.**

Morphology of the blends and composites depends upon compounding compositions, rheological properties, physical characteristics of the components, their intrinsic melt viscosity, the presence of other ingredients and the mixing conditions. Detailed investigations on phase morphology development, phase co-continuity and phase stability of polymer blends have already been studied [34]

1.3.3 Mechanical properties

1.3.3.1 Tensile strength

The ability of a material to resist breaking under tensile stress is one of the most important and widely measured properties of materials used in structural applications. The force per unit area (MPa or psi) required to break a material in such a manner is the ultimate tensile strength or tensile strength at break. Tensile strength is an important characteristic of polymeric materials because it indicates the limit of final stress for most applications**.** Tensile strength measurement serves as an overall performance indicator. Values below 1000psi usually mean that most mechanical properties are poor, and values above 2000 psi point to generally good mechanical properties. For dynamic applications, a minimum of 1000 psi is usually specified. Tensile strength is also used as a measure of elastomers deterioration during service. The tensile strength of a material quantifies how much stress the material will endure before suffering permanent deformation. This is very important in applications that rely upon a polymer's physical strength or durability. For example, a rubber band with a higher tensile strength will hold a greater weight before snapping. In general, tensile strength increases with polymer chain length and crosslinking of polymer chains.

1.3.3.2 Hardness

Hardness is one of the most widely used properties in the specification of rubbers. Hardness can also be varied to meet specific needs. The shore durometer scale, which runs from 0 to 100, the higher the number the harder the material. There are some relationships between hardness and several mechanical properties of elastomers. For example, the lower the hardness, the lesser is the tendency for the elastomer to creep or flow. Elongation decreases as hardness increases. Tensile strength generally increases with hardness up to 50 on the durometer scale, and then falls off; its hardness continues to increase.

Toughness is the energy of the sample absorbed before it breaks and there are three cases; brittle (strong and not tough), Plastic (strong and tough) and elastomeric (neither strong nor tough). The physical properties of composite materials are generally not isotropic (independent of direction of applied force) in nature, but rather are typically orthotropic (different depending on the direction of the applied force or load).

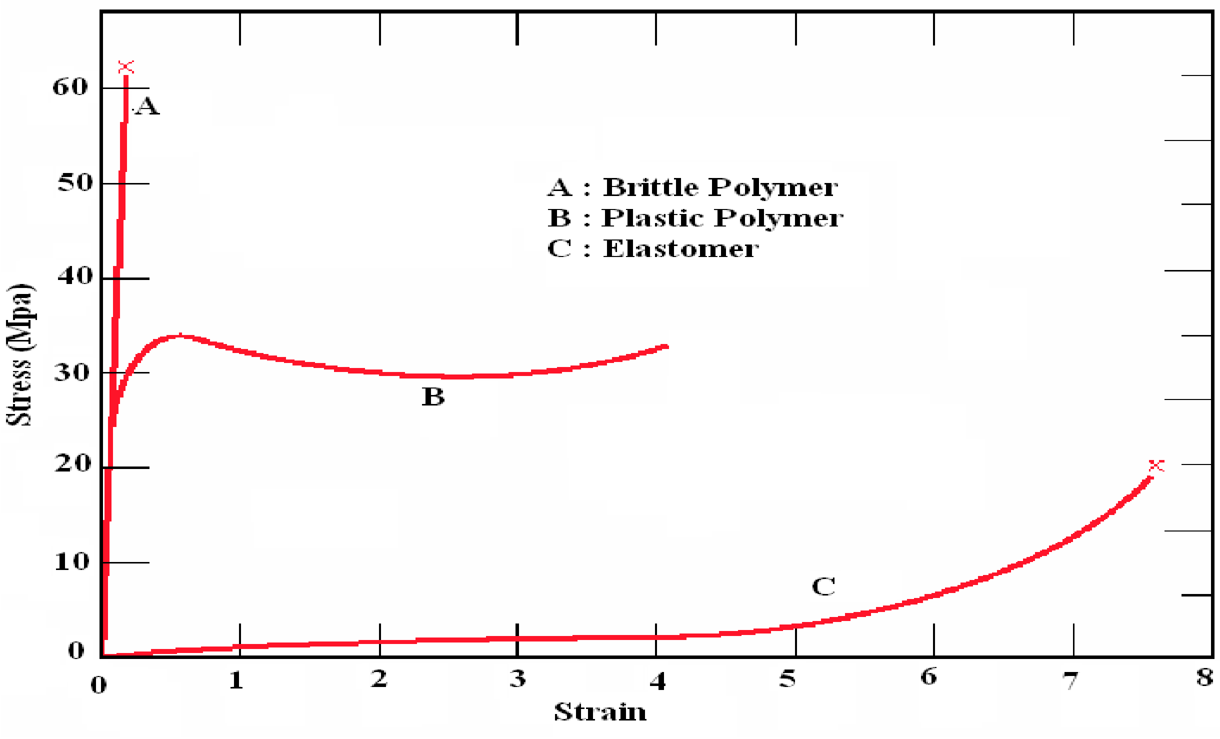


Figure 1.5 Schematic representation of Stress-Strain curve of polymers

For instance, the stiffness of a composite panel will often depend upon the orientation of the applied forces and/or moments. Panel stiffness is also dependent on the design of the panel.

1.3.3.3 Young's modulus

In solid mechanics, Young's modulus, also known as the tensile modulus, is a measure of the stiffness of an isotropic elastic material. Young's modulus is the ratio of stress, which has units of pressure, to strain, which is dimensionless; therefore, Young's modulus has units of pressure. It can be experimentally determined from the slope of a stress-strain curve created during tensile tests conducted on a sample of the material. Low tensile modulus indicates easy deformation of the sample.Elastomers have low modulus values. It is also commonly, but incorrectly, called the elastic modulus or modulus of elasticity, because Young's modulus is the most common elastic modulus used, but there are other elastic moduli measured, too, such as the bulk modulus and the shear modulus.The SI unit of modulus of elasticity (E, or less commonly Y) is the pascal (Pa or N/m^2 or $m^{-1}\cdot kg\cdot s^{-2}$). The practical units used are megapascals (MPa or N/mm^2) or gigapascals (GPa or kN/mm^2).The Young's modulus calculates the change in the dimension of a bar made of an isotropic elastic material under tensile or compressive loads. For instance, it predicts how much a material sample extends under tension or shortens under compression. Some calculations also require the use of other material properties, such as the shear modulus, density, or Poisson's ratio. It also helps in selection of materials for particular structural applications. Young's modulus quantifies the elasticity of the polymer. Like tensile strength, this is highly relevant in polymer applications involving the physical properties of polymers, such as rubber bands. The modulus is strongly dependent on temperature.

1.3.3.4 Compression set

This characteristic refers to the percentage of deflection or distortion remaining in an elastomer after a load is removed. It **is** comparable to creep or cold flow in plastics, and type and size of loading. In general, compression set values are about 20 percent less than shear, and tension creep is about 30 percent more than shear.

1.3.3.5 Tear resistance

Elastomers as a class have low tear strength. If tear strength is extremely low, small nicks or cuts can cause catastrophic failure, and under flexing, failure will quickly occur. In addition, elastomers with poor tear strength generally has low abrasion resistance.

1.3.3.6Abrasion resistance

Because many elastomer applications involve friction and wear, abrasion resistance is usually an important consideration. Generally, abrasion resistance improves with an increase in hardness. However, for some kinds of abrasion, for example, where small particles are involved, relatively soft elastomers perform better.

1.3.3.7 Elongation at break

It gives what happens to the sample while trying to break it. It is a type of deformation and is a change in shape that anything undergoes under stress. The sample deforms by stretching and becomes longer called elongation.

$$\%\ \text{elongation} = \frac{L \times 100}{L_0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ 1.1$$

where L=length of sample after stretching and L_0 = original length.

1.3.4 Deterioration resistance and Polymer degradation

All elastomers undergo changes in properties with time because of oxidation. This deterioration, which is referred to as aging, is affected by many different environmental factors such as sunlight, heat and ozone, all of which accelerate oxidation. Aging results in loss of resilience, a decrease of hardness, and eventual cracking.

Polymer degradation is a change in the properties—tensile strength, colour, shape, etc. of a polymer or polymer-based product under the influence of one or more environmental factors such as heat, light or chemicals such as acids, alkalis and some salts. These changes are usually undesirable, such as cracking and chemical disintegration of products or, more rarely, desirable, as in biodegradation, or deliberately lowering the molecular weight of a polymer for recycling. The changes in properties are often termed "aging". In a finished product such a change is to be prevented or delayed. Degradation can be useful for recycling/reusing the polymer waste to prevent or reduce environmental pollution. Degradation can also be induced deliberately to assist structure determination.

1.3.5 Oil resistance

This is an important criterion in the selection of elastomers because many of their applications involve an environment of hydrocarbon fluids such as a oil and gasoline. Resistance to oils is monitored based on how many the elastomers swells in the presence of oil.

1.3.6 Thermal properties

The term thermal analysis (TA) is frequently used to describe analytical experimental techniques which investigate the behaviour of a sample as a function of temperature. This definition is too broad to be of practical use. In this discussion, TA refers to conventional TA techniques such as differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermogravimetry (TG), thermomechanicalanalysis (TMA) and dynamic mechanical analysis (DMA).

Thermal analysis is an important tool in the characterization of polymeric materials. During the fabrication of new products from polymers, acknowledge of the thermal stability of their components is essential. The threshold temperature for breakdown determines the upper limit of temperature in fabrication. Optimization of the processing temperature and time with an understanding of the matrix, the reinforcing element and the interface can lead to a best balance of composite properties.

(TGA) can help in understanding the degradation mechanism and thus assist any effort to enhance the thermal stability of a polymeric material. This analysis needs only a small quantity of the sample. It is possible to quantify the amount of moisture and volatiles present in the composites which have a deteriorating effect on the properties. Thermogravimetric data provides the different stages of thermal breakdown, weight of the material in each stage; threshold decomposition temperature etc.TG curves provide information about the nature and conditions of degradation of materials. The thermal stability of individual polymers can be enhanced to greater extent by blending it with other polymers or by reinforcing with fibres. Composites usually have better thermal properties than the corresponding components in the system [35].

1.3.7 Electrical properties

Electrical resistivity, dielectric constant, tangent of the dielectric loss angle (tanð) and dielectric strength are key parameters which determine the usefulness of elastomers as potential insulators in wire and cable applications. The electrical properties of rubbers, apart from the dielectric constant, differ widely but can be further altered by compounding and as a result of the susceptibility of the polymer and or the compound to pick up moisture. Dielectric constant can be widely varied by the choice of additives.

1.3.8 Dynamic properties

Dynamic mechanical properties refer to the response of a material as it is subjected to a periodic force. These properties may be expressed in terms of a dynamic modulus, a dynamic loss modulus, and a mechanical damping term. Typical values of dynamic moduli for polymers range from 10^6-10^{12} dyne/cm2 depending upon the type of polymer, temperature, and frequency. dynamic mechanical measurements over a range of temperatures provide valuable insight into the structure, morphology and properties of polymeric blends and composites. Dynamic mechanical thermal analysis (DMTA) has proved to be an effective tool in the characterization studies of viscoelastic materials [36-38].

1.3.9 Sorption and permeation properties

Towards the end of 20 th 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. Transport studies are of considerable importance when we come across problems like designing a barrier material or tubes for transporting liquids and gases [39].

Molecular transport of organic solvents through polymeric materials has been the subject of both technological and fundamental interest for a variety of applications such as food packaging, controlled drug release, reverse osmosis etc.

Polymers are now used as structural engineering materials and knowledge of the performance of polymer under the influence of external factors such as solvent, temperature etc. is essential for their successful applications.

The transport of small molecules through a polymer membrane occurs due to random molecular motion of individual molecules. The driving force behind the transport process which involves sorption, diffusion and permeation is the concentration difference between the two phases. The transport process slowly tries to equalize the concentration difference or the chemical potential of the penetrant in the phases separated by the membrane.

Permeation is the migration of fluids through the thickness of a polymeric material. It is a major concern particularly when elastomers are used in chemical handling and processing industries. Permeation can be evidenced by swelling, blistering and discoloration. Although the mechanism is not well understood, the presence of ethanol in fuel facilitates the permeation of hydrocarbons through certain elastomers and thermoplastics, and to a lesser degree in thermoset products. Permeation refers to the mass transport of a substance (or solvent) through membrane that is driven by a chemical potential or activity gradient. It is dependent on numerous factors, such as solvent-material interaction, diffusivity of fluids through a material, the surface-area-to thickness ratio of the nonmetal and the degree of crosslinking (e.g., elastic contraction) in a material. Permeation is essentially a three-step process which covers an instant liquid-uptake on the polymer. The permeability of gases in polymers is a property inherent to their structure, which results, firstly, from the absorption of fluids by the material, then, from the diffusion of these products through the polymer matrix [40].

Knowledge and understanding of the diffusion process and diffusion coefficients is thus of importance both theoretically and experimentally. The assumed mechanisms of the diffusion process for small penetrants in rubbery and glassy polymers are quite different. Knowledge of both types of system is required. Measuring diffusion coefficients for small penetrants in polymeric matrices is often time-consuming and difficult. The ability to predict diffusion coefficients for these systems from first principles, or by extension from existing data is clearly desirable. A small amount of unfilled volume is associated with the end of a polymer chain. This volume is called the free volume and is schematically represented in the diagram below. For a given mass of polymer the amount of free volume will depend on the number of chain ends, hence the number of chains and hence the degree of polymerisation .Free volume is the fraction of the volume not occupied by the polymer. This concept has found uses in discussing physical properties such as viscosity, diffusion in liquids, viscoelasticity, electrical conductivity, the glass transition and plastic yielding. Early attempts to predict diffusion consist in trying to relate the diffusion coefficient (*D*) of a hypothetical penetrant to the fraction of the volume that is free volume (voidageV -2fraction) and possibly some other information obtained from the detailed structure, in addition to the pure quantity, of the free volume. The free volume theory implies that the voidage fraction is the dominant content as *D* is proportional to both the kinetic velocity and the probability of finding enough free volume for the hopping of the penetrant. More recent models have tried to take into account the distribution of the free volume and even its dynamical redistribution as the polymer evolves performing thermal motion with time.

1.4 Theory of molecular transport

For the membrane separation processes, a well-established mass transport model is essential. Several models have been used to describe these processes like solution-diffusion model [41, 42], the pore-flow model [43], and the irreversible thermodynamics model [44].

Among them, the solution-diffusion model seems to be accepted by many of the membrane researchers. According to this model, the mass transport process is considered to consist of three consecutive steps: (i) sorption of the penetrant from the feed to the matrix; (ii) diffusion of the penetrants with in the matrix; and (iii) desorption of the penetrant from the matrix on the downstream side of the matrix. The transport process slowly tries to equalize the concentration difference or the chemical potential of the penetrant in the phases separated by the membrane. If a concentration gradient is established across some arbitrary reference section in the polymer, a net transport of penetrant occurs in the direction of decreasing concentration. A schematic representation of the steps involved in the solution-diffusion model in polymers is shown in Figure 1.6.Diffusion behaviours can be classified into three categories [45]: (i) Fickian diffusion, in which the rate of diffusion is much less than that of sorption and the sorption equilibrium is rapidly established. (ii) Sorption-controlled process, in which the diffusion rate is very rapid, compared with the sorption rate and therefore sorption is the key step for the transfer process. (iii) Non-Fickian diffusion or anomalous diffusion, which occurs when the diffusion rate and the sorption rate are comparable.

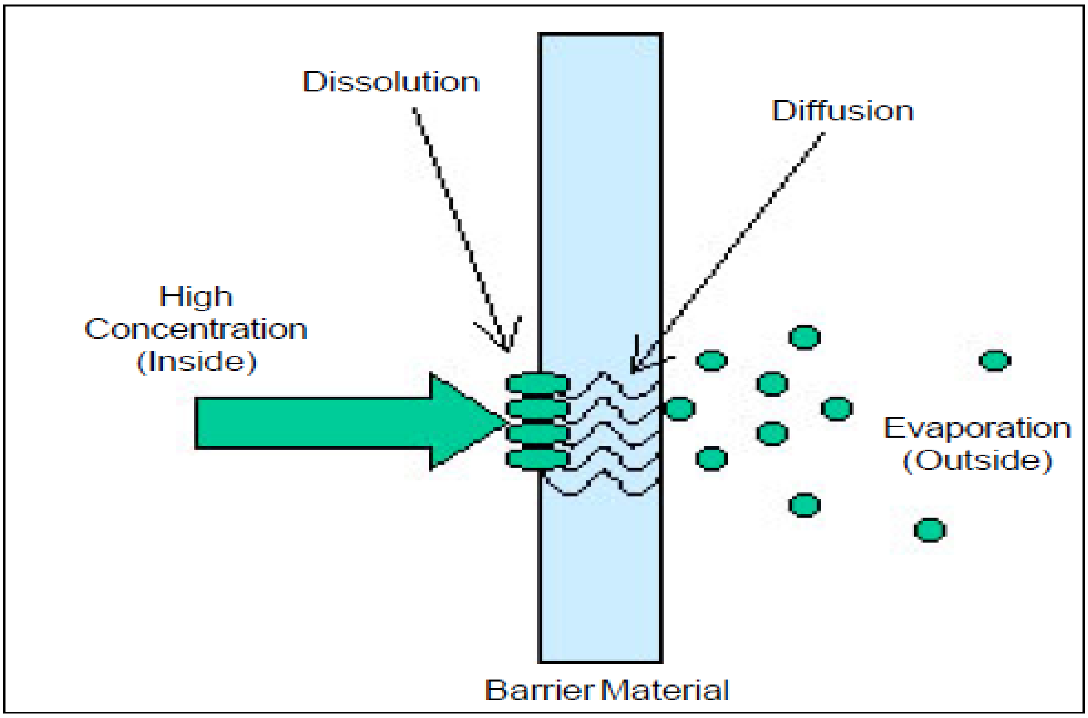


Figure 1.6 Schematic representation of solution –diffusion model

Among these three kinds of diffusion behaviours, the non-Fickian diffusion, which commonly occurs in the case of liquid penetrants and glassy polymer membranes, is the most complicated one.

According to Fick's first law of diffusion, the diffusive flux *J* (the amount of penetrant passing through a plane of unit area normal to the direction of flow during unit time) in the *x*-direction of flow is proportional to the concentration gradient $\frac{\partial c}{\partial x}$ as:

$$J = -D\frac{\partial c}{\partial x} \quad \ldots \ldots\ldots\ldots\ldots\ldots\ldots\ldots 1.2$$

where *D* is the diffusion coefficient and *c* the concentration of the diffusing molecule. This equation is applicable when the diffusion is in the steady state.

On the other hand, Fick's second law describes the unsteady state transport process, which is given by the rate of change of the penetrant concentration at a plane within the membrane, as:

$$D\frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t} \dots\dots\dots\dots\dots\dots .1.3$$

This is an ideal case in which the membrane is isotropic and *D* is independent of distance, time and concentration. Depending on the boundary conditions, there are many solutions available for Equation (1.2). When the diffusion rate *J* achieves a steady value (no longer varies with time) a material balance requires that it also be independent of *x*, in which case Equation (1.1) can be integrated to give,

$$\int_0^h J dx = -\int_{c=c_1}^{c=c_2} D(dc) \dots\dots\dots\dots\dots\dots\dots\dots..1.4$$

$$J = -\frac{1}{h}\int_{c=c_1}^{c=c_2} D(dc) \dots\dots\dots\dots\dots\dots\dots 1.5$$

Equation (1.4) indicates the steady-state diffusion rate which is inversely proportional to the overall membrane thickness *h* for a given set of boundary conditions. To complete the integration, the variation of *D* with *c* must be known. In some systems, the diffusion coefficient does vary with concentration because the van der Waals forces are high between the diffusing molecules themselves and between the diffusing molecules and the polymer chains. When there are relatively weak intermolecular forces of attraction between the diffusing molecules and the polymer chains, the solubility is low and the polymer structure is not significantly altered. Under these circumstances *c* can vary without affecting *D*, and Equation (1.4) then becomes:

$$J = -\frac{D}{h}[C_2 - C_1] \dots\dots\dots\dots\dots .1.6$$

where c_2 and c_1 are the concentrations of the diffusing molecules dissolved at the downstream and upstream polymer-membrane faces respectively. In many cases, it is the pressures or partial pressures *p* of a gas or vapour above the faces of the polymer film, rather than the surface concentration, which are known. These quantities are related by Henry's law, which states that:

$$C = Sp \ldots\ldots\ldots\ldots.1.7$$

where *S* is the solubility constant for a given gas-polymer system. The combination of Equations (1.5) and (1.6) gives the well-known permeation equation:

$$J = DS\left[\frac{p_2 - p_1}{h}\right] \ldots\ldots\ldots\ldots\ldots.1.8$$

The product *DS* is called the permeability coefficient, *P*, so that:

$$P = DS \ldots\ldots\ldots\ldots.1.9$$

1.5 Factors affecting transport process

i) Nature of the polymer

The transport behavior for a given penetrant varies from one polymer to another. Transport property depends on the free volume within the polymer and on the segmental mobility of the polymer chains. The segmental mobility of the polymer is affected by the extent unsaturation, degree of cross linking, degree of crystallnity and nature of the substituents. The glass transition temperature of polymers has a profound influence on transport properties. Polymers with low glass transition temperature possess greater segmental mobility and will have higher diffusivity. It is found that diffusivity is decreased when the extent of unsaturation in the polymer backbone is lowered by hydrogenation. This is because unsaturation in the polymer chains provides for segmental mobility whereas saturation tends to restrict it. The introduction of bulky or polar substituents on the poymer chain influences the transport process. It has reported that rubbers containing large number of substituent methyl groups have lower diffusivities [46].For instance, the low permeability of butyl rubber is due to sluggish segmental motion of the polymer chains caused by the sterric hindrance of the two pendant methyl groups on every other main chain carbon atom [47]. For polymers with the same substituent pattern, it is the flexibility of the backbone that dominates permeation property. The substitution of bulky functional groups in the side chain appears to have a greater influence on decreasing diffusivity than substitution of these groups in the polymer backbone [48].It was also reported that the polymer molecular weight, significantly influences the transport process .As molecular weight increases, the number of chain ends decreases. The chain ends repeat a discontinuity and may form sites for permeant molecules to be sorbed into glassy polymers. 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. Thus transport phenomenon is strongly related to the structure of the elastomers.

Permeability is affected by the crystallinity of the polymer. It has been observed that the crystalline region put up stiffer resistance to a penetrating molecule the amorphous region. In other words, crystalline polymers, in general, are far less permeable than the amorphous one [49, 50].Crystallites act as physical crosslinks that prevent a high degree swelling and therefore shows a lower permeability, compared to the amorphous polymer. Crystallinity has also a great influence on the dissolution of the feed mixture in the membrane during transport process, because this will occur in the amorphous part of the polymer. Only because of the absence of polar groups in their flexible chains, elastomers absorb organic liquids preferentially, with respect to water and the flexible chains of the elastomer cause a relatively high permeability [51]. Polymers with these properties are excellent candidates as membrane materials for the removal of organics from water .Many of the hydrophobic polymers show good chemical and thermal stability, which is a reason to choose such a polymer as basic material and try to improve its separation properties by some kind of chemical modification.

For mixtures of two organic liquids three kinds of mixtures can be distinguished: i)polar/apolar, ii)polar/polar and iii)apolar/apolar mixtures. For the removal of the polar component from the first mentioned mixture, polymers with polar groups should be investigated and for the removal of the apolar component completely, apolar polymers are favourable. The polar/polar and apolar/apolar mixtures are mostly very difficult to separate especially when the two components have similar molecular size.

ii) Nature of crosslinks

The transport properties of polymers are strongly dependent on the distribution of crosslinks within them. An uncrosslinked polymer will not usually dissolve in a solvent if the solvation energy is not enough to break the strong covalent bonds between the macromolecules. Depending on the distribution of crosslinks or crosslink density, however, such materials may admit significant amounts of solvent, become softer and swollen as they do so. The swelling by fairly lightly crosslinked materials is generally reversible and, given appropriate conditions, the solvent that has entered a crosslinked structure can be removed and the polymer can be returned to its original size. Heavily crosslinked polymers have a dense three-dimensional network of covalent bonds in them, with little freedom for motion by the individual segments of the molecules involved in such structures. The mass transport process is very tortuous in these types of polymer matrices. However, crosslinked polymers will not dissolve since the crosslinks set an obstacle, transport property is reduced at high levels of crosslinking. For the same polymer with the same crosslink density, transport phenomena depend on the nature of the cross links. It was reported that in benzene solution, crosslink networks swell more than the corresponding bulk cross linked networks having the same crosslink density. Unnikrishnan [52] et al. has investigated the effect of cross links on the diffusion and transport of aromatic hydrocarbons through natural rubber membranes. It was found that NR crosslinks with conventional vulcanization absorbs the highest amount of solvent whereas the crosslinked using peroxide system takes the lowest due to the difference in the crosslnks present in them. Peroxide and sulfur are the most widely used crosslinking agents for uncured natural elastomers. The chemical reaction consisting in the addition of sulfur to the double bonds of the rubber molecules are always involved in the vulcanization of rubber with sulfur, which constantly forms the three dimensional networks . For peroxide curing, the free radical produced by peroxide is the driving force for peroxide crosslinking, which is much faster than sulfur cure. Free radicals are atoms or molecular fragments with unpaired electrons, which are in unstable state and tend to react with other materials to make the electron to pair with another.

iii) Effect of plasticizers

Addition of plastcizers to a polymer results in increased segmental mobility and usually in an increased penetrant transport [53].

iv) Nature of the penetrant

The diffusivity of a penetrant in an amorphous polymer matrix is governed by the penetrant size [54] and interactions with the polymer as well as by the shape, connectivity and time scales of thermal rearrangement of unoccupied space within the polymer[55]. The size and shape of penetrant molecule will influence its rate of transport within the polymer matrix [56]. A decrease in diffusivity with an increase in the size of the penetrant has been reported by many investigators [57] The effect of polymer molecular weight on transport properties is generally found to be very low. Several experimental studies revealed that the diffusion and permeability coefficients were not strongly dependent on the molecular weight presumably because the samples involved were of sufficiently high molecular weight .The permeant’s shape also has noticeable effects on permeability. For example, flattened or elongated molecules have a higher diffusion than spherical molecules of equal molecular volume [58]. Because of the absence of polar groups in their flexible chains, elastomers absorb organic liquids preferentially, with respect to water and flexible chains of the elastomer cause a relatively high permeability. Polymers with these properties are excellent candidates as membrane materials for the removal of organics from water. As energy costs rise, membrane technology for separating gases is likely to play an increasingly important role in reducing the environmental impact and costs of industrial processes [59].

v) 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. The significant role of fillers on the diffusion process has been identified by several researchers [60, 61]. Introducing fillers into polymers can substantially modify the properties and cost of the material. Loading of filler particles into a polymer matrix is known to affect mechanical and transport properties of composite polymers [62-67]. Previous studies have shown that filler content may alter sorption and transport properties [68-71].The presence of certain chemical modifiers was found to affect the thermal properties of polymer systems [72].Particulate fillers can increase the strength of an amorphous rubber more than 10-fold [73]. However, in most systems to achieve the full benefits of the effects offered by the filler, the interaction between the filler and the polymer matrix must be optimised. Although, it should be noted that optimising does not necessarily mean maximising the strength of adhesion between filler and matrix, in some instances this causes embrittlement, and then a lesser level of interaction is needed. If the inert filler used is compatible with the polymer matrix, the filler will take up the free volume within the polymer matrix and creates tortuous path for the permeating molecules. 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 [74].

vi) Temperature

The diffusibility and temperature are related by Arrhenius relationship

$$D = D_o\left(e^{\frac{-E_D}{RT}}\right) \quad \text{.......} \quad 1.10$$

and heat of solution of the penetrant in the polymer,Do,So,Po are pre-exponential factors.

$$S = S_o\left(e^{\frac{-\Delta H_s}{RT}}\right) \quad \text{.......} \quad 1.11$$

$$P = P_o\left(e^{\frac{-E_P}{RT}}\right) \quad \text{.......} \quad 1.12$$

where, E_D and E_P are activation energies of diffusion and permeation, ΔH_S

Knowledge and understanding of the diffusion process and diffusion coefficients is thus of importance both theoretically and experimentally. The assumed mechanisms of the diffusion process for small penetrants in rubbery and glassy polymers are quite different. Knowledge of both types of system is required. Measuring diffusion coefficients for small penetrants in polymeric matrices is often time-consuming and difficult. The ability to predict diffusion coefficients for these systems from first principles, or by extension from existing data is clearly desirable.

1.6 Permeation in everyday life

- Packaging: The permeability of the package (materials, seals, closures, etc) needs to be matched with the sensitivity of the package contents and the specified shelf life. Some packages must have nearly hermetic seals while other can (and sometimes must) be selectively permeable. Knowledge about the exact permeation rates is therefore essential.
- Tires: Air pressure in tires should decrease as slowly as possible. Therefore it is good to know which gas permeates least through the rubber wall.

- Insulating material: Water vapour permeation of insulating material is important as well as for submarine cables to protect the conductor from corrosion.

- fuel systems: To meet legal regulations, e.g. CARB (California Air Resource Board) for Low Emission Vehicles, it is essential to use barrier materials for fuel hoses and tanks.

1.7 Free volume Theory

The presumption that molecular transport is regulated by free volume was first introduced by Cohen and Turnbull in 1959[75].From the Cohen and Turnbull perspective, the hard sphere molecules that constitute an idealized liquid exist in cavities or cages formed by nearest neighbours. Thus, the total volume of the liquid could be divided into two components: occupied volume and free volume. A small amount of unfilled volume is associated with the end of a polymer chain. This volume is called the free volume and is schematically represented in the diagram below.

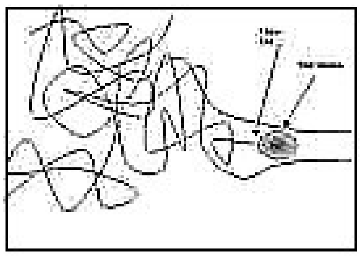


Figure 1.7 Schematic representation of free volume in polymers

For a given mass of polymer the amount of free volume will depend on the number of chain ends, hence the number of chains and hence the degree of polymerisation .Free volume is the fraction of the volume not occupied by the polymer [76].

The diffusivity of a dilute penetrant in an amorphous polymer matrix is governed by the penetrant size and interactions with the polymer as well as by the shape, size, connectivity and time scales of thermal rearrangement of unoccupied space within the polymer. In a high temperature melt (T>Tg), openings among chains that are capable of accommodating the penetrant undergo rapid redistribution in space. One can envision that the penetrant is ”carried along” by density fluctuations caused by thermal motion of surrounding chains. As in free volume picture of the liquid state diffusion, one could envision that a penetrant molecule resides in a certain position of the polymer matrix until the motion of surrounding chains, modified by the penetrant’s presence, leads to the formation of a cavity ,at a distance commensurate with the penetrant’s diameter, into which the penetrant can move. After the move, the cavity in which the penetrant was originally accommodated is closed. A succession of such small random moves of the penetrant constitutes diffusion. In this high- temperature melt limit, formation of a cavity of sufficient size to accommodate the penetrant can be viewed as the rate controlling step for a move. The time scale between moves is thus set by the relaxation time of density fluctuations on the length scale of the penetrant diameter within the polymer matrix. This concept has found uses in discussing physical properties such as viscosity, diffusion in liquids, viscoelasticity, electrical conductivity, the glass transition and plastic yielding. Early attempts to predict diffusion consist in trying to relate the diffusion coefficient (D) of a hypothetical penetrant to the fraction of the volume that is free volume and possibly some other information obtained from the detailed structure, in addition to the pure quantity, of the free volume. The free volume theory implies that the voidage fraction is the dominant content as D is proportional to both the kinetic velocity and the probability of finding enough free volume for the hopping of the penetrant. More recent models have tried to take into account the distribution of the free volume and even its dynamical redistribution as the polymer evolves performing thermal motion with time. Takeuchi and Okazaki [77] have suggested a simple integral expression of the cluster size distribution that shows very good correlation with the self-diffusion coefficient of penetrant particles of He and O_2 for their hypothetical polymer models. However, the lack of further interest in that expression by the same or other authors, probably indicates that their model was oversimplified or unrealistic in some other way.

Swelling experiments are important because they give valuable information about the service performance of composites in liquid environment and also to study the characteristics of rubber / fibre interface. These studies are useful when composites are used for oil seals, marine articles etc. On absorption of liquid the material undergoes a diffusion process, which involves transfer of liquid to the interior of the article. By this , the article swells as a whole and this leads to the gradual deterioration in physical and mechanical properties and premature failure of the article. When rubbers absorb liquids its' volume increases and this phenomenon is known as 'swelling' by which deterioration in properties happens. Raw rubbers are completely soluble in certain liquids; but vulcanized rubbers are virtually insoluble because chemical crosslinks between the rubber chains prevent rubber molecules becoming surrounded by the liquid and restrict the deformation. Chemical structure and composition of rubber compound, and test piece size and shape, rubber / liquid ratio, temperature, time, presence of filler etc. influence the swelling behavior of elastomers.

Swelling of rubbers by liquids is a diffusion process. Initially the liquid concentration at the surface of a rubber component is high, while the liquid concentration in the bulk of the component is zero. Subsequently the liquid diffuses into the rubber just below the surface and to the bulk of the rubber, until the concentration of the liquid is uniform through out the component and equilibrium swelling is reached. Swelling of elastomers can mainly be governed by various polymer structure properties, such as:

- Glass Transition Temperature: Swelling will be decreased in an elastomer with a high Tg, that is, in a polymer with little free volume available for absorption of liquid.

- Crosslinking: Since crosslinks set an obstacle against swelling, swelling is reduced at high levels of crosslinking. The greater the number of cross links per unit volume, the shorter the average length of rubber chains between cross links and lower the degree of swelling.
- Fillers: Swelling is reduced by the use of high filler loadings. At high filler loadings, less free volume is available in elastomer to absorb fluid.Some other additional factors which can influence swelling can be summarized, as follows:
- Increasing liquid viscosity lowers the rate of absorption and the equilibrium mass uptake level.
- Increasing temperature may increase swelling by a modest amount.
- During liquid immersion, soluble non-bound ingredients in the elastomer can be removed by leaching; this is usually (but not always) a small effect.

The degree of swelling depends upon the compatibility of the rubber and liquid on a molecular scale. It also depends on the amount and type of filler present in the rubber. The rate at which swelling proceeds depends on the relative molecular size of the diffusing liquid molecules.

When a polymer fragment is added to the solvent, the forces of attraction or dispersion start acting between them depending on their chemical nature, polarity and solubility parameter. When this solvent – solute interaction become more powerful than the solute – soluble interaction, the forces holding the polymer segments together become weak and the solvent molecular forces their way between the segments, break the segment – segment contact, surround individual segments and establish contact with them.

Elastomers, as crosslinked products, are insoluble in liquids as far as the cross links are not destroyed. They show, however a greater or lesser volume increase, the extent of which is a function of compatibility factors, and this increase with time until equilibrium – swelling rate has been attained. This absorption of liquid is associated with three-dimensional expansion of network structure. The loosing of cohesive bond causes a large number of mechanical properties to deteriorate, e.g. tensile strength, tear strength and hardness. Their process is theoretically reversible. If no material extraction takes place by virtue of swelling process, then the original property state is obtained after full-scale reversal of swelling. This seldom occurs however since the swelling media eg:- stabilizers, antioxidants and plasticizers are practically dissolved out. This causes changes in ageing properties on subsequent reversal of swelling. For these reasons, chemicals that are highly difficult to extract are used and a low level of swelling is target.

The solubility parameter concepts provide a useful approach to decide on the compatibility of elastomeric with liquids i.e., capability of the individual component substances in either an immiscible polymer blend or a polymer composite is to exhibit interfacial adhesion .The solubility parameter may be regarded as a measure of intermolecular attraction and is numerically equal to the square root of cohesive energy density, polymers and compounding ingredients having closely similar solubility parameter values are likely to be compatible and this is often considerable value when dealing with unfamiliar materials.

$$\partial = \left[\frac{L - RT}{MD}\right]^{1/2} \qquad \text{1.13}$$

where L= latent heat of evaporation
R= gas constant
T= absolute temperature
M= molecular weight
D= density

This concept predicts that a solvent with a solubility parameter similar to that of a polymer will swell or dissolve the polymer, depending on whether it is or is not cross linked. If two chemical species have the same, or similar, solubility parameter values, upon mixing, they are likely to have a strong affinity for one another. Hence an elastomer will have a tendency to absorb a liquid of similar ð, and be swollen by it. Therefore, an elastomer, exposed to an immiscible liquid mixture, will eventually swell as if it is exposed to the more compatible liquid (i.e., the one with the nearest solubility parameter), even if the sample does not directly contact that liquid in a pure form.

The maximum thermodynamic compatibility of two materials and hence their penetration, occurs when both have similar solubility parameter. The more dissimilar the solubility parameter becomes (ii) the greater the difference between the elastomer and the swelling medium, the less the volume increase that can be expected.

As the difference between the solubility parameters of polymer and solvent increases, their affinity for each other decreases. However, for those elastomers which are inclined to swell significantly in some liquids, a good indication of which liquids cause larger swelling in a particular elastomer can be estimated from knowledge of their respective solubility parameters. The most frequently used unit for solubility parameter in the literature is $(cal/cm3)^{1/2}$.

Unfortunately, this concept does not always work. The solubility parameter of a fluorocarbonrubber lies in the range of 6.3-8.3,while that of hexane is 7.3.Hexane does not swell a fluorocarbon rubber,contrary to the prediction based on solubility parameters ,because fluorocarbon rubber is polar and hexane is not. As in general rule, non-polar solvents will swell nonpolar rubbers, and polar solvents will swell polar rubbers.

Chemical reaction and hydrogen bonding in the elastomer or liquid can override the simple solubility parameter value. Solubility parameter will not give the rate of penetration of a liquid into an elastomer. The rigidity of three-dimensional structure will play a part in the amount absorbed. The tendency of a polymer to swell in a given solvent decreases as the molecular weight of the polymer increases and with increase in crosslinking.

The solubility behavior of polymers can be predicted to a reasonable extent by applying the Hildebrand relation, which connects the energy of mixing of two compounds to their individual energies of vaporization [78]

$$\frac{\partial E_{\text{mix}}}{\phi_1 \phi_2} = \frac{V}{(\partial_1 - \partial_2)} \text{ .... } 1.14$$

where $ðE_{\text{mix}}$ is the energy of mixing; $ø_1$ and $ø_2$,the volume fraction of the components, Vis the toal volume of one mole of the mixture and $ð_1$,$ð_2$ are the Hildebrand solubility parameter of both components, defined by

$$ð = (\text{Cohesive energy density})^{½} = \left(\frac{\partial E_{\text{vap}}}{V_m}\right)^{1/2} \text{ .... } 1.15$$

where $ðE_{\text{vap}}$ is the energy of vapourisation and V_m is the molar volume. From the equation 1.6,it is clear that a smaller difference in ð value between two compounds results in diminished energy of mixing. A decrease in $ðE_{\text{mix}}$ gives a higher degree of swelling and eventually complete solubility may result.

The penetration rate varies considerably with the rubber type and with the liquid type. The higher the viscosity the lower the penetration rate. The assessment of the swelling behavior of thick walled articles requires not only the actual media resistance but also knowledge of the time laws of the diffusion process. Whilst the edge zone of the elastomer swell up readily the swell front only move slowly into the inside, so that the mechanical performance of moulded parts, can be retained for a long period of time. It is understandable that swell resistance can also be influenced to a pronounced extent by compounding and particularly through the type and quantity of the filler selected, although also through the degree of crosslinking. Readily extractable oils in the rubber blend can lead to an apparently lower level of swelling in the case of swelling due to fuels or oils. This is due to the fact that part of the fuel or oil uptake is compensated by oil extraction. The diffusion or permeation through a rubber moulding can be reduced through barrier forming layer fillers.

Influence of fillers on swelling is relatively small compared with effect of rubber liquid interaction. However, there is a very pronounced decrease on matrix swelling with some filler.

T. K. Kwei et al.[79] studied the effect of filler loading on sorption and a marked decrease in the sorption of organic vapors was noted at low relative pressures, even with very low filler content.

Interaction between macromolecules and various solvents may cause localized disruption of intermolecular cohesive forces resulting in structural rearrangement.

1.8 Flory – Rehner Theory

The contact of rubbery polymers with organic solvents can be well explained by absorption and diffusion phenomena. The molecular mass between crosslinks can be calculated by using the following, Flory-Rehner equation.

$$M_c = \frac{-\rho_r V_s V_r^{1/3}}{\ln(1-V_r)+V_r+\chi V_r^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 1.16$$

Where Mc is the molecular mass of the polymer between crosslinks. Vs, the molar volume of the solvent and χ, the interaction parameter given by the Hilde brand equation.

$$\chi = \beta + V_s(\delta_s-\delta_p)^2 RT \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 1.17$$

Where ‘β’ is the lattice constant, R, the universal gas constant, T, the absolute temperature and δ_s and δ_p are the solubility parameter of the solvent and polymer respectively.

1.9 Kraus equation

Kraus has studied the degree of cure in particulate filler-reinforced vulcanizates by swelling method. The degree of restriction exerted by reinforcing filler is given by the equation.

$$\frac{V_{r_0}}{V_r} = 1 - m\left[\frac{f}{(1-f)}\right] \quad \text{...}$$

1.18

Where V_{r_0} is the volume fraction of rubber in the unfilled vulcanizate, V_r the volume fraction of rubber in the filled vulcanisate after swelling as calculated from the equilibrium swelling data equation, f, the volume fraction of filler and ‘m’ the polymer-fibre interaction parameter.

1.10 Lorenz and Parks Equation

The restriction to swelling exerted by filler reinforced composites has been investigated by Lorenz and parks by the following relation.

$$\frac{Q_f}{Q_g} = ae^{-z} + b \text{...} \quad 1.19$$

Where Q is defined as the grams of solvent per gram of composite, the subscripts ‘f’ and ‘g’ refer to filled and gum vulcanizater respectively, ‘z’ the weight of the filler per unit weight of rubber ‘a’ and ‘b’ are constants. The ratio Q_f/Q_g reflects the restriction to such of the rubber matrix in the neighbourhood of filler particles. The higher Q_f/Q_g values, the lower will be the extent of interaction between the fibres and matrix

1.11 Report of earlier study

Tailoring of heterogeneous polymer-polymer systems with balanced physical properties for specific applications is a frequent task in material engineering. Physical properties of such systems being structure dependent,the properties can be modified by changing the structure of the system.ie., by changing their crystallinity, nature and degree of crosslinking ,incorporation of compatibilizers and fillers etc. A number of systematic studies have been reported in the literature on this regard [80-92].

There exist interesting reports on the molecular transport through different polymer membranes[93-119].Sony C .George et al. [120] studied the molecular transport of aromatic hydrocarbons through crosslinked SBR in the temperature range (25–65°C). SBR has been vulcanized by four different vulcanizing techniques viz., conventional, efficient, dicumyl peroxide and a mixture consisting of sulfur and peroxide. SBR vulcanized with EV system showed highest solvent uptake tendency and that vulcanized with peroxide showed the lowest. The influence of penetrant size on sorption behaviour of SBR has been examined. The thermodynamic constants such as standard entropy, standard enthalpy and first-order kinetic rate constant have been evaluated. A correlation between theoretical and experimental sorption results was evaluated. The polymer—solvent interaction parameter (χ) was also computed from the diffusion data.

Morphology can affect the properties of polymeric materials.Viveca Lonnberg & Paul Starck [121]compared the weather resistance of different thermoplastic elastomer blends by measuring the change in hardness,tensile modulus,tensile strength and elongation at break.hardness and modulus of the materials changed to a very small extent during the exposure period .The elongation of the partly cross linked PP/EPDM decreased drastically due to the migration of the plasticizing oil. Also tensile strength of all TPEs decreased. The mechanical properties of two-phase composites made up of a continuous polymer phase and particulate filler phase have been studied in great detail. The mechanical properties of particulate-filled composites are affected by a number of parameters such as filler orientation, filler/matrix adhesion and filler shape [122]. The sorption and diffusion characteristics of 70/30 ethylene propylene diene monomer rubber (EPDM)/acrylonitrile butadiene rubber (NBR) blends loaded with black fillers such as ISAF (intermediate super-abrasion furnace), HAF (high abrasion furnace) and SRF (semi-reinforcing furnace) have been investigated by K. C. Manoj et al.[123]. The penetrants used were benzene, toluene and xylene. Filled samples have been found to show a reduced solvent uptake compared to the unfilled sample for the given blend ratio. The observations have been correlated with the morphology of the systems. Blends loaded with ISAF exhibited the lowest liquid uptake among black filled systems which has been attributed to the better filler reinforcement and enhanced crosslink density of the matrix. The extent of particulate filler reinforcement has been studied by using Kraus theory. The unfilled and filled systems have been found to exhibit non-Fickian transport behaviour. The effect of fillers on the cure and mechanical properties of the blends have also been investigated. Among the black filler loaded systems used, the ISAF mix showed the highest maximum torque value. The improvement in the cure and mechanical properties has been observed to be the highest for ISAF filled samples followed by HAF and SRF filled systems, which is in compliance with the observation from the sorption studies. Anusree et al. [124] studied the permeation of aromatic solvent vapours through natural rubber/EVA blends with reference to the effect of blend ratio.The regular reduction in the rate of solvent vapour permeation with increase in EVA content in the blend has been attributed to the semicrystalline nature of EVA. A. F. Younan et al. [125] from the electrical and mechanical investigations, found that the use of silica and calcium carbonate in EPDM/CR blends could improve these properties. Electrical Conductivity Behaviour of Chemical Functionalized MWCNTs Epoxy Nanocomposites. Nanocomposites were investigated as function of MWCNTs concentration [126]. MWCNTs and surfactant additive MWCNTs nanocomposites gave higher electrical Conductivity than functionalized MWCNTs nanocomposites. Masoud Frounchi et al.[127] studied the barrier properties of PP/EPDM blend nano composites and found that the bariier property was enhanced by the organoclay. Gunasekaran et al. [128]tried a noval approach ,using infrared spectral measurements, for the evaluation of the various physic-mechanical properties such as tensile strength, elongation and hardness of NR/NBR and NR/EPDM blends. The results obtained were in good agreement with the data resulted from other standard methods. Sowmya Ganapathi-Desai et al. [129] tested composite membranes for recovering volatile organic compounds (VOCs) from dilute aqueous solutions and found that this method can offer potentially cleaner and cost-effective means of recovering VOCs from contaminated streams. Unnikrishnan et al. [130] studied the effect of different fillers on the swelling nature of crosslinked NR using carbon black and silica fillers. 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**.** Swelling experiments are important because they give valuable information about the service performance of composites in liquid environment and also to study the characteristics of rubber / fibre interface. Chao Ying WAN et al.[131] studied the mechanical properties of Carboxylated Poly (vinyl chloride) and Polyurethane membranes and found that the properties vary with concentration of the filler.*D.* Felhõs1 et al. [132] studied the visco elastic properties of EPDM .to investigate the rolling friction whereby a steel ball is rolling on a rubber plate and the results describes a general method on how to consider the viscoelastic behavior of rubber materials. Jian-hua Cao et al. [133] studied the separation of propane from propane/nitrogen mixtures using PDMS composite membranes by vapour permeation. The electrical properties of polymeric composites were studied by several workers [134-136]. A. M. Y. El-Lawindy [137] found that electrical conductivity of polymers can be provided by incorporation of conductive materials such as carbon black. The introduction of carbon black allows them to envisage the elaboration of polymers possessing the conductive properties of carbon black and the varied properties of polymers. The effect of blend ratio on properties of chloroprene rubber/natural rubber (CR/NR) blends was investigated by *P.* Sae-oui1 et al.[138].The mechanical properties and the resistance to degradation of the silica-filled CR/NR blends were found to be governed by the blend morphology. Samantha Oliveira Vilea et al. [139] studied the synthesis and properties of conductive polymer composites obtained by mixing polyaniline with clay. The results suggest polyaniline chain linearization in a clay medium. M.S.Khan et al. [140] investigated the mechanical and tribological properties of PTFE filled EPDM composite. They found that EPDM reinforced with electron modified PTFE powder demonstrated improvement in the above mentioned properties. Yasin Khan [141] investigated the hydrophobic characteristics of EPDM composite insulators and found that EPDM insulator loses its hydrophobic properties proportional to the intensity of UV radiations The pysico-mechanical properties of EPDM/HDPE blends with different cure system were studied by Zenovia Moldovan and others [142] and could obtain the best thermoplastic vulcanizates. Sujith et al. [143] used Acrylonitrile butadiene rubber (NBR) as acompatibilizer for natural rubber–poly (ethylene-co-vinyl acetate) (NR–EVA) blends, vulcanized by sulfur. A significant reduction in solvent uptake was observed for compatibilized samples. This has been explained in terms of the increased interfacial adhesion between NR and EVA components of the blends in the presence of the compatibilizer. Nina Vranjes et al. [144] investigated the influence of the EPDM on blend properties of Blends of isotactic polypropylene (iPP) and high density polyethylene(HDPE) with and without ethylene-propylene-diene (EPDM) terpolymer as compatibilizer. Elongation at break and impact strength was significantly increased with EPDM addition. The sorption of n-alkanes, viz. hexane, heptane and octane by cross-linked natural rubber/poly(ethylene-co-vinyl acetate)(NR/EVA) blends has been studied[145] at 28, 38, 48 and 58 -C, with special reference to the effects of EVA content, crosslinking systems, penetrant nature and temperature. The solvent transport was found to decrease with increase in EVA content in the blends. The effects of blend ratio on the transport characteristics have been correlated with the phase morphology of the blends, using scanning electron micrographs and optical micrographs. Among the three vulcanizing systems, viz. sulphur (S), dicumyl peroxide

(DCP) and a mixed system (S + DCP) employed for the matrix, the DCP cross-linked blends exhibited the lowest solvent uptake.

The dynamic mechanical behaviour of uncrosslinked and crosslinked styrene butadiene rubber/poly(ethylene-co-vinyl acetate) (SBR/EVA) blends was studied with reference to the effects of blend ratio, crosslinking systems, a compatibilizer viz. maleic-anhydride grafted poly[styrene-b-(ethylene-co-butylene)-b-styrene](SEBS-g-MA),frequency and temperature[146]. The two separate tan δ peaks, obtained during DMA, indicated the immiscibility of SBR/EVA system. The damping properties increased with SBRcontent for uncrosslinked and crosslinked blends. In the case of crosslinked systems, depending upon the type of crosslinking agent used, the glass transition temperature (Tg) of SBR phase has been found to be shifted to higher temperatures. The damping characteristics of the blends were observed to be affected by the variations in frequency. The addition of the compatibilizer improved the storage modulus and reduced the damping properties. These results have been correlated with the morphology of the blends, attested by scanning electron micrographs. The thermal behaviour of styrene butadiene rubber (SBR)/poly (ethylene-co-vinyl acetate) (EVA) blends was studied [147] by using thermogravimetry (TG) and differential scanning calorimetry (DSC). The effects of blend ratio, cross-linking systems and compatibilization on the thermal stability and phase transition of the blends were analyzed. It was found that the mass loss of the blends at any temperature was lower than that of the components, highlighting the advantage of blending SBR and EVA. The addition of compatibilizer was also found to improve the thermal stability. DSC studies indicated the thermodynamic immiscibility of SBR/EVA system even in the presence of the compatibilizer.

Varghese et al. [148] studied the effects of blend ratio,crosslinking systems and fillers on the morphology,curing behavior, mechanical properties and failure mode of acrylonitrile butadiene rubber (NBR) and EVA blends. They used three different crosslinking systems,namely,sulphur, dicumyl peroxide and a mixtureof the two and found that the mixed system exhibited better mechanical properties.The dynamic mechanical studies, impact resistance and scanning electron microscopic studies of ethylene propylene diene terpolymer-polyvinyl chloride and methyl methacrylate grafted EPDM rubber –PVC blends were undertaken by Singh.D et al. [149]EPDM showed less improvement while a six fold increase in impact strength was noticed with the grafted EPDM. The scanning electron micrographs of EPDM-PVC showed less interaction between the phases in comparison to MMA-g-EPDM-PVC blends. Bothros et al. [150] found that the mechanical properties, the weight swelling values and the dielectric constant values of EPDM-PVC blends showed linear behavior versus the blend ratios after the incorporation of the MMA-EA-AA terpolymer. Yulin Feng et al. [151] observed that the strength and modulus can be increased by the addition of filler into polypropylene composites. The dynamic mechanical properties of single polymer composites of poly(methyl methacrylate) (PMMA) reinforced with electrospun PMMA nanofibers of different diameters are reported [152].Dynamic mechanical analysis showed a pronounced improvement in the storage modulus of the composites compared to the matrix.

1.12 Objective of the present work

EPDM is an elastomer which is generally used in conjunction with other elastomers and modifiers. It is non polar, amorphous material with low physico-mechanical properties which limit its apllication in such areas. Blending or copolymerizing EPDM with other elastomers or modifiers substantially improves the performance of the final EPDM elastomer product. The flexibility, rigidity and softness characteristics are just a few examples of how the end product of EPDM can be changed when it is combined with other elastomers and modifiers. Since the overall performance of the EPDM increases dramatically, it has become extensively used in making automotive tire sidewalls, coverstrips, wires, cables, hoses, belting gaskets, appliances, footwear, roofing barriers and sporting goods. When the new EPDM elastmers are created, their mechanical properties become substantially different from the original EPDM material. Hence Dynamic Mechanical Analysis (DMA) of EPDM provides an accurate means of characterizing the effects of blending or copolymerizing with other materials.

There are a few studies on EPDM/PVC blends [153] but no systematic study has yet been carried out for the preparation and transport characterization of EPDM/PVC composites, highlighting the combined effects of component ratio, mode and type of crosslinking etc on their physical and mechanical properties. Therefore a systematic investigation has been carried out on EPDM/PVC composites with the following major objectives.

- Development of EPDM/PVC composites with different crosslinking systems
- Preparation of dynamically vulcanized EPDM/PVC composites.
- Study of mechanical , electrical properties of EPDM/PVC composites
- Study of vapour permeation and molecular transport properties of EPDM/PVC composites with special reference to the effects of:
  Filler loading

Crosslinking systems
Crosslinking techniques

- To examine the ageing characteristics of the composites under varying conditions
- Support the above findings by the evaluation of :
  Cure characteristics (by Rheometry)
  Morphology [by Scanning Electron Microscopy (SEM)]
  Crystallinity (by X-ray Diffractomertry).

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Chapter 2

Materials and Experimental Methods

Summary

The specification of the materials used and the experimental methods followed for the present investigation are given in this chapter. The characteristics of the materials, formulations of the composites and sample preparation techniques have been discussed. The methodologies for the examination of transport properties, mechanical properties, ageing characteristics, crystallinity and morphological features have been given.

2.1 Materials

2.1.1 Ethylene Propylene Diene Monomer Rubber (EPDM)

Ethylene Propylene Diene Monomer Rubber (EPDM), a terpolymer of ethylene,propylene and a non-conjugated diene, is one of the most versatile, fastest growing rubbers having both specialty and general –purpose applications[1].This choice is based on the common use as general-purpose rubber, in addition to their distinguished property [2].

Heat resistance up to 130 °C with sulphur acceleration systems and upto 160°C with peroxide cured compounds. Excellent resistance to heat, oxidation, ozone and weather ageing are expected to provide continued value in demanding automotive construction and mechanical goods applications [3,4]. EPDM is made from ethylene, propylene and a cross linking monomer. EPDM contains a difunctional comonomer, either ethylidene-norbornene (ENB) or dicyclopentadiene (DCPD). These comonomers are there to provide cross linking sites for vulcanization. Because these reactive sites are pendent (not part of the main backbone chain), there are no weak points on the main chain. This is unlike for example Natural rubber or SBR, where these necessary reactive sites are along the main chain. This means that the reactive entities in the atmosphere like ozone can easily attack and degrade these materials. This also explains why EPDM is on the order of 100 to 1000 times more resistant to ozone than Natural Rubber, even containing antiozonant stabilizers. The processing, vulcanization and physical properties of EPEs are largely controlled by the characteristics of ethylene content, diene content, diene content, molecular weight and molecular weight distribution. The chemical structure of EPDM terpolymer is shown in Figure 2.1.The diene shown is ethylidene-norbornene (ENB), which is the most widely used diene in EPDM terpolymers due to its ease of incorporation and higher reactivity towards sulphur vulcanization.

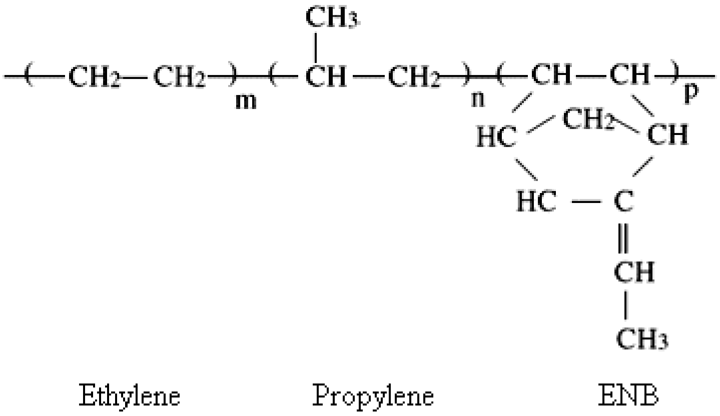


Figure 2.1 Structure of EPDM

Ethylene Propylene Diene Monomer Rubber (EPDM), used in the present investigation was Herlene-502 obtained from Herdilla Unimers Limited, Navi Mumbai,India, the characteristics of which have been given in Table 2.1. It is fast curing, light coloured,non-staining and capable of accepting large quantities of mineral black.

Table 2.1 Characteristics of EPDM

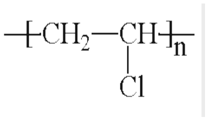
Product name	Herlene-502(EPDM)
Mooney viscosity,ML $_{1+4}$ at 125^{o}C	60.00
Ethylene/Propylene, weight ratio	62/38
Ethylene norbornene weight percentage	4
Molecular distribution	Broad
Specific gravity	0.86
Volatile matter(weight percentage)	0.7
Ash(weight percentage)	0.15
Colour Solubility parameter(MPa)$^{1/2}$	Light amber 8.6

2.1.2 Poly vinyl chloride (PVC)

Poly (vinyl chloride) is one of the most widely used polymers in many industrial applications [5]. PVC possesses a low level of crystallinity and derives its rigidity as a plastic from its high glass transition temperature. Commercial PVC is slightly (5% to 10 %) crystalline. It is a normal impact, high corrosion resistant polyvinyl chloride. Because of its exceptional corrosion resistance, it is ideally suited for applications where maximum chemical resistance is necessary. Their high strength-to-weight ratios, cost efficiency, ease of fabrication and economic balance make it the material of choice.

Table 2.2 Basic characteristics of PVC

Sl. No.	**Property**	**Value**
1	Density gm/cc	1.2-1.6
2	Tensile strength Ps	9000
3	Elongation %	2-2.5
4	Water absorption %	0.1-1
5	Solubility parameter CAL$^{1/2}$ cm$^{3/2}$	9.4
6	Glass transition temp ^{0}C	83



$-\!\!\left[CH_2-\underset{Cl}{CH}\right]\!\!_n-$

Figure.2.2 Structure of PVC

PVC used for the work was obtained from Sigma Aldrich. The basic characteristics of PVC are given in Table 2.2.

2.1.3 Rubber Chemicals

Rubber is seldom used alone. Almost always a number of additives are used. There are a wide variety of ingredients from which the rubber compounder can choose to modify the physical and chemical properties of an elastomer. The objectives in using a particular ingredient might be one or more of the following:

1. To improve the physical properties of the rubber
2. To improve the processing properties
3. To cross link the rubber compound
4. To control the rate of cure
5. To prolong the service life of the rubber
6. To extend the service life of rubber
7. To reduce the cost of rubber compounds.

Vulcanization is a chemical process performed on rubber to strengthen it by causing polymer molecules to interlink with other polymer molecules. Different chemicals used as vulcanizing agents for crosslinking the matrix were elemental sulphur (specific gravity 1.9) and dicumyl peroxide (DCP; 40 % active, specific gravity(1.55). Sulphur used in the study is rhombic sulphur .DCP does not require any accelerators and activators as they do not respond to accelerators. It has the property of self activation. Both EPDM and PVC can be vulcanized (cross linked) by peroxides effectively.

Other chemicals used such as zinc oxide, stearic acid and mercatobenzothiazyl disulphide (MBTS) were of commercial grade. MBTS acts as the accelerator .Accelerators are organic compounds which when added to the rubber mix increases the rate of vulcanization and thus increases the properties of vulcanization. Accelerators require activators for full effects. ZnO and Stearic acid are the most popular activator systems and are used in the present work .It is seen that ZnO react with stearic acid to form zinc stearate, which is soluble in the rubber and in this form facilitates the cross linking process.

2.1.4 Solvents

The solvents used in the study such as aromatic hydrocarbons (benzene, toluene and xylene) and aliphatic hydrocarbons (1-propanol and 2-propanol) were obtained from E. Merck (India) Ltd. They were of reagent grade and were distilled twice to ensure purity. The fuels petrol, Kerosene and diesel used were also of commercial grade. The solubility parameters values of elastomers and solvents are given in Table 2.3 and the physical properties of the solvents used are given in table 2.4

Table 2.3 Solubility parameter values of elastomers and solvents

Polymers	**ðCal$^{1/2}$ cm$^{-3/2}$**	**Solvents**	**ðCal$^{1/2}$ cm$^{-3/2}$**
PE	8	ACETONE	9.74
PP	7.9	BENZENE	9.22
SBR	8.1-8.5	CYCLOHEXANE	8.2
NR	8.1	CHLOROFORM	9.3
BR	8.5	CARBON TETRA CHLORIDE	8.6
PS	8.5-9.6	METHYLENE CHLORIDE	9.7
PVC	9.6	TOLUENE	8.9
PET	10.7	WATER	23.6
PAN	15.4	PROPANOL	12
EPDM	8.6	XYLENE	8.83

Table 2.4 Physical properties of the solvents

Solvent	Molecular Weight	Density (Kg/m^3)	Boiling point (^{o}C)
Benzene	78.11	874	79
Toluene	92.14	867	109
Xylene	106.17	860	137
1-propanol	60.10	803	97.2
2-propanol	60.10	783	82.3
Petrol	80-100	710-737	30-150
Kerosene	150-170	810-817	140-230
Diesel	170-330	820-950	240-350
Methylene chloride	84.9	1330	39.6
Chloroform	120	1483	61
Carbon tetra chloride	154	1586	77

2.2 Experimental Methods

2.2.1 Mixing and compounding

The mixing of EPDM with PVC in different ratios was done on a two roll (Fig. 2.3) mixing mill (150 x300 mm), with a nip gap of 1.3 mm and a friction ratio 1:1.4. The roll mill was provided with a metal tray under the roll collect dropping from the mill. The rolls rotate on parallel horizontal axis and the distance between the roller surfaces can be adjusted. First the process was mastication. This was done to break the long chain of bonds in rubber matrix. The rubber becomes a perfectly homogeneous mass, capable of being made into sheets after the addition of chemicals. The process involves passing rubber 3-4 times with a nip gap of 4mm, 2mm and 1mm successively. The EPDM was masticated for two minutes and PVC powder then added. After 4 minutes, other ingredients were added in the following order: zinc oxide, stearic acid, MBTS and sulphur. The processing time after the addition of each component added was about 2 minutes. Details of formulations and mixing schedules are given in Table 2.5. and table 2.6. respectively. The details of the sample designations are given in Tables 2.7 and 2.8 .The first letter of the sample codes being used for sample designation represents the vulcanizing agent viz., sulphur (S),DCP(C) and mixed (M) .For dynamically vulcanized sulphur system(3phr),the letter D is used. The first superscript on S represents the PVC loading. The second digit 1, 2, 3, 4 and 5 represent amounts of sulphur in the different composites; 100/0 EPDM/PVC, 100/2.5 EPDM/PVC, 100/5EPDM/PVC,100/7.5 EPDM/PVC and 100/10 EPDM/ PVC respectively. For example, S13 represents 3phr sulphur cured 100/2.5 EPDM/PVC composite and C1 represents DCP cured 100/0 EPDM/PVC composite, ie., pure EPDM.

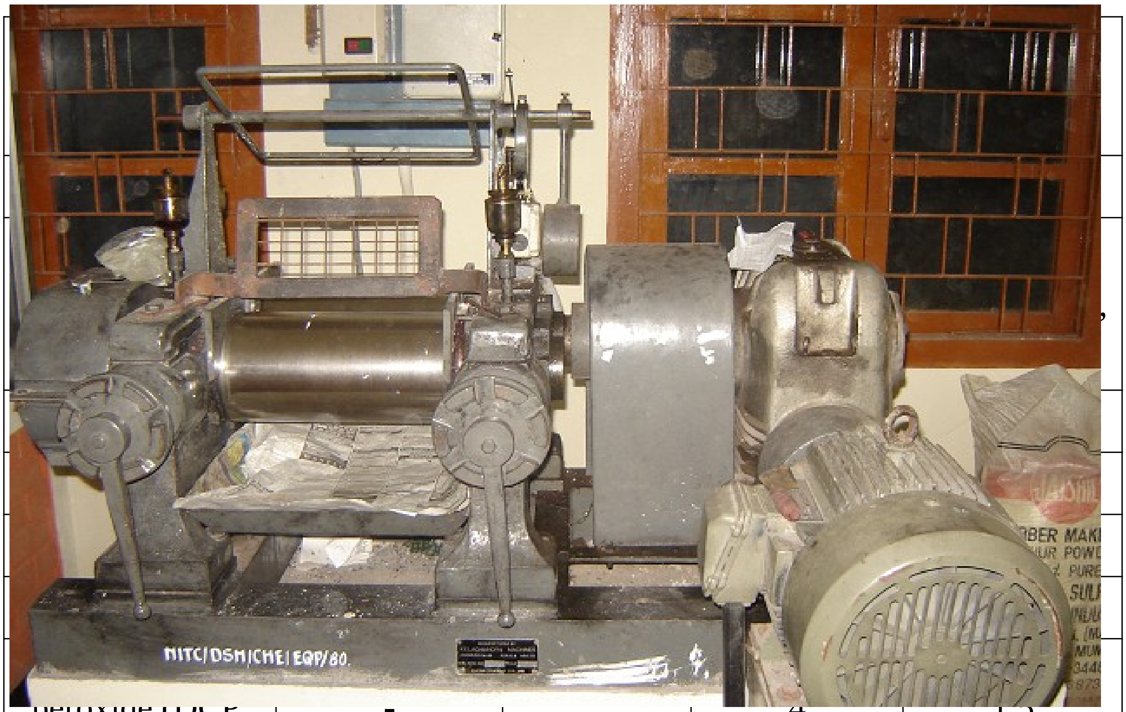


Figure 2.3 Two roll mill

Table 2.5 Formulation of mixes (phr[1])

peroxide (DCP, 90% active)	-		4	1.5

[1]Parts per hundred rubber

[2] Mercaptobenzothiazyl disulphide

Table. 2.6 Mixing schedule for the ingredients of EPDM /PVC composites

Mixing order	Ingredients	Mixing time (min)	Cumulative time (min)
1	EPDM	3	3
2	PVC	3	6
3	ZnO	2	8
4	Stearic Acid	2	10
5	MBTS	2	12
6	Sulpur	3	15

Table 2.7. Sample designations of sulphur cured composites

Sample designation	**EPDM**	**PVC**	**Sulphur**
S12	100	0	2
S22	100	2.5	2
S32	100	5	2
S42	100	7.5	2
S52	100	10	2
S 13	100	0	3
S 23	100	2.5	3
S 33	100	5	3
S 43	100	7.5	3
S 53	100	10	3
D 1	100	0	3
D 2	100	2.5	3
D 3	100	5	3
D 4	100	7.5	3
D 5	100	10	3

Table 2.8 Sample designations of DCP and mixed cured composites

Sample designation	**EPDM**	**PVC**	**DCP**	**Sulphur**
C1	100	0	4	
C2	100	2.5	4	
C3	100	5	4	
C4	100	7.5	4	
C5	100	10	4	
M1	100	0	1.5	1.5
M2	100	25	1.5	1.5
M3	100	5	1.5	1.5
M4	100	7.5	1.5	1.5
M5	100	10	1.5	1.5

2.2.2 Evaluation of cure characteristics

The cure characteristics of the compounds were determined according to ASTM d 2084 by using Zwick rheometer model ODR at 170 ^{0} C. The minimum torque, maximum torque and scorch time were determined from the rheographs.

2.2.3 Moulding of the samples

The compounded composites were compression moulded at 170 degree for optimum cure time using a hydraulic press (Fig. 2.4) having electrically heated platens, under a load of 5 MPa to get sheets(mould dimension :150X150X2 mm^3) and membranes(The average thickness of the membranes was 0.23-0.25 mm). Before preheating silicon oil is applied on the mould to prevent sticking. The pieces are cut from the compounded sheet and placed in the heated mould and mould is closed and pressure is applied for a definite period for completing the cure and the sample is taken out by releasing the pressure and opening the mould. The moulding was done at a pressure of 100Kg/cm^2 and 150^{0}C temperature. Within the mould cavity, because of heat, rubber behaves like a fluid and flows from a higher pressure location to a lower pressure location. Thus rubber fluid completely matches with the contour of the cavity. The overall flow process is partially or fully accompanied with the vulcanization reaction after the achievement of the desirable state of cure, the moulded article is taken out of the cavity. The excess polymer will flow out of the mould, which is called the flash.

The equipment used in the compression moulding may be described for general purpose as consisting of flat plates up on which the mould parts may be fastened. These plates are capable of being moved towards one another as pressure is applied. The movable plates are held on rams, which in term form the part of the hydraulic pressure. The press used for conventional compression moulding has two or more platens, which are heated either electrically or more commonly by saturated stream under pressure. The lower platen is moved on a hydraulic ram set at the bottom of the machine towards the fixed upper platen, as the press is closed. The mould is opened when pressure is released and either the weight of the platen separates the die cavity parts.The pressure exerted during moulding can be calculated from cross sectional area of the moulding material up on which the pressure is exerted.The moulds were cooled and the cured sheets were conditioned before testing (one day maturation at room temperature) and from the moulded sheets, appropriate samples were cut to make the test specimen.

Figure 2.4 Hydraulic press

2.2.4 Examination of transport characteristics

For diffusion experiments, circular samples of diameter 19.6mm and 2mm thickness were punched out from the vulcanized sheets and were dried in vacuum desiccators over anhydrous $CaCl_2$ at room temperature for about 24 hours. The original mass and thickness of the samples were measured before sorption experiments. They were then immersed in about 20 ml solvents taken in closed diffusion bottles, kept at constant temperature in an air oven. The samples were removed from the bottles at periodic intervals, dried for about 5 minutes between filter papers to remove the excess solvent on their surfaces and weighed immediately using an electronic balance (Shimadzu, Libror AEU-210,Japan) that measured reproducibly within ± 0.0001 g. They were then placed back into the test bottles. The process was continued until equilibrium swelling was achieved (no further increase in solvent uptake was detected). Since the weighing was done within 40 seconds, the error associated with the evaporation of solvents is negligible . Similar procedure was adopted by other researchers [6]. The experiments were triplicates in most cases and the deviation was within ±0.08 to 0.1 mole percentage. Thickness and diameter of the specimen after equilibrium swelling were also measured. The up take of liquid by the polymer during swelling is expressed as moles of liquid sorbed by 100g of the polymer. The mole percentage uptake Q_1 for the composite sample is determined as [7].

2.2.4.1 Calculation of Q_t (mol %)

$$Q_t = \frac{\text{Massof solventsorbed/ Molarmassof solvent}}{\text{Massof polymersample}} \times 100 \text{ .... } 2.1$$

The sorption data is evaluated by plotting the mole percentage uptake (Q_t) of the solvent versus square root of the time for different solvents. The Q_t values obtained thereby have been plotted as a function of square root of time, to construct the sorption curves.

2.2.4.2 Swelling co-efficient

Equilibrium swelling measurements of vulcanizates is a measure of swelling resistance of rubber composites. In order to asscess the extent of swelling behaviour of the composites, gum and fibre filled vulcanizates are swollen in a suitable solvent at room temperature and the swelling parameters are evaluated by the following equation.

$$\text{Swelling coefficient } (\alpha) = \left[\frac{W_2 - W_1}{\rho_1 S}\right] \text{ .... } \quad 2.2$$

Where W_1, the initial weight of the sample, W_2, the final swollen weight of the sample and ρ_s, the density of the solvent used.

2.2.4.3 Vapour permeability

The vapour permeability was determined by the measurement of the weight loss of small vials filled with solvents and tightly closed by a membrane of 0.23-0.25 mm thick.The weight loss was proportional to the time, area of membrane and pressure inside and outside of the vials (considered zero outside) and inversly proportional to the thickness of the membrane[8].The experiments were triplicates in most cases and the deviation was within ±0.001 to 0.003 mole percentage.The results of the vapor permeation results were expressed by plotting the amount of vapor permeated, Mt, verses time, t.Experiments were conducted at different temperatures by immersion of the permeation apparatus int water contained in a thermostated bath with controlled temperature. The permeability,P, can be used as a quantitative tool to predict the barrier performance of the material.Permeability describe how easily a fluid is able to move through the matrix and is given by[9],

$$\mathrm{P} = \frac{QL}{\Delta PAt} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..2.3$$

where ‘L’ is the thickness of the membrane and ‘Q’ is the molar quantity of solvent orberd through the material of area ‘A’ during a time ,t, at a steady state condition. ‘ΔP ‘ is the difference in partial pressure of the solvent across the membrane.

2.2.5 Investigation of mechanical Properties

The test specimens were punched out from the moulded sheets using a die.The thickness of the dumbbell specimens was measured using a micrometer having accuracy of 0.01mm.Tensile strength tests of composite samples were conducted on computerized Universal Testing Machine (Tinius Olsen H10KS USA).Specimens of dimension 100mmx10mmx5mm were used for analysis. Tensile test was conducted in accordance with ASTM D-412 test method using the specimens at a cross head speed of 500 mm/minThe sample of 10 cm length was clamped into the two jaws of the machine. Each end of the jaws covered 2 cm of the sample. Tensile test was studied over the rest of 6 cm gauze length. Reading of the tensile strength instrument for Newton force and extension was initially set at zero. The test was conducted at the constant strain rate of the order of 0mm/mm.Tensile stress was applied till the failure of the sample and load-extension curve was obtained. Each sample was tested for seven times and standard deviation, coefficient of variance and standard error was calculated. The tensile strength and elongation at break were calculated using the equation,

$$\text{Tensile strength} = \frac{\text{Load failure}}{\text{Cross section}} \dots\dots\dots\dots\dots\dots\dots .2.4$$

$$Elongation\ at\ break = \frac{Displacement\ at\ failure}{Effective\ gauge\ length} X100 \dots\dots..2.5$$

The tensile strength of a material quantifies how much stress the material will endure before suffering permanent deformation. This is very important in applications that rely upon a polymer's physical strength or durability. For example, a rubber band with a higher tensile strength will hold a greater weight before snapping. In general, tensile strength increases with polymer chain length and crosslinking of polymer chains.

The rate at which a sample is pulled apart in the test can range from 0.2 to 20 inches per minute and will influence the results. The analogous test to measure tensile properties in the ISO system is ISO 527. The values reported in the ASTM D638 and ISO 527 tests in general do not vary significantly and either test will provide good results early in the material selection process. Separate tensile test methods are commonly applied to polymer films (ASTM D882) and elastomers (ASTM D412).

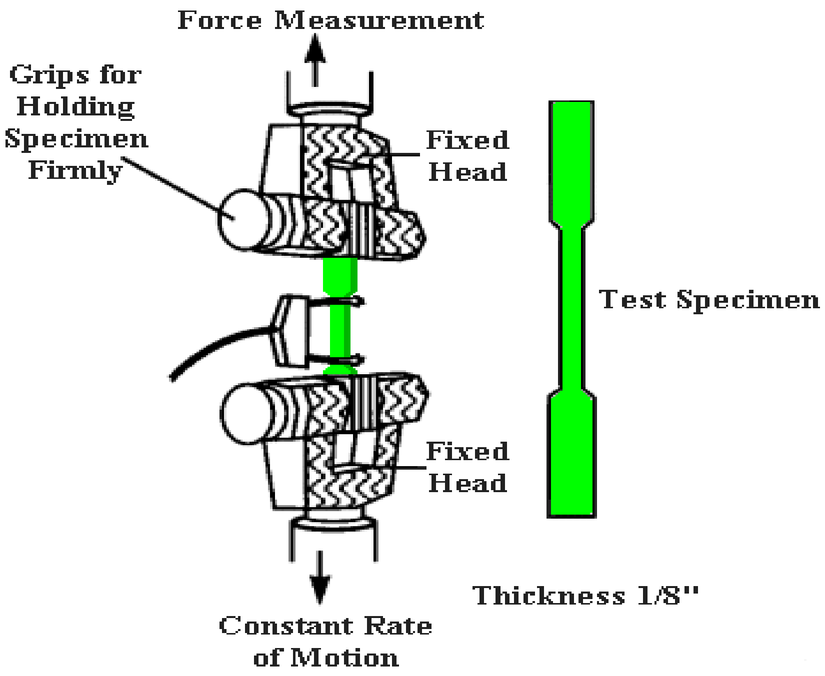


Figure 2.5 Tensile measurement

The tear strength was examined as per ASTMD-624 using 90^{o} angle test pieces. The experimental condition of temperature and cross head speed for the tear measurements were same as in the case of tensile testing. The tear strength was calculated using the equation,

$$Tensile\ strength, N/mm = \frac{Load\ failure(N)}{Thickness(mm)} \ldots\ldots..2.6$$

Tear strength data were averaged over at least five specimens.

2.2.6 Morphological studies

The samples for Field Emission Scanning Electron Microscopy (FESEM) were prepared by cryogenically fracturing them in liquid nitrogen.They were sputter coated with gold and morphology examination were performed on a scanning electron microscope (JEOL-JS IN-T330-A-SEM; ISS Group, Whittington, Manchester, U.K).

2.2.7 X-ray Diffraction Studies

X-ray diffraction patterns of the samples were recorded with an X-ray diffractometer using Ni-filtered CuK∞ radiation from Philips X-ray generator. The angular range was 5 to 40°.The samples of the same thickness and area were exposed. The operating voltage and the current of the tube were kept at 55KV and 190 mA respectively throughout the course of investigation. From the X-ray diffraction patterns, the change in crystallinity of the composite samples was determined [9].

2.2.8 Ageing Property

(a) Accelerated ageing and weather ageing

Accelerated ageing of the compression moulded specimens was carried out in an air-circulated ageing oven at 100°C for three days. The ageing characteristics of the samples were studied by measuring the changes in different mechanical properties such as tensile strength, modulus and elongation at break of the aged samples. The samples were exposed to natural weathering (all environmental effects such as rain, sunlight, wind etc). The natural exposure was conducted for a period of 4 months from August 2011 to November 2011. The specimens were attached to a rack with a rack holder and were placed on the roof of our research building. Samples were collected to study of the effect of weathering. Scanning electron microscopy (SEM) on the surface of specimens before and after the exposure were carried out to study effect of natural weathering on structure and morphology by using Jeol JSM-6360LV Scanning Electron Microscope. The mechanical properties were also investigated. The samples were immersed in organic solvents like toluene, carbon tetra chloride and diesel for 24 hours ,dried in an air oven for 24 hours and the mechanical properties determined.

(b) Physico-chemical properties of composites

The behavior against weathering conditions was studied by the swelling behavior in different solvents and chemical resistance behavior against acids and bases. Swelling behavior of the composite samples was evaluated by studying the swelling in different solvents like water, saline water and organic liquids like toluene, carbon tetra chloride and diesel. For the swelling test, the specimens were dried in an oven for a specified time at a particular temperature and then cooled in a desicator. Known weight (W_1)of the initial samples were immersed in 100 ml of different solvents and 10 %sodium chloride solution at room temperature for 7 days. The samples were filtered and the excess solvent was removed with the help of filter paper, patted dry with a lint free cloth and then final weight (W_f) was noted. The percent swelling was calculated from the increase in initial weight in the following manner.

$$\text{Percent swelling } (P_s) = \left[\frac{W_f - W_i}{W_i}\right] \text{x } 100 \ldots\ldots\ldots\ldots\ldots\ldots \quad 2.10$$

For the chemical resistance test, the dried specimens were immersed in 100 ml of 1 N NaOH and 1N HCl for different intervals of time (22-144 hours).After this, the samples were filtered out, dried and weighed. The percent chemical resistance (P_{cr}) was calculated in terms of weight loss in the following manner:

$$\text{Percent chemical resistance } (P_{cr}) = \left[\frac{Wi - W_{aci}}{W_i}\right] \text{x } 100 \ldots\ldots\ldots \quad 2.11$$

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Chapter 3

Mechanical Properties and Morphology of EPDM/PVC Systems

Summary

The effects of composite ratio and vulcanizing systems on the mechanical properties, such as stress–strain behaviour, Young’s modulus, tensile strength and elongation at break and cure characteristics of EPDM/PVC systems were studied.DCP vulcanized system possess higher torque than sulphur crosslinked ones.Composite with 7.5 phr PVC Samples prepared by using sulphur as the vulcanizing agent exhibited comparatively better mechanical properties. The amount of crosslinking agent also affects the values of mechanical properties. Dynamically vulcanized composites exhibited better properties than static samples. The morphology and crystalline properties have also been studied for complementing the observations related to the sorption characteristics to be discussed in the preceding chapters.

Part of contents of this chapter have been

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3.1 Introduction

Raw rubber, either polar or non polar, has poor physico-mechanical properties. To improve these properties, some ingredients such as accelerators, activators, antioxidants, softeners, and white and black fillers were added to the rubber vulcanizates. In polymer systems, fillers not only reduce the cost of the material but also reinforce the rubber and improve the properties of the rubber compounds. Polymer blends and composites are being used extensively for the development of a wide spectrum of products. Unfortunately, the demands for many applications need a set of properties that most of single polymers cannot fulfill. Mixing of properly selected polymers has been a widely accepted technique to develop high performance matrices to meet the demands for new materials. Fillers often increase the performance of polymeric products. The degree of improvement depends on the choice of filler origin, particle size and shape, the fraction of filler and the surface treatment promoting interaction between the polymer matrix and filler. The addition of fillers to polymers is a fast and cheap method to modify the properties of the base materials. For this reason, particulate filled polymers have been, and continue to be, the subject of increasing interest in both industry and research. In this way, strength, stiffness, electrical and thermal conductivity, hardness and dimensional stability, among other properties can be tailored to the required values [1]. One of the largest areas of application for polymers, polymer blends and composites on this basis are electronic and electrical industries. In many industrial applications, rubber articles are used as electrical insulators since rubbers in general are one of the families that have better dielectric properties. The study of these properties would provide useful information about the behaviour of molecules when they are under the influence of an electric field.

Polymers contain a very low concentration of free charge carriers, and thus they are non-conductive and transparent to electromagnetic radiation. For that reason they are not capable for being used as enclosures for electronic equipment as they cannot shield it from outside radiation or prevent the escape of radiation from the component. They also cannot provide protection against electrostatic discharge in handling sensitive electronic devices. These drawbacks have led to the growth in the research for electrically conductive polymers. Conductive polymers can be either inherently conductive (such as polyaniline) or insulating polymers filled with conductive particles. A critical concentration of filler, beyond which the polymer composite becomes conductive, is referred to as the percolation threshold. At this point a conductive network is formed through the matrix. This permits the movement of charge carriers in the fillers through the polymeric matrix, and so the composite achieves a certain degree of electrical conductivity. Conductive polymers have many advantages over metallic conductors. They can be easily shaped with low cost technologies; they have light weight; they provide corrosion resistance and they can offer a wide range of electrical conductivities. Numerous fillers can be compounded into the insulating matrix in order to achieve different conductivity range [2].

A number studies have been reported on the mechanical , electrical , thermal and morphological properties of polymeric systems[3-16].The electrical and thermal conductivity of systems based on epoxy resin (ER) and poly(vinyl chloride) (PVC) filled with metal powders have been studied[17] . Copper and nickel powders having different particle shapes were used as fillers. It was found that the shape and the spatial distribution of dispersed filler particles are the important factors controlling the electrical and thermal properties of metal-filled polymer systems. As the temperature is raised above ambient, mechanical properties (eg. tensile and tear strength) decreases, the rate of decrease being dependent on the particular elastomer used and the compound formulation. Long term exposure to elevated temperatures, or aging, results in a permanent change in all the properties of a rubber compound. Mechanical properties are generally improved as the hardness increases. Tensile strength measurement serves as an overall performance indicator. Kazuya Okubo et al.,[18] studied the development of composites for ecological purposes (Eco-composites) using bamboo fibers and their basic mechanical properties. The tensile strength and modulus of PP based composites using steam-exploded fibers increased about 15 and 30%, respectively, due to well impregnation and the reduction of the number of voids, compared to the composite using fibers that are mechanically extracted. Bamboo fiber bundles have a potential ability to work as the reinforcement of polymer matrix.

Thermal analysis of polymers is an important characterization tool as it plays a major role in the use of polymeric materials in many consumer oriented applications [19]. Fabrication of a variety of articles and their end uses need a detailed understanding of the thermal degradation of polymers. Further, a change in heat flow and stability of polymers will give some idea on the extent of chemical interaction occurring between the components, their bond strength, activation energy, melting temperature and degradation kinetics. Stipanelov et al. [20] investigated the thermo-oxidative degradation of PVC/CPE blends of various compositions by means of differential scanning calorimetry (DSC) and thermogravimetry (TG). By using DSC, it was found that all the investigated PVC/CPE blends were immiscible. The main reaction of PVC and CPE degradation at moderate temperatures was dehydrochlorination. In spite of the chemical similarity of the investigated polymers, thermo-oxidative stability and degradation mechanism were different. It was also found that CPE had a stabilizing effect on the thermooxidative degradation of PVC. Maria-Daniela Stelescu [21] investigated the mechanical properties of EPDM/PVC blends with special refence to the crosslink agents and found that the properties depend upon the vulcanizing system used. Bussaya Rattanasupa et al. [22] investigated the the influence of vulcanization system on the mechanical properties of $CaCO_3$ filled vulcanizates and discovered that the mechanical properties increased with sulphur concentration.

Several authors have used the rheographs to analyse the processing characteristics of polymer systems [23,24]. Oluranti Sadiku-Agboola [25] reviewed the importance of the rheological properties of polymer mixtures in the development of the phase structure and the importance of considering the stress and/or strain history of a material sample in a rheological investigation is discussed. Finally, the outlook on the past, present and future developments in the field of polymer rheology are given. The review concludes with a brief discussion on the opportunities and challenges in the field of polymer blends and blend rheology. The effect of filler content and size on curing characteristics and mechanical properties of oil palm wood flour (OPWF) reinforced epoxidized natural rubber (ENR) composites has been studied[26]. The cure (t_{90}) and scorch times of all filler size decrease with increasing OPWF content. At any filler content, larger OPWF particle size show shorter t_{90} and scorch time. The torque values increase with an increase in fibre content and OPWF with smallest particle size shows the highest torque. Increasing OPWF content in ENR compound resulted in reduction of tensile strength and elongation at break but increased tensile modulus, tear strength and hardness. Again, the composites filled with smaller OPWF size showed higher tensile strength, tensile modulus and tear strength.

The ethylene–propylene–diene monomer (EPDM) rubber compound is being increasingly demanded in many engineering areas due to its excellent electrical property and oxidation-resistance— e.g., automobile and electrical applications. Since the EPDM has a viscoelastic nature as in other polymeric materials, it has a strong dependence of dynamic mechanical behavior on temperature and frequency. The EPDM compound is often reinforced with the various particles (such as carbon blacks, silica, glass beads, etc.) because of its low stiffness and low tensile strength (i.e., 6.8 and 12.5 MPa, respectively). When the particles are incorporated into the matrix material to produce composites, the interaction between particles and matrix (i.e., interface behavior) is an important factor to influence the composite property in addition to the properties of the particle and the matrix material, respectively. Also, continuous break-up and rearrangement of particles take place due to the dynamic loads applied to the composite specimens. All these factors affect the viscosity change and dynamic elastic moduli of the composites.

In the present discussion, EPDM has been mixed with PVC and characterized with special emphasis on the effects of composition, nature of crosslinking system used, type of vulcanization and temperature on the cure, morphological, mechanical ,electrical and thermal characteristics of the system.

3.2 Results and discussion

3.2.1 Cure characteristics from Rheometric Data

Polymers are complicated materials to characterise rheologically because there are many factors that influence their flow properties. Examples of factors that influence the flow behaviour may include: Processing temperature; Rate of flow; Residence time etc. Furthermore the rheological properties of polymers are in between those of a liquid and a solid. This leads to time dependence of the flow properties and other important characteristics.

The curing behaviour of the composites was studied by a Monsanto rheometer (R-100) at a cure temperature of 170°C. The initial decrease in torque is due to the softening of the matrix. Torque then increases due to the formation of C-C crosslinks between the macromolecular chains.The leveling off is an indication of the completion of the curing process. The maximumtorque (*MH*) is a measure of crosslink density and the stiffness of the blend matrix. The increase in torque observed with time is due to the crosslinking of blends. The optimum cure time was calculated from the rheometric torque-time curve. Figure 3.1 shows the rheograph sulphur cured 100/7.5 EPDM/PVC composites cured at 160 and 170 ^{0}C. Many of the properties were found to be higher for composites vulcanized at 170°C The following observations based on Figure 3.1 are worth mentioning;

i. The cure rate has been found to be very slow at 160°C.

ii. At the temperature of 170°C, the cure rate is substantially high, so that the curing process gets completed within a reasonable time period.

iii. Plateau region without any tendency of reversion indicates good thermal stability of all composites at an elevated temperature

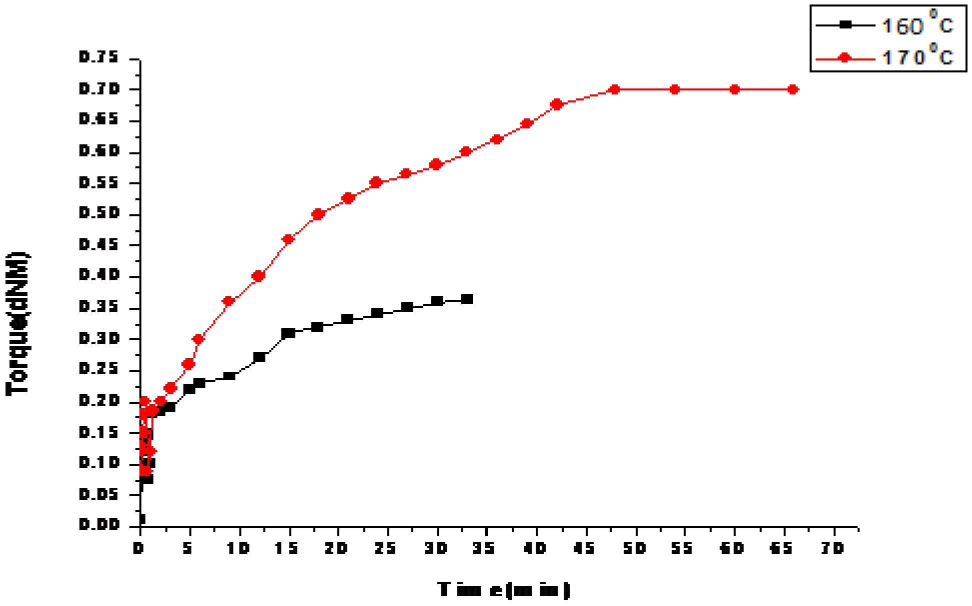


Figure 3.1 Rheograph sulphur cured 100/7.5 EPDM/PVC composites cured at 160 and 170 ^{0}C

Results show that cure time decreases as temperature of curing is increased from 160 to 170°C.For example the optimum cure time for sulphur cured 100/7.5 EPDM/PVC composites were found to be reduced from 28 minutes to 26 minutes. Processing and final properties are dependent on the composition. The torque at any time is dependent on the composition. This composition of rubber and plastic components determines the structure and its potential end use properties. Figure 3.2shows a comparison of the rheographs of the three different curing systems.

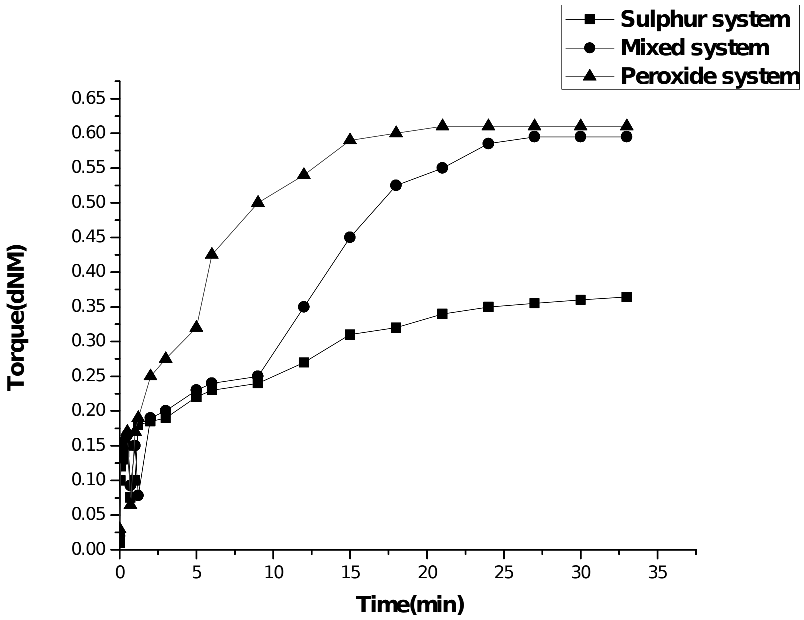


Figure 3.2 Rheograph of different crosslinked 100/5 EPDM/PVC composites

It can be seen that the maximum torque is greater for DCP cured samples, when compared to sulphur cured composites, the mixed system occupies an intermediate position. Table 3.1 shows the effect of formulation on the optimum cure time of peroxide cured composites. As expected, it can be seen that with increasing filler content, optimum cure time decreases.

Table 3.1 Cure characteristics of DCP cured EPDM/PVC composites as a function of PVC composition .

Sample	Sample code	Cure time,t_{90}(min) DCP cured
100/0 EPDM/PVC	C1	16
100/2.5EPDM/PVC	C2	13.6
100/5 EPDM/PVC	C3	12.8
100.7.5EPDM/PVC	C4	9.4
100/10 EPDM/PVC	C5	11.8

3.2.2 Mechanical Properties

3.2.2.1 Effect of PVC loading and crosslinking systems

The assessment of the performance of a polymer material can be made in terms of certain physico-mechanical properties like tensile strength, tear strength, elongation at break and modulus.The effects of different crosslinking system on the stress-strain behavior of the EPDM/PVC composites are given in Figure 3.3.The sulphur and mixed systems showed almost similar stress-strain behavior and the initial modulus values were closer to each other. However, for the peroxide-cured system, the initial modulus was very high. This was probably because of the rigid C-C network in them.

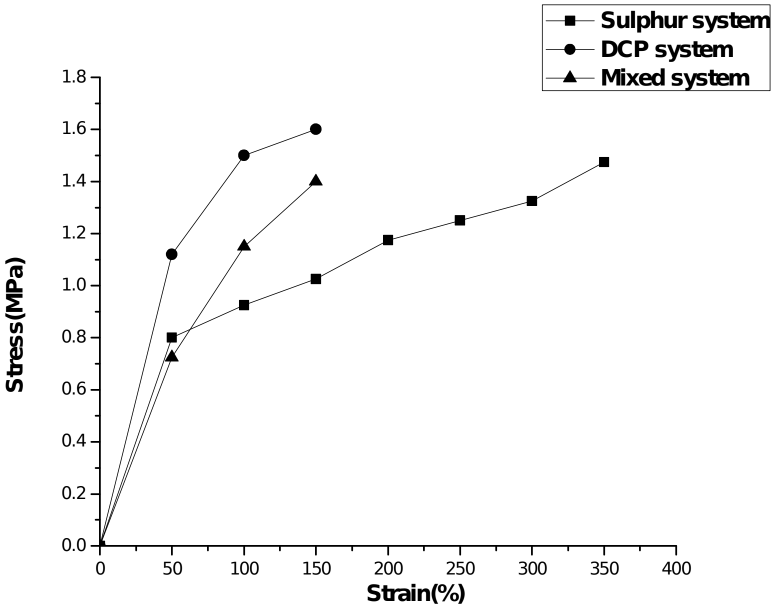


Figure 3.3 Effect of different curing systems on the Stress-Strain behavior of the 100/7.5 EPDM/PVC composites

Tensile strength is an important characteristics of polymeric materials because it indicates the limit of final stress for most applications. There is a gradual increase in the tensile strength with PVC loading as given in table 3.2. The initial drop at lower level of filler in sulphur system is a result of dilution effect in a strain crystallizing matrix such as EPDM. The tensile strength of sulphur system in many cases are greater than that of DCP system. This can be explained on the basis of the nature of the crosslink formed between macromolecular chains during vulcanization. In sulphur vulcanizing system, polysulphidic linkages are formed and these long S-S linkages are flexible whereas in the peroxide system, C-C linkage are formed, which are very rigid. In mixed system ,both the S_S and C-C linkages are formed and the network formed during different vulcanization technique are given in figure 3.4.The short and rigid C-C bond break easily ,under a stress, compared to flexible C-C and S-S linkages. The highly flexible C-S and S_S linkages are capable of with standing a higher stress. So the sulphur vulcanising system shows better mechanical properties. At 5-7.5 phr PVC loading, tensile strength is higher than the pure EPDM. Tear strength and modulus show the same trend. Better interaction and smaller particle size helps it better arrest or deviate the tear cracks, resulting in higher tear resistance. Normally, in the cases of conventional composites tensile strength increases with increasing filler loading until a maximum point is reached; whereby the filler particles are no longer adequately separated or wetted by rubber phase. Since agglomerates in composites can act as obstacles to chain movement and may cause failure under stress, the elongation at break shows a decrease with filler content.

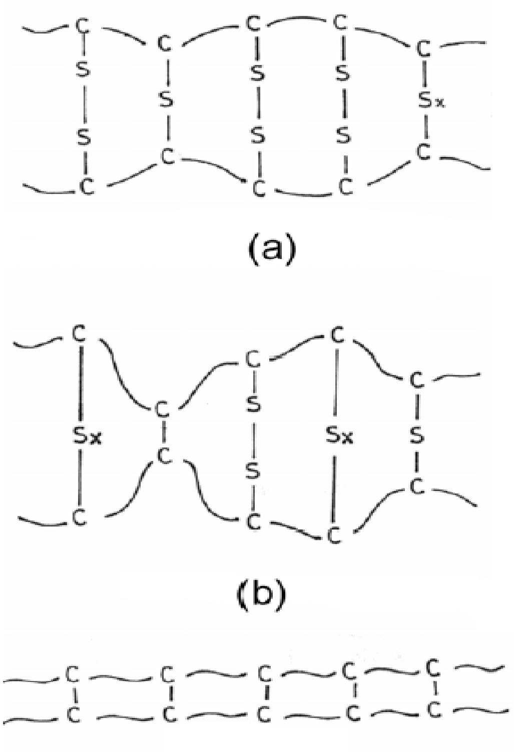


Figure 3.4 Cross linking with sulphur, DCP and mixed systems

Table 3.2 Mechanical properties of dynamically vulcanized EPDM/PVC composites

Sample	Tensile srenght(MPa)	Tear strenght (N/mm)
D1	1.82	1.49
D2	1.83	1.75
D3	1.94	2.26
D4	2.04	2.38
D5	1.79	1.86

Agglomerates can become stress concentrators in building up stresses in composites quicker than usual and cause earlier rupture compared to unfilled samples. Modulus is an indication of the relative stiffness of the material The 100 % modulus increases with increasing EPDM composition due to the low stiffness for EPDM. The increase in modulus with increasing filler loading is expected since the addition of filler increases the stiffness of the composites, which in turn decreases the elongation at break [27]. As elongation is reciprocal to the stiffness of a material [28], the results show that the filler imparts a greater stiffening effect than that of unfilled one.

For sulfur vulcanized composites, elongation at break decreases with increasing amount of filler loading as given in figure 3.5. Pure EPDM has got maximum value since it has greater chain mobility. As the incorporation of PVC particle into the rubber reduces elasticity of rubber chains and leads to more rigid rubber vulcanizates matrix. At higher loading, molecular mobility decreases owing to the formation of physical bonds between filler particles and polymer chain.100/7.5 EPDM/PVC composite shows maximum Tear strength as shown in figure 3.6.

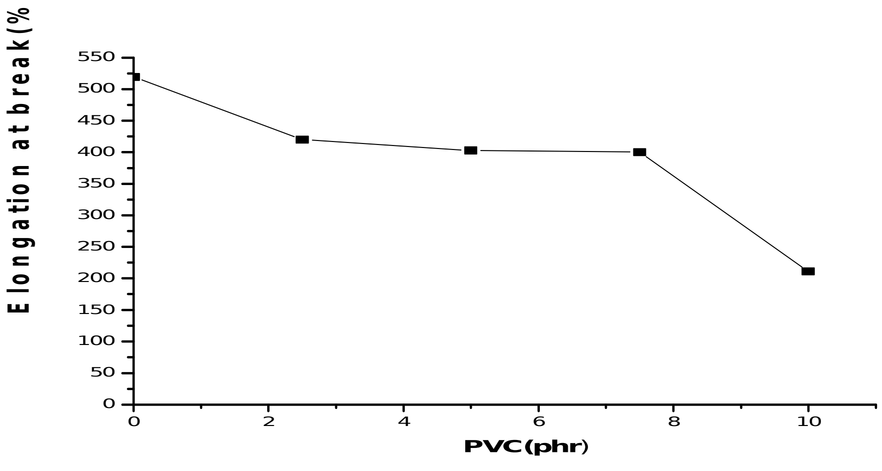


Figure 3.5 Effect PVC loading on the % Elongation at break of sulphur[3phr] cured EPDM/PVC composites

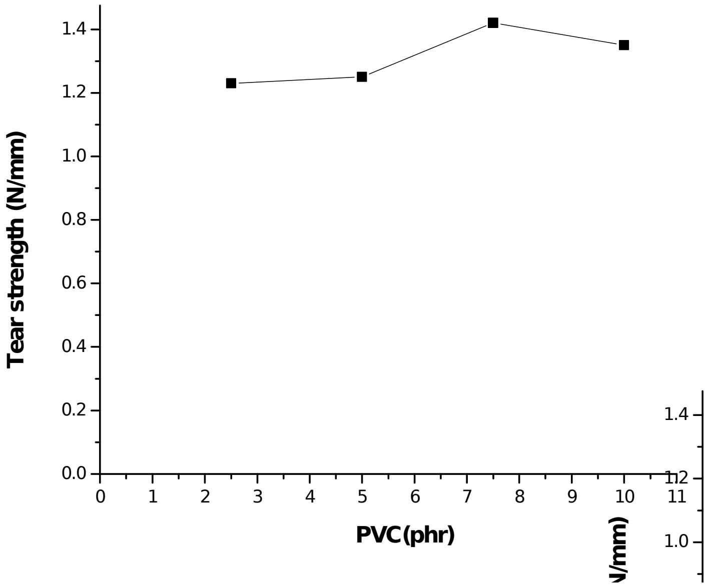


Figure 3.6 Effect PVC loading on the tear strength of sulphur[2phr] cured EPDM/PVC composites

The mechanical properties of the composites vulcanized by the two different crosslinking systems are given in the Table 3.3. Tensile strength measurement serves as an overall performance indicator. The tensile strength increases steadily with an increase in PVC concentration up to 7.5 phr PVC loading due to the increased thermoplastic hard component in it. Pure EPDM shows the lowest modulus and fails at fairly low stresses. As the PVC content in the blend increases, there is an increase in stress with increasing strain. Figure 3.7 shows the variation in the modulus of the composites crosslinked with the two different curing systems with PVC loading. Here, the composite materials exhibit optimum mechanical properties for 7.5 phr PVC loading. The composite with DCP system show more brittle type behavior than that with the sulphur system. This has been due to the presence of flexible polysulphidic linkage in sulphur system. Also, the DCP cured system showed lower elongation at break compared to sulphur cured system.This was attributed to the rigid C-C crosslinks between the macromolecular chains in the DCP system..

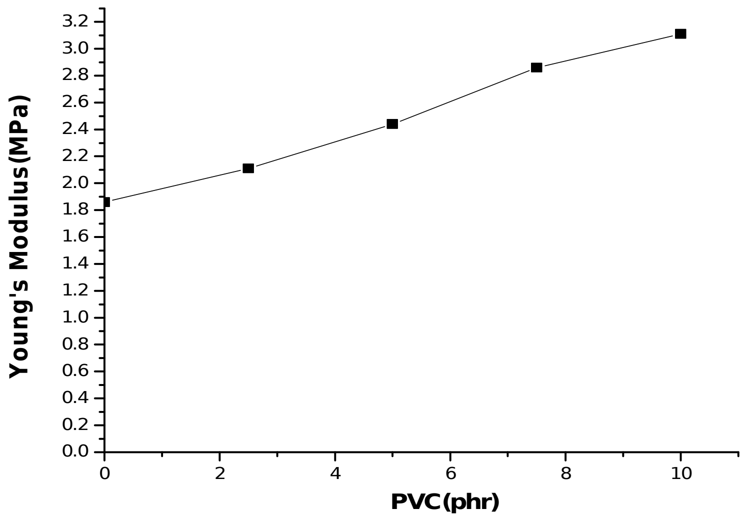


Figure 3.7 Effect of PVC loading on the modulus of the sulphur cured EPDM/PVC composites

Table 3.3 Effect of crosslinking system on mechanical properties of EPDM/PVC composites

Sample	**Young'smodulus (MPa)**		**Tensile strenght**		**Elongation at break(%)**			
EPDM/ PVC	Sulphur	Sulphur	Sulphur	DCP	Sulphur	DCP	Sulphur	DCP
100/2.5	2.11	1.45	1.45	1.14	1.45	1.14	420	117
100/5	2.44	1.4	1.4	1.15	1.4	1.15	402.77	88
100/7.5	2.86	1.48	1.48	1.4	1.48	1.4	400.17	194
100/10	3.11	1.20	1.20	1.04	1.20	1.04	211.21	54

3.2.2.2 Effect of dynamic vulcanization

Dynamic vulcanizing has enhanced the overall mechanical properties. The tensile strength of dynamically vulcanized composites are greater than the statically vulcanized samples for all the composites. For a less dispersed system, the tensile strength of the composites decreases due to the inability of the filler to support stresses transferred from matrix. The better tensile strength of dynamically vulcanized samples can be attributed to the better dispersion. Figure 3.8 shows the effect of type of vulcanization technique on tensile strength of sulphur cured EPDM/PVC composites. Table 3.4 shows the effect of vulcanization technique on mechanical properties of EPDM/PVC composites.

Table 3.4 Effect of type of vulcanization on mechanical properties of EPDM/ PVC composites

	Tensile Strenght (MPa)		**Modulus 100%(MPa)**	
EPDM/PVC	Static	Dynamic	Static	Dynamic
100/2.5	1.45	1.76	0.92	1.13
100/5	1.4	1.96	0.94	1.15
100/7.5	1.48	1.93	0.94	0.94
100/10	1.20	1.79	0.97	1.1

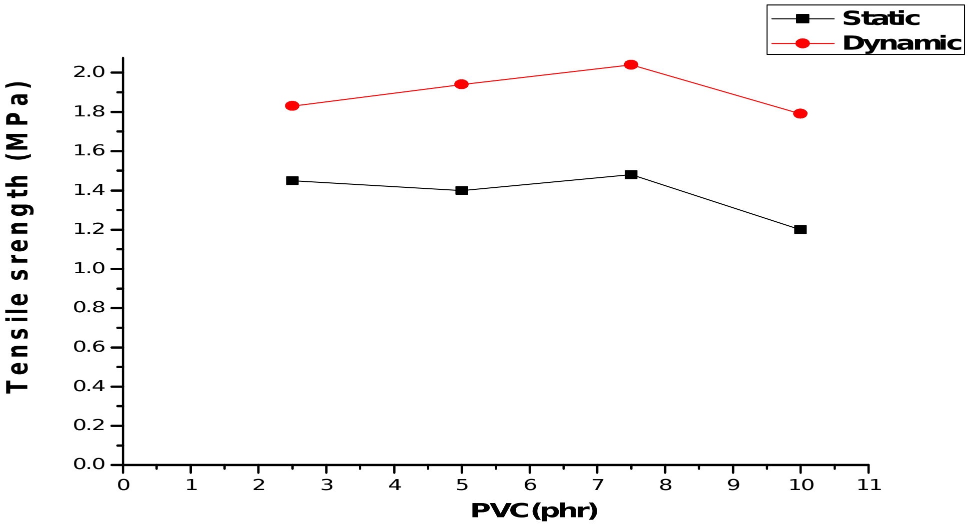


Figure 3.8 Effect of type of vulcanization technique on tensile strength of sulphur cured EPDM/PVC composites

3.2.2.3 Effect of concentration of sulphur

The torque increases with increase in sulphur concentration. This is due to crosslinking of rubber phase and thereby exerting greater resistance to the rotation of Brabender mixing rotors. Figure 3.9 shows the effect of sulphur concentration on torque values of different EPDM/PVC composites. The cure time decreases with increase in sulphur concentration . It can be seen that tensile strength increases with increase in sulphur concentration. Result for tear strength also exhibits a similar trend. The introduction of crosslinks into the elastomer phase is responsible for enhancement of these properties. The crosslink density increases with increase in sulphur concentration. This means that the number of the individual macromolecular chains increases, albeit they become shorter, stiffer and require more energy to cause failure. The incorporation of sulphur also increases the Young's modulus since the modulus is directly proportional to the number of crosslinks formed; the data obtained can be used to assess the crosslink density. It can be seen that the elongation at break value, E_b, increases with sulphur concentration for all the composites. E_b value increases with crosslink density as the crosslinked rubber particles can be strained to very large extensions before failure. The results are tabulated in table 3.5.

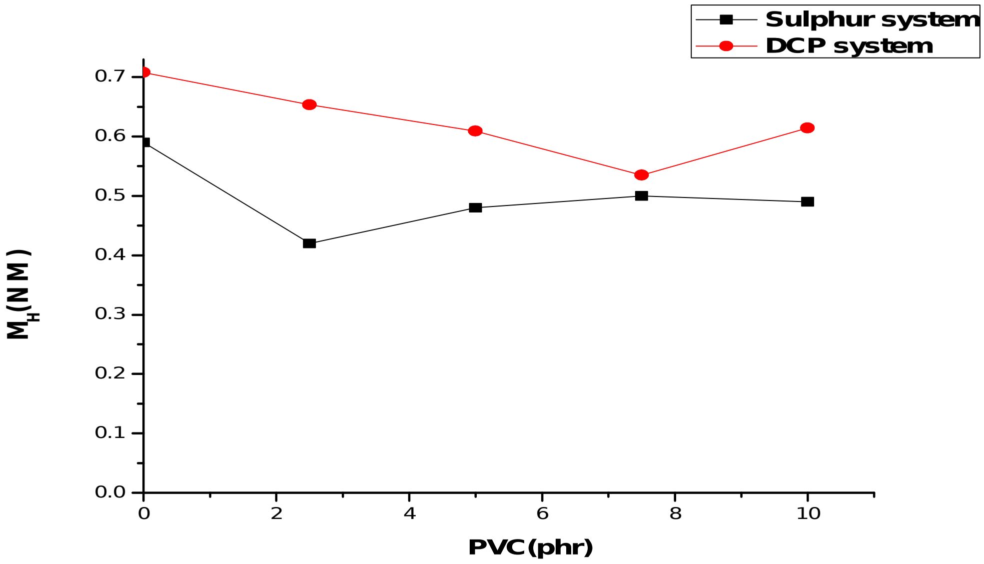


Figure 3.9 Effect of sulphur concentration on maximum torque values of different EPDM/PVC composites

Table 3.5 Effect of concentration of sulphur on mechanical properties of EPDM/PVC composites

System	Tensile Strength (MPa)		Young'modulus (MPa)	
EPDM/PVC	S=2phr	S=3phr	S=2phr	S=3phr
100/2.5	1.13	1.45	1.78	2.11
100/5	1.19	1.4	1.94	2.44
100/7.5	1.25	1.48	1.96	2.86
100/10	0.88	1.20	1.46	3.11

3.2.3 Crosslink density from tensile properties

The behavior of different vulcanizing system towards mechanical properties could be related to the morphology and crosslink density of the system [29].The crosslink density of the blends was calculated from the tensile values using the kinetic theory of elasticity.

$$\nu = \frac{\sigma}{\left(\lambda - \frac{1}{\lambda^2}\right)RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.1$$

The molar between crosslinks ,M_c is an important structural parametrr for characterizing crosslinked polymer systems. The magnitude of M_c controls the solvent transport through such systems discussed in coming chapters. M_c was calculated by the equation,

$$M_c = \frac{1}{2\nu} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 3.2$$

Where ν is the degree of crosslinking.

The calculated values of crosslink density and molar mass between crosslinks are given in table3.6a and 3.6 b.It is observed that crosslink density increases with increase in PVC and increase in concentration of sulphur and also with DCP crosslinking.

Table 3.6a Effect of PVC loading and concentration of sulphur on crosslink density of static vulcanized EPDM/PVC composites

EPDM/PVC	**Crosslink density, v** (2phr sulphur)	**Molar mass between crosslinks, Mc**	**Crosslink density, v** (3phr sulphur)	**Molar mass between crosslinks, Mc**
100/0	1.54	0.3246	1.79	0.2793
100/2.5	1.71	0.2918	2.03	0.2462
100/5	1.86	0.2677	2.35	0.2129
100/7.5	1.88	0.2650	2.75	0.1818
100/10	1.93	0.2584	2.99	0.1670

Table.3.6 b Effect of crosslinking system on crosslink density and molar mass between crosslinks 100/5 EPDM/PVC composites

100/5 EPDM/PVC	**v**	**Mc**
Sulphur (Static)	2.35	0.2129
DCP (Static)	2.39	0.2090

3.2.4 Crystallinity

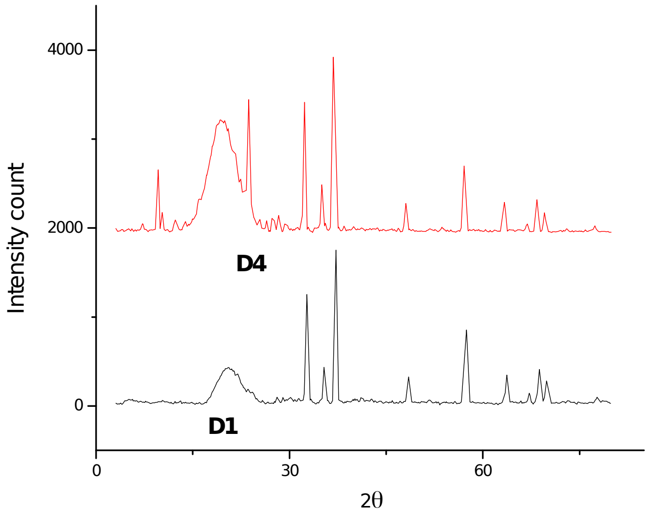
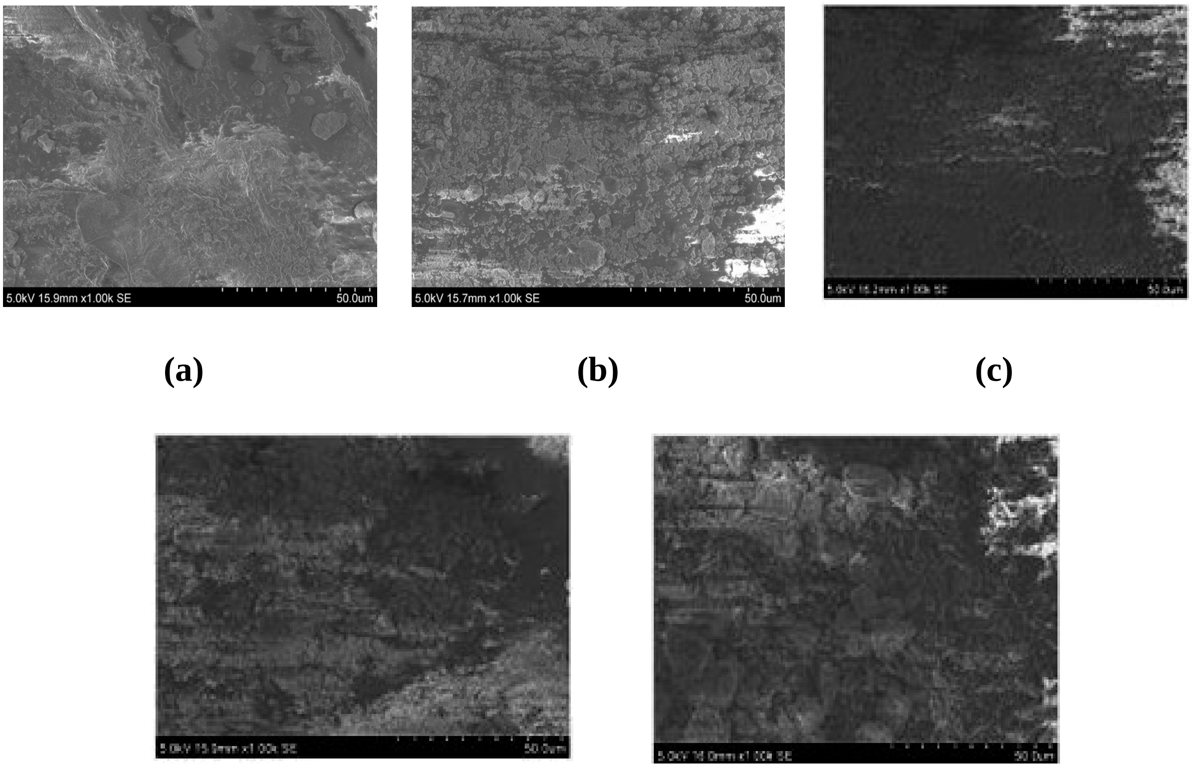


Figure.3.10 X –ray diffraction pattern of dynamically vulcanized (D1) 100/0 EPDM/PVC and (D4) 100/7.5 EPD/PVC composites.

Figure 3.10 shows the X-ray diffraction patterns of pure EPDM and 100/7.5 EPDM/PVC composite crosslinked by sulphur. In D_1 (pure EPDM), there is no crystalline peak appearing but in D_4 sample, peaks with d spacing is appearing.ie., the matrix becomes more crystalline with PVC loading.

3.3 Morphology

The morphology of a system depends upon the concentration of the dispersed phase. Figure 3.11 (i) shows Scanning Electron Micrographs of sulphur cured EPDM/PVC composites Figure clearly shows the PVC domains that distributed in the EPDM matrix.This restricts the path of solvent vapours. The increase in dispersed domain size with increasing proportion of PVC in 100/10 EPDM/PVC composite is associated with the coalescence or recombination of the dispersed domains. Figure 3.11 (ii) Scanning Electron Micrographs of DCP cured EPDM/PVC composites. Here, due to the improvement in filler dispersion, the composites display significantly finer morphology. The dynamic vulcanization produces a fine dispersion [30] of the rigid PVC particles in EPDM matrix as can be seen from FESEM in Figure 3.11 (iii). Here,the microhetrogenity between EPDM and PVC is redueuced due to the improved interfacial adhesion.This generates a matrix with relatively lower free volume for solvent permeation.

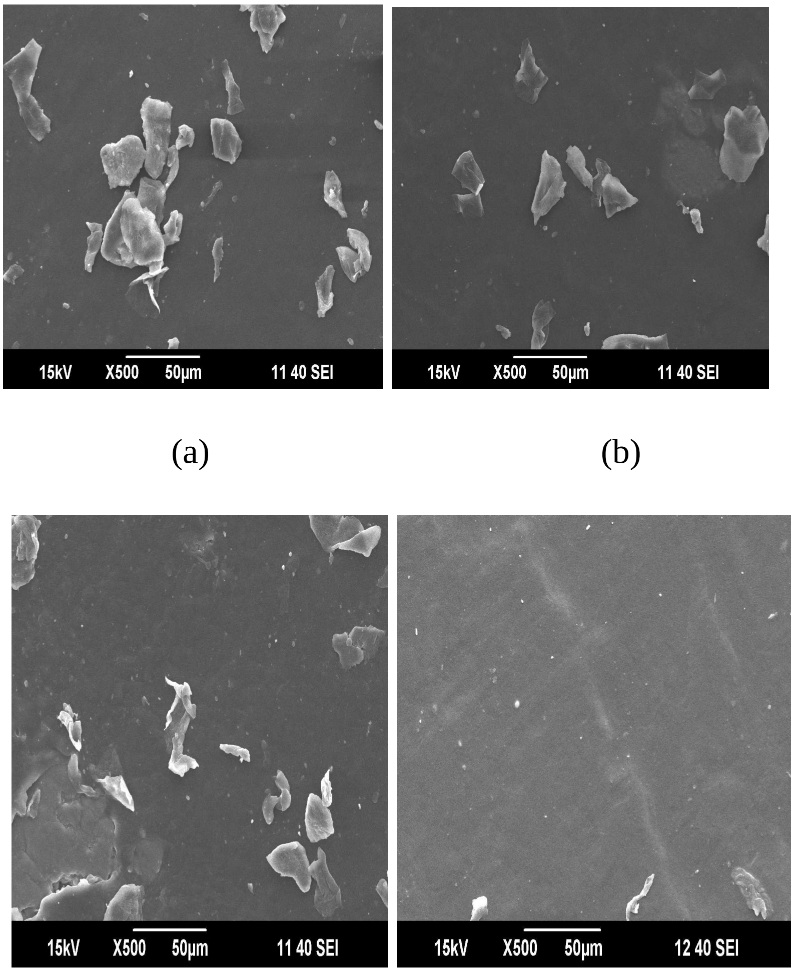


(a) **(b)** **(c)**

(d) **(e)**

Figure 3.11(i) Scanning Electron Micrographs of sulphur cured EPDM/PVC composites;

(a) 100/0 EPDM/PVC (b) 100/2.5 EPDM/PVC (c) 100/5 EPDM/PVC (d) 100/7.5 EPDM/PVC and 100/10 EPDM/PVC

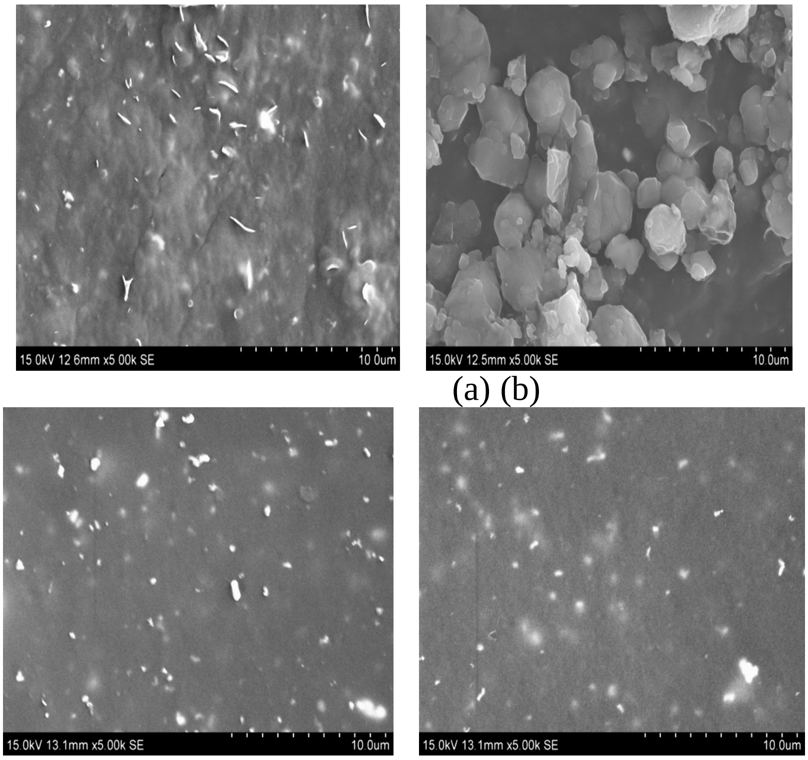


(a) (b)

(c) (d)

Figure 3.11(ii) Scanning Electron Micrographs of DCP cured EPDM/PVC composites;

(a) 100/2.5 EPDM/PVC (b) 100/5 EPDM/PVC (c) 100/7.5 EPDM/PVC and (d) 100/10 EPDM/PVC



(a) (b)

(c) (d)

Figure 3.11 (iii) Scanning Electron Micrographs of Dynamically vulcanized sulphur cured EPDM/PVC composites;(a))100/2.5 EPDM/PVC (b) 100/5 EPDM/PVC (c) 100/7.5 EPDM/PVC and (d) 100/10 EPDM/PVC

3.4 Conclusion

The mechanical, thermal and dielectric properties of EPDM/PVC composites were investigsted with special reference to the effect composite ratio and vulcanizing system.DCP vulcanized system possess higher torque than sulphur crosslinked ones. Samples prepared by using sulfur as the vulcanizing agent showed comparatively better mechanical properties. Mechanical properties, structure and morphology of the system depends upon the processing methods and vulcanizing techniques due to difference in the extent of mixing. The amount of crosslinking agent also affects the values of mechanical properties Dynamically vulcanized composites exhibited better mechanical properties than statically vulcanised samples. The morphology and crystalline properties have also been studied for complementing the observations of the sorption characteristics.

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Chapter 4

Vapour permeation through EPDM/PVC polymeric systems

Summary

Vapour permeation of three aromatic solvents viz, benzene, toluene and xylene and aliphatic propanol through EPDM and EPDM/PVC composites has been studied. The reduction in the rate of solvent vapour permeation through the membrane with increase in PVC content has been attributed to the stiff and rigid nature of the PVC. This is due to the better dispersion of PVC in the rubber matrix which blocks the solvent transport through the vulcanizates. The morphology of the composites is complementary to the observations. The vapour permeability decreases with increase in size, chain length and with introduction of side chain . The flat benzene ring easily diffuses through the available free volumes of the blend than toluene and xylene which contain methyl groups that make it difficult to locate a hole of the appropriate size in the composite. Hence, permeation was lower with toluene and xylene.

In the case of benzene/ propanol mixtures, it has been found that when propanol content increases, the vapour permeation rate decreases. This indicates less interaction of propanol towards EPDM/PVC membranes, which can be explained by their solubility parameter values. Azeotropes at the azeotropic point give vapour of the same composition as the azeotropic liquid and thus cannot be further concentrated by normal distillation no matter how efficient the fractionating column used.

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4.1 Introduction

The investigation on permeability and selectivity of a membrane are important to understand its fundamental functions for practical applications [1-3]. Permeation process through any material is a combination of sorption and diffusion and occurs by a solution-diffusion mechanism [4] which can lead to useful levels of selectivity. According to the solution-diffusion model, vapour permeation consists of three consecutive steps; (1) sorption of the permeant from the feed liquid to the membrane, (2) diffusion of the permeant in the membrane and (3) desorption of the permeant to the vapour phase on the downstream side of the membrane(Figure 4.1). Each component in the vapour feed dissolves in the membrane polymer at its upstream surface, much like gases dissolve in liquids, then diffuse through the polymer layer along a concentration gradient to the opposite surface where they ‘evaporate’ into the down stream gas phase[5]. The components in the membranes usually consist of separate phases and so the material needs to be treated as a composite. The presence of crystallinity reduces permeability and good membranes should be capable of high fluxes. The usual physical picture is to think of a semi crystalline polymer in terms of a simple two-phase model; one phase being amorphous and the other being crystalline. In the typical case, the crystals do not sorb or transmit penetrant molecules. Usually the continuous phase dominates the permeation process[6].Thin film composite membrane consisting of two or more polymer layers that can tolerate wide pH ranges, higher temperatures, and harsh chemical environments and that have highly improved water flux and solute separation characteristics have been developed. Vapour permeation is similar in principle to pervaporation [7].The only difference concerns the feed, which is a mixture of vapours or vapors and gases. As in pervaporation, the permeate partial pressure is maintained by use of a vacuum or an inert sweep gas [Figure 4.2]. There is no change of phase involved in its operation. Thus, compared to pervaporation, the addition of heat equivalent to the enthalpy of vaporization is not required in the membrane unit and there is no temperature drop along the membrane.

Operation in the vapour phase also eliminates the effect of the concentration polarization prevalent in liquid phase seperations, such as pervaporation .

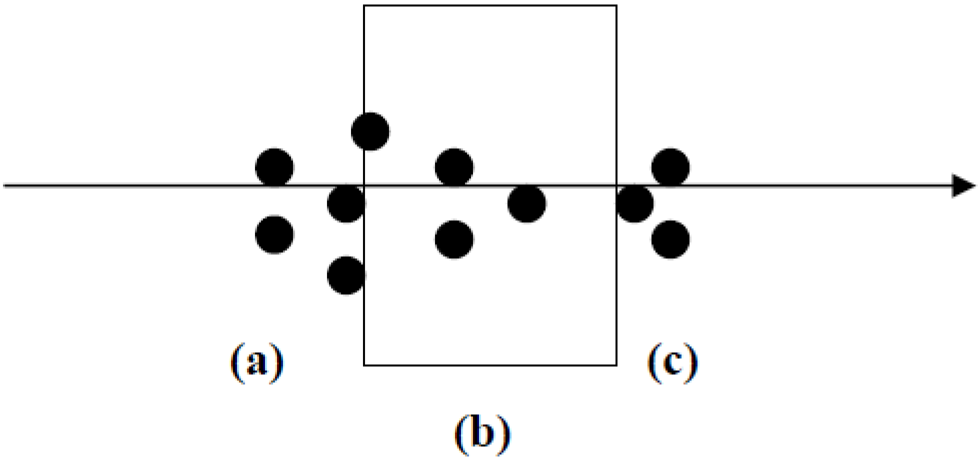

Figure 4.1 Schematic representation of different stages in vapour permeation :(a) Adsorption onto polymer surface, (b) Diffusion through bulk polymer, (c) Desorption into external phase

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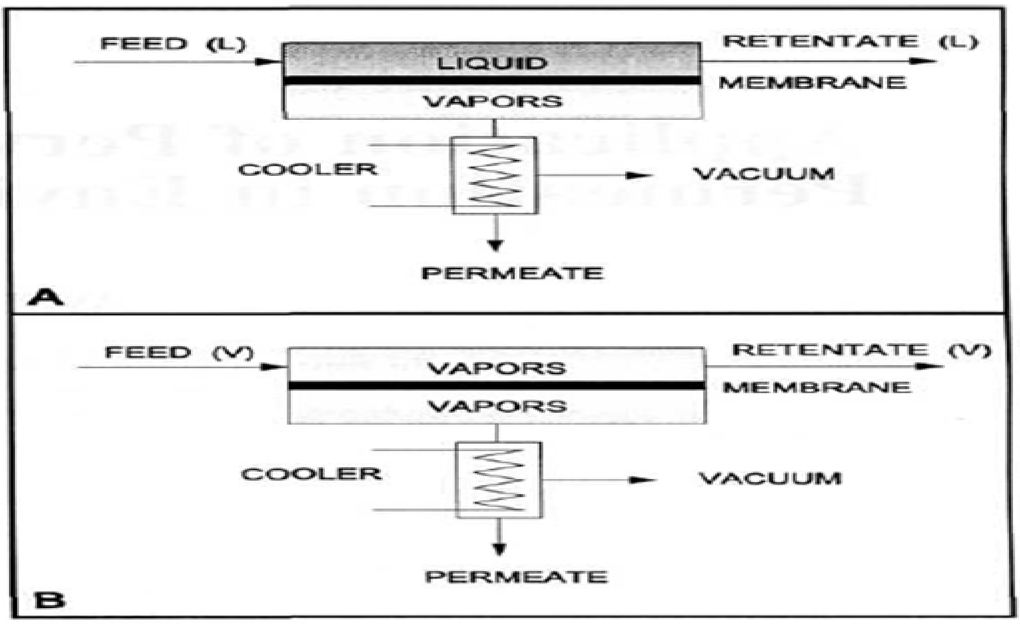


Figure 4.2 Schematic representation of (a) pervapouration and (b) vapour permeation.

Pervaporation and vapor permeation are the most well-known membrane processes for the separation of liquid and vapor mixtures allows variety of possible application areas:

Dewatering of organic fluids like alcohols, ketones, ethers etc;

i. Separation of mixtures from narrow boiling temperatures to constant (azeotrope)
ii. Removal of organic pollutants from water and air streams;
iii. Separation of fermentation products;
iv. Separation of organic-organic liquid mixtures.

Vapour permeation offers the unique feature of studying the transport process of a single permeant through a dense membrane under various upstream activities and promises greater simplicity in technical design and significant opportunities for energy savings. Such characteristics can by no means be obtained by pervaporation, where the modification of the upstream activity of a component can only be achieved by adding another compound to the mixture. The effective membrane area requirement for vapour permeation is lower than that for pervaporation. Vapor transport offers one the unique ability to study structure–property relationships in polymers. By using this technique, even difficult separation of azeotropic mixture can be performed. This process offers direct practical conclusion for the understanding and rational design of volatile organic components (VOC) vapour recovery from contaminated air stream and is more advantageous than classical VOC control process. Compared with other conventional separation technologies, vapour permeation as well as pervaporation have quite a few practical advantages in common:

- Simple operation and control
- Reliable prerformance
- High flexibility
- Unproblamatic part-load operation
- High product purity (no contamination by entrainer)

- No environmental pollution (no entrainer emission)
- High product yield.
- Low specific energy consumption
- Compact design (low space requirement, minimum height)
- Short erection time (prefabricated and preassembled units)
- Uncomplicated capacity enlargement (due to modular construction design)

Membrane-based chemical separations constitute an emerging research area and industrial technology. The objective is to develop membranes that selectively transport a particular target molecule and reject (or transport at much lower rates) other molecules that might be present in the feed solution.

In order to obtain a good permeation rate and a high degree of separation for a feed mixture, it is essential to choose the right membrane as well as the optimum operating conditions. Since usually a single polymer does not possess the optimum properties for a given separation, new membranes have to be developed to achieve the desired balance of properties [8]. Membranes with many interesting applications can be developed from different polymeric materials. Novel membranes can be prepared by various methods like copolymerization, blending and use of thin film composites.

4.1.1 Polymer selection criteria

A polymer to be used for the preparation of gas and vapor separating membranes should have the following intrinsic properties: (1) high selectivity for the components to be separated, (2) high permeability for the permeating components, and (3) high life expectance under operating condition, good thermal, chemical and mechanical stability. For the mixture of two organic liquids or vapors, again three kinds of mixtures can be distinguished: polar/apolar, polar/polar and apolar/apolar mixtures. For the removal of the polar component from polar/apolar mixture polymers with polar groups should be chosen and for the removal of the apolar component completely apolar polymers are favorable. The polar/polar and apolar/apolar mixtures are very difficult to separate, especially when the two components have similar molecular sizes. In principle all kinds of polymers can be used for these systems, the separation has to take place on the basis of differences in molecular size and shape, since no specific interaction of one of the two components can take place.

There exist interesting reports on the vapour permeation through different polymer membranes [9-11] and use of thin film composites. It has been reported that the permeation depends upon a number of factors like composition, method of formation, type of cross linking agents used, nature and size of the penetrants, temperature etc. For example, a decrease in diffusivity with an increase in the size of penetrant has been reported by many investigators [12-14]. Haraya and Hwang [15] have conducted permeation studies in a series of polymers for selecting appropriate polymers for the separation of O_2/Ar mixtures. Masoud Frounchi etal [16] studied gas barrier properties of PP/EPDM blend composite and found that the permeability decreased with PP content in the composite. S. AnilKumar etal [17] studied the permeability of n-alkanes through EVA membranes and found that the rate increased with introduction of cross links to a certain extent due to increase in free volume of the crystalline polymer. Sowmya Ganapathi-Desai etal [18] tested composite membranes for recovering volatile organic compounds (VOCs) from dilute aqueous solutions and found that this method can offer potentially cleaner and cost-effective means of recovering VOCs from contaminated streams.It has been reported that the permeation depends upon a number of factors like composition, method of formation, type of cross linking agents used, nature and size of the penetrants, temperature etc.

This chapter presents an investigation on the vapour permeation characteristics of EPDM/PVC composites vulcanized by sulphur,DCP and a mixture system of sulphur and DCP,in the temperature range of 28-48 ^{0}C.The effect of filler loading, size and shape of penetrant molecule and vulcanization technique on the permeation through EPDM/PVC composites have been discussed.

4.2 Results and Discussion

4.2.1 Effect of PVC loading

The permeation of a penetrant into the polymer matrix depends on the polymer morphology,which controls the propagation of a molecule from one slab to another.Any morphoilogical factor that modify either the structure or the flexibility of the polymer chains will be expected to change the diffusivity of the molecule.Owing to the two phase morphology,the transport of organic solvents through EPDM/PVC membrane is highly interesting. Figure 4.3 shows the amount of benzene vapours permeated through pure EPDM and 100/2.5 EPDM/ PVC system. It has been observed from the figure that EPDM membrane shows higher permeability than the PVC loaded system due to the flexible nature of the chains that creates more free volume in the matrix. Pure EPDM is amorphous with flexible macromolecular chains which readly undergo rearrangement to allows the passage of penetrants.As the PVC content increases,the blend offers greater resistance to the vapour penetrant molecules leading to lower permeation. Adding PVC to EPDM phase improves the barrier property due to the combination of two phenomena; the decrease in area available for diffusion as a result of impermeable PVC occupying free volume and the increase in the distance a molecule must travel to cross the film as a result of the tortuous path it follows around the the impermeable PVC particles.

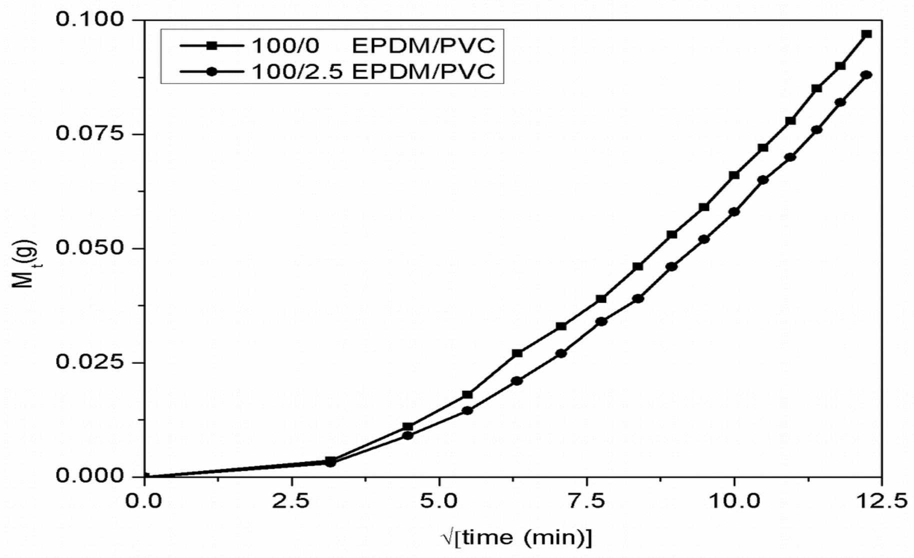


Figure 4.3 Effect of PVC loading in EPDM on permeation of benzene

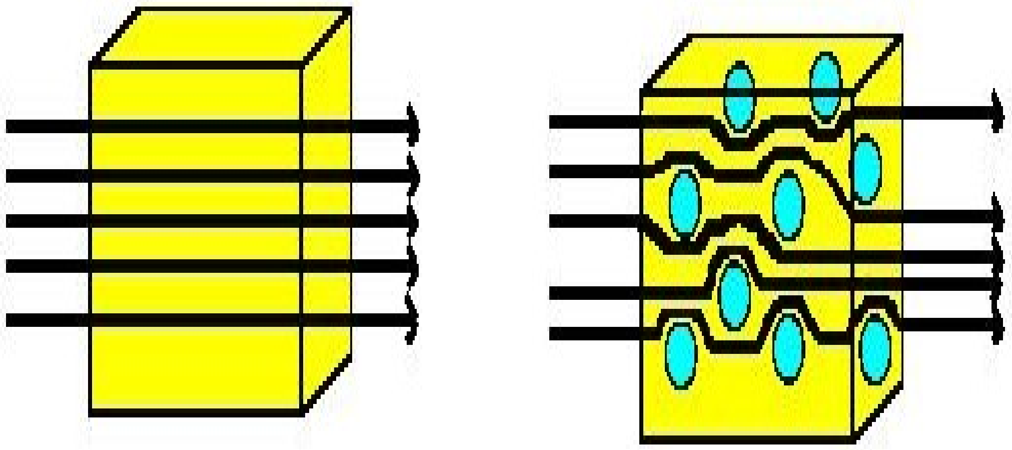


Figure 4. 4 Schematic representation of permeation through (a) pure EPDM and (b) EPDM/PVC composite

Figure 4.4 shows a schematic representation of permeability through pure EPDM and EPDM/PVC composites. Figure clearly shows the PVC domains that distributed in the EPDM matrix which restricts the path of solvent vapours.

4.2.2 Effect of amount of PVC

Figure 4.5 shows the amount of benzene permeated through membranes with varying amount of PVC.It can be seen that the vapour permeation decreases with increase in PVC content in the composite upto 7.5 phr PVC and then the permeability increses in 10 phr PVC.This may be due to optimum loading in 7.5 phr PVC .ie., due to the better dispersion of PVC in the rubber matrix which blocks the solvent transport through the vulcanizates and the non uniformity after the optimum loading.

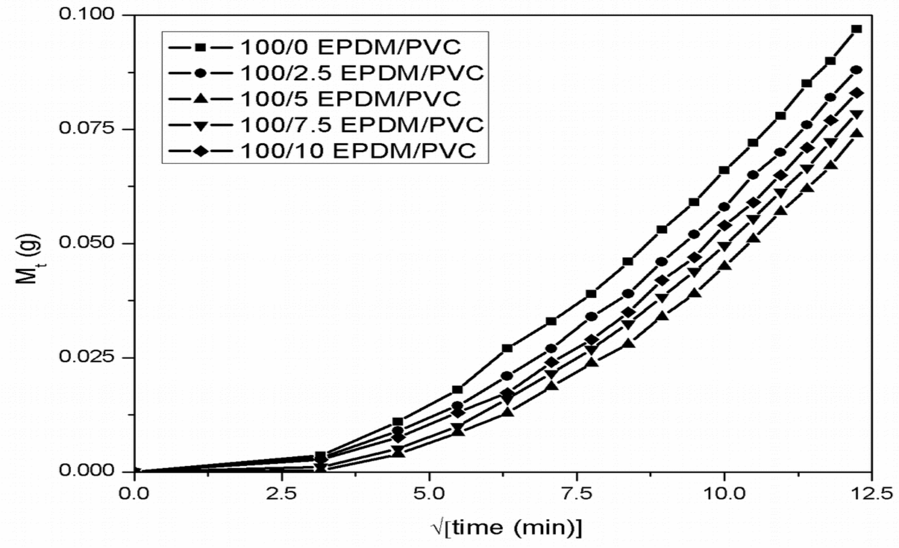


Figure 4.5 Effect of amount of PVC on the vapour permeation of benzene through EPDM/ PVC composite

It is clear from the FESEM figure 3.11(i) (a), (b), (c), (d) and (e) that the uniformity of the dispersed PVC particles increases up to 7.5 phr.After that the dispersion of PVC in EPDM matrix is non uniform. This may be attributed to the tendency of rigid PVC to form aggregates or agglomeration of the dispersed domains occurs which impede the solvent penetration into the rubber matrix That may be the reason for maximum torque value for 7.5 phr samples.This makes the particles larger and non-uniform, leading to an unstable morphology.Here, voids tend to occur at interface which leads to an increase in free volume. To complement the above observations, the volume fraction of polymer composites (φ) in the toluene swollen sample has been computed by the Equations

$$\phi = \frac{w_1/\rho_1}{\frac{w_1}{\rho_1} + \frac{w_2}{\rho_2}} \quad \text{..} \quad 4.1$$

Where, w_1 is the weight of the blend sample, ρ_1 is the density of polymer composite,$w_2$the weight of solvent in the swollen sample and ρ_2 is the density of solvent. The values of the volume fraction and interaction parameter are given in table 4.1. There is a regular increase in the volume fraction values with increase in PVC content of the composites. From these, interaction parameter values can be calculated.

$$\chi = \frac{-[\ln(1-\phi)+\phi]}{\phi^2} \quad \text{...} \quad 4.2$$

These results are complementary to the observed *Q*∞ values.

Table 4.1 Volume fraction of EPDM/PVC composites in tolune

EPDM/PVC	Volume fraction	Interaction parameter, χ
100/0	0.2588	0.610
100/2.5	0.2834	0.620
100/5	0.2980	0.630
100/7.5	0.3096	0.636
100/10	0.3155	0.640

4.2.3 Nature of the penetrants

The size,shape and side chain of the penetrant molecule is found to influence its rate of permeation through the polymer membrane.The vapour permeation curves of EPDM/PVC (5phr) for the three aromatic solvents ,benzene,toluene and xylene is given Figure 4.6. As expected,as the size of the permeant molecule increases, the permeation rate of the solvent vapours decreases. The order of permeation is benzene> toluene> xylene. This is because the smaller molecules find it easier to diffuse into free volumes whereas the larger ones, on account of the pendant groups around them find it difficult to locate themselves in the vacant sites.

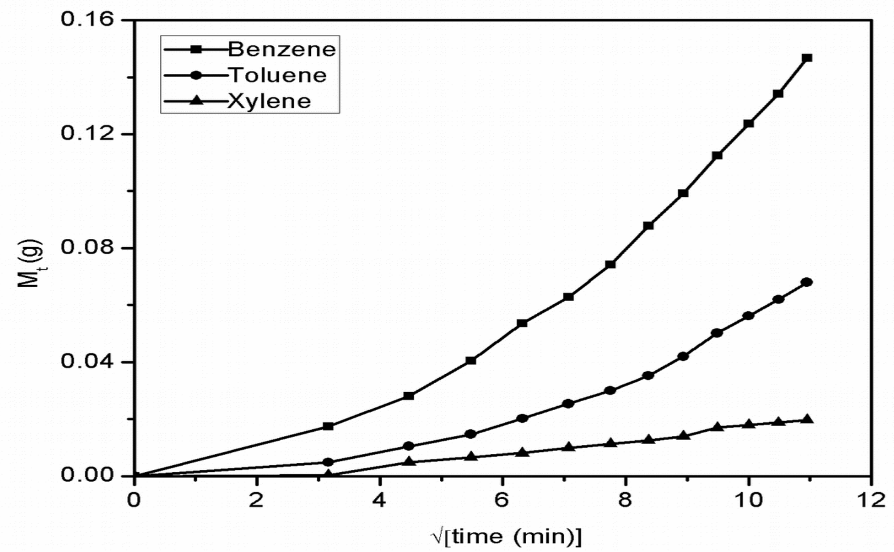


Figure 4.6. Effect of different penetrants on the vapour permeation through 100/5 EPDM/ PVC composite membrane

Figure 4.7 shows the difference in vapour permeation of 1- propanol and 2- propanol; molecules having same molecular weight, but different structures.

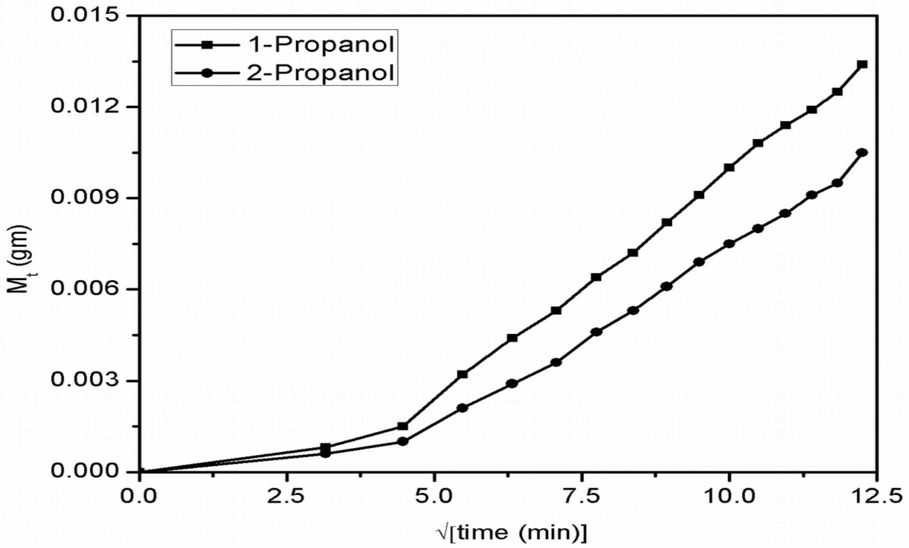
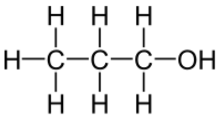
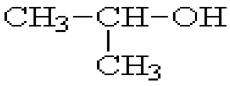


Figure 4.7 Permeation of Propan-1 ol and propan-2 ol through 100/5 EPDM/ PVC composite membrane.

It has been found that 1- propanol has greater permeation compared to 2- propanol.This can be due to the CH_3- side chain of 2- propanol, that can not easily pass through the matrix.





$$\mathrm{CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH}$$

1-propanol 2-propanol

The permeability,P, can be used as a quantitative tool to predict the barrier performance of the material.Permeability describe how easily a fluid is able to move through the matrix and is given by(2.5)

$$P = \frac{QL}{\Delta PAt}$$

Where ‘L’ is the thickness of the membrane and ‘Q’ is the molar quantity of solvent orberd through the material of area ‘A’ during a time ,t, at a steady state condition. ‘ΔP ‘ is the difference in partial pressure of the solvent across the membrane.

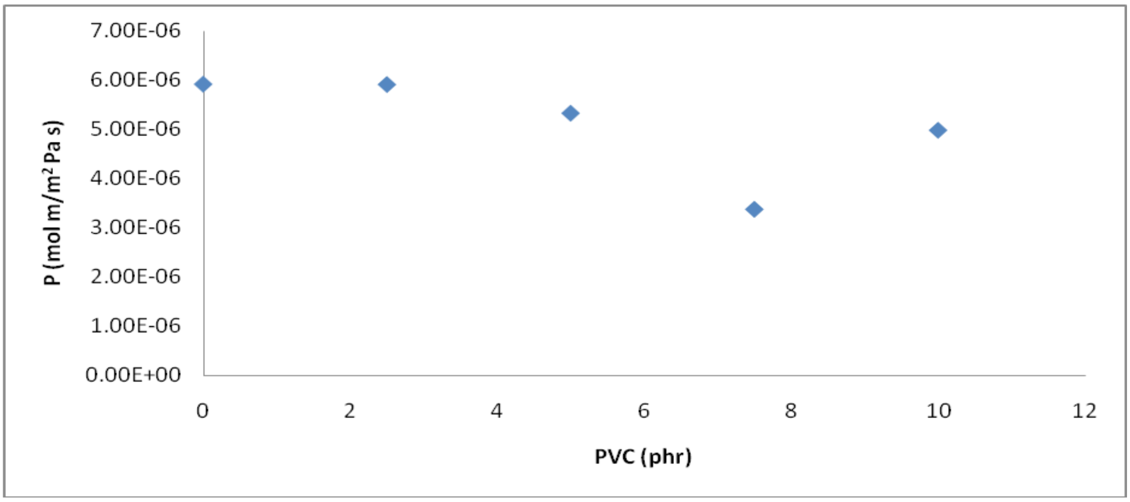


Figure 4.8. Variation of permeability on the composite ratio in benzene.

The values have been found to decrease with increase in PVC content in the composites as can be seen from figure 4.8.This is dues to the increase in rigidity of the membrane,which affects the diffusion and desorption characteristics.The P values of the three aromatic liquids have been found to follow the order: benzene> toluene > xylene as per their molecular size.

4.2.4 Effect of liquid mixtures

Figure 4.9 shows the difference in permeability between benzene and 1- propanol vapours through 100/ 5 EPDM/PVC membranes.It can be seen that pure benzene permeates at a higher rate than pure propanol.

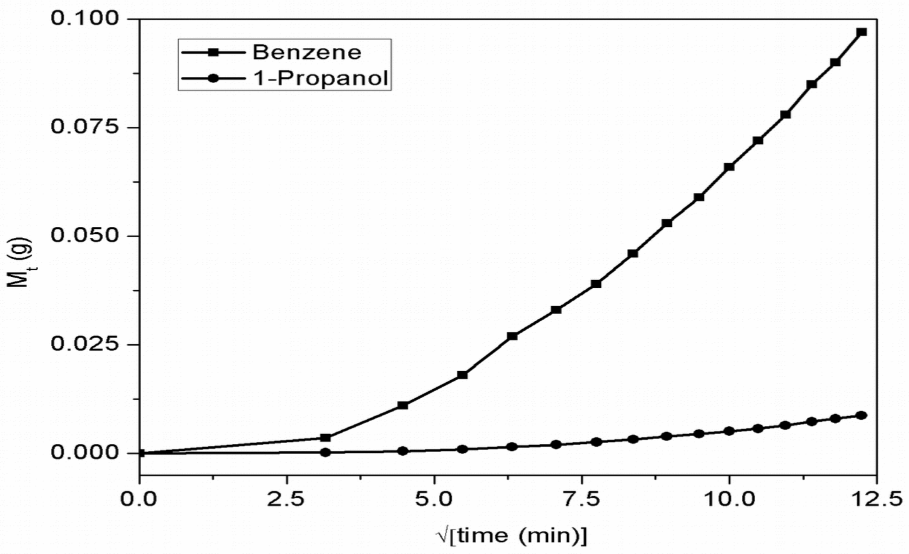


Figure 4.9 Permeability of 100/5 EPDM/ PVC membrane for propan-1 ol and benzene

Figure 4.10 shows the effect of benzene/ propanol mixtures on the vapour permeation behavior of 100/5 EPDM/PVCcomposite membrane. It has been found that 100% benzene permeates in a higher rate than 100% propanol.ie., the uptake of aromatic solvent is higher than aliphatic solvent for the composites. This clearly indicates the high interaction of benzene to the EPDM/ PVC membranes than propanol.This can be explained by their solubility parameter values (EPDM- 8.6, benzene-9.15, 1-propanol- 11.97 in $(cal/cc)^{1/2}$), The polymer-solvent interaction will be high if their solubility parameter values were closer. From the Figure, it has been found that as the propanol content in the mixture increases, the M_t values have been found to decrease.This clearly indicates the higher permeability of benzene than propanol through EPDM/PVC membrane. In the case of a liquid mixture, separation is obtained because the membrane has the ability to transport one component more readily than the other even if the driving forces are equal . [When a mixture of liquids, vapors or gases is fed to the membrane a part of the mixture will permeate through the membrane, which is the permeate stream. The remaining part, which does not permeate, is the retentate stream].

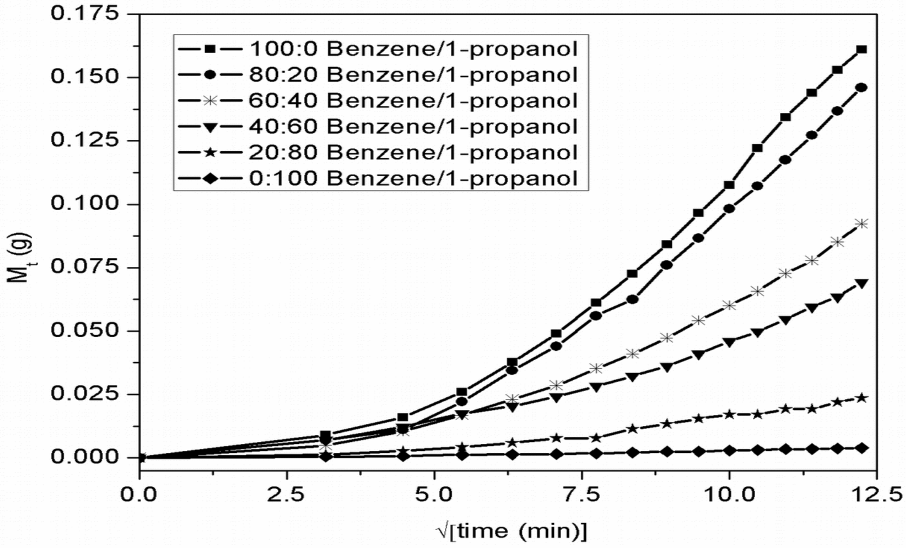


Figure 4.10 . Effect of liquid mixture compositions on the permeability of 100/5 EPDM/ PVC composite membrane

Figure 4.11 shows the permeation of azeotropic mixtures of benzene/ 1- propanol and benzene/ 2- propanol.The liquid mixture composition was analyzed by an Abbe refractometer upon completion of the vapour permeation studies.It was found that after two and half hours, the concentration of benzene in the permeate decreased from 82 % to 78% and from 58 % to 55 %

respectively. The composition of the benzene/1-propanol mixtures before and after vapor permeation for 21/2 hrs through 100/5 EPDM/PVC membrane are given in table 4.2.

Table 4.2. Composition of the benzene/1-propanol mixtures before and after vapor permeation after 21/2 hrs through a 100/5 EPDM/PVC membrane.

Pure composition of benzene/1-propanol	**Composition of the benzene/1-propanol permeation after 21/2 hrs**
80/20	78/22
60/40	55/45
50/50	42/48
40/60	33/67
20/80	11/89

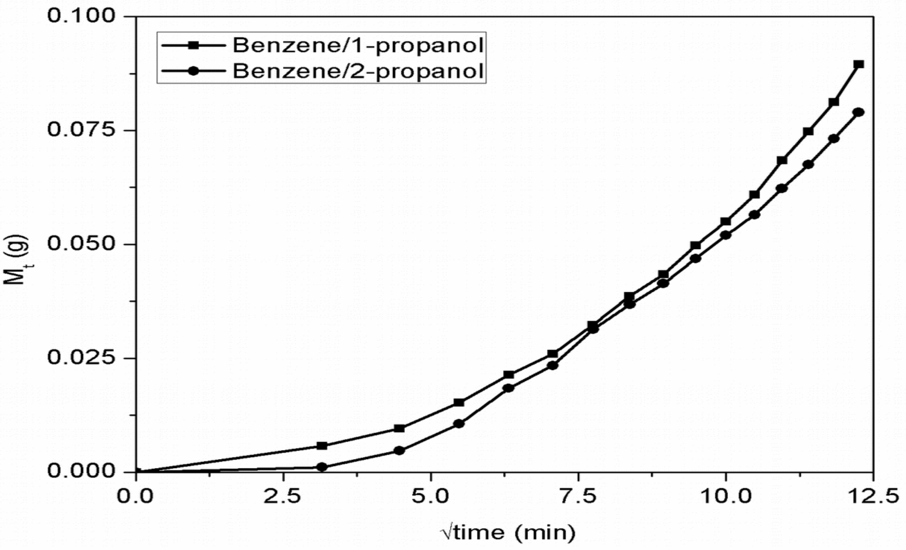


Figure 4.11 Permeation of azeotropic mixtures of benzene/1- propanol and benzene/ 2-propanol

4.2.5 Effect of type of vulcanization

Figure 4.12 shows the effect of the type of vulcanization techniques on the permeation behavior of 100/5 EPDM/ PVC membranes, using benzene as permeant. It is observed that dynamically vulcanized samples showed a lower permeation compared to the corresponding statically vulcanized one.

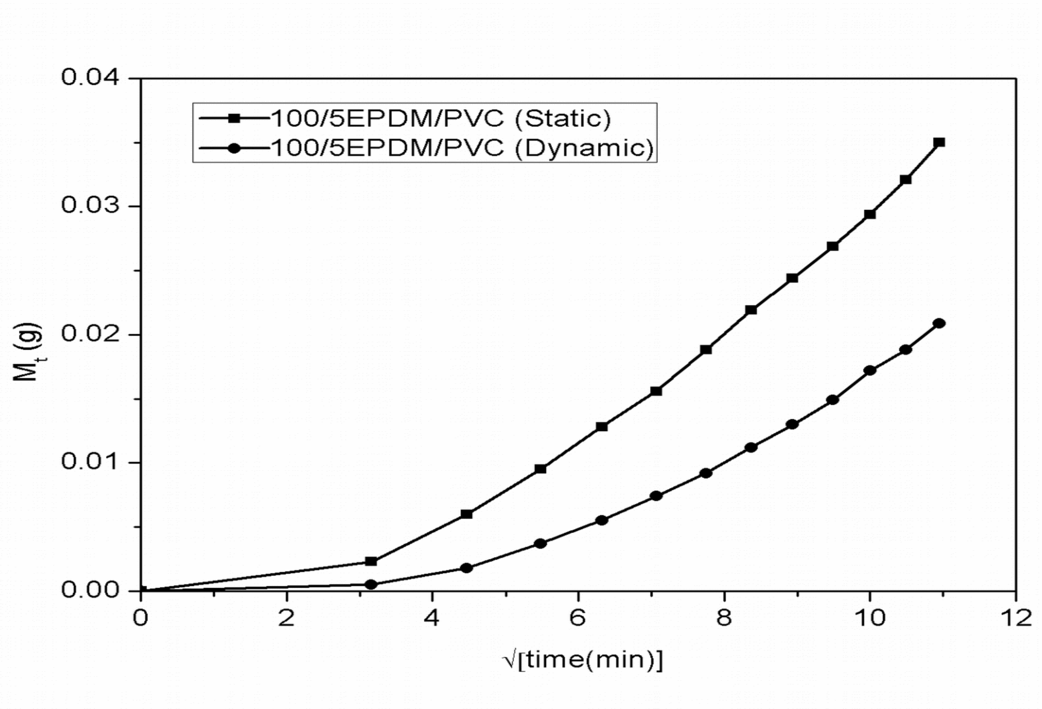


Figure 4.12. Effect of the type of vulcanization techniques on benzene permeation behaviour of 100/5 EPDM/ PVC composite membranes

The dynamic vulcanization produces a fine dispersion [19] of the rigid PVC particles in EPDM matrix as can be seen from FESEM in Figure 3.13(i) and 3.13 (iii). This generates a matrix with relatively lower free volume for solvent permeation.

4.3 Conclusion

Permeation of three aromatic solvent vapours viz, benzene, toluene and xylene, and aliphatic propanol through EPDM and EPDM/PVC composites has been studied .The reduction in the rate of solvent vapour permeation through the membrane with increase in PVC content has been attributed to the stiff and rigid nature of the PVC. This is due to the better dispersion of PVC in the rubber matrix which blocks the solvent transport through the vulcanizates.

The morphology of the composites is complementary to the observations. Of the three aromatic vapours used, the trend is in the order: benzene > toluene > xylene.This is in accordance with their molecular size. The vapour permeability decreases with increase in chain length and with introduction of side chain in isomeric solvents. In the case of benzene/ propanol mixtures, it has been found that when propanol content increases, the vapour permeation rate decreases. This indicates less interaction of propanol towards EPDM/PVC membranes, which can be explained by their solubility parameter values. Thus membranes separate mixtures by discriminating the components on the basis of physical or chemical attributes, such as molecular size, charge, or solubility. This means that the membrane is selective for some components of a mixture and let them permeate through, while other components will not permeate through the membrane. Dynamically vulcanized samples showed enhanced permeation compared to the corresponding statically vulcanized composites. Azeotropes at the azeotropic point give vapour of the same composition as the azeotropic liquid and thus cannot be further concentrated by normal distillation no matter how efficient the fractionating column used. Thus an alternative means to effect separation of such mixture is highly desirable.In the case of a liquid mixture, separation is obtained because the membrane has the ability to transport one component more readily than the other even if the driving forces are equal.

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Chapter 5

Molecular Transport of Chloromethanes Through EPDM/PVC systems

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Summary

Using a continuous gravimetric method, the kinetics of mass uptake and the equilibrium sorption behaviour of thick EPDM/PVC composit films has been studied for the three halogenated hydrocarbons; ethylene chloride, chloroform and carbon tetrachloride, which are part of the homologous series of the chloromethanes, as probe molecules at different temperatures.Suiphur, peroxide and a mixture of sulphur and peroxide were used for crosslinking the matrix. The dependence of the transport property on crosslink density,nature of penetrants ,type of crosslinking system and temperature was studied. A peculiarity can be seen among the group of chloromethanes, i.e. sorption increases with increasing number of chlorine atoms or molar volume, as it would be predicted from simple solubility parameter considerations. The mechanism of transport was found to be deviated slightly from Fickian trend. The differences in the equilibrium uptake can be explained on the basis of morphological changes.

5.1 Introduction

Long-term stability and performance of polymeric membranes in solvent and mixed solvent media can be reduced due to sorption and swelling of the membrane matrix. For this reason quantification of sorption and swelling is of major importance for the development of future applications of membrane processes in solvent and mixed solvent media. It is important to understand phenomena like swelling and sorption that contribute to a reduction of the life-time of the membrane. The transport phenomenon is a complex process with a variety of industrial applications. Solvent sorption and diffusion are the limiting factors of polymer end-use applications because these processes might change the mechanical properties and sometimes cause destruction in polymer structures. An investigation of the causes of such phenomena requires a thorough knowledge of the solvent-transport characteristics . Polymer composites have attracted in recent years a great deal of interest. In most cases, fillers are used as additives for improving the behavior of the host polymeric matrix [1].

Reports on the transport of small molecules into selected polymer membranes are available in the literature. [2-9] .The sorption equilibria and kinetics of three volatile organic compounds (VOCs)—benzene, chloroform, and acetone—in a newly developed divinyl-terminated poly(dimethylsiloxane) (PDMS[vi])–oligo polymer were studied[10]. The sorption uptake of each VOC by the polymer was measured gravimetrically at different VOC partial pressures at a constant temperature and at different temperatures between 24 and 50°C. The rate of VOC sorption was monitored until equilibrium was established. Maya Jacob et al., [11] evaluated the water absorption characteristics of the Natural rubber composites with reference to fiber loading. The influence of temperature on water sorption of the composites is also analyzed. Moisture uptake was found to be dependent on the properties of the biofibers. The mechanism of diffusion in the gum sample was found to be Fickian in nature, while in the loaded composites, it was non-Fickian. Sisal and oil palm fibers were subjected to different treatments such as mercerization and silanation. The effect of chemical modification on moisture uptake was also analyzed. Chemical modification was seen to decrease the water uptake in the composites

5.2 Results and discussion

5.2.1 Effect of PVC Loading

Figure 5.1 shows the amount of carbon tetra chloride sorbed throughs statically vulcanised pure EPDM and EPDM/ PVC systems. It has been observed from the figure that EPDM shows higher sorptrion than the PVC loaded system due to the flexible nature of the chains that creates more free volume in the matrix. Adding rigid PVC to EPDM phase improves the barrier property due to the reduction in free volume or microvoids.Increase in PVC content also restricts the macromolecular chain mobility resulting in a tortuous path for the diffusion of the penetrants

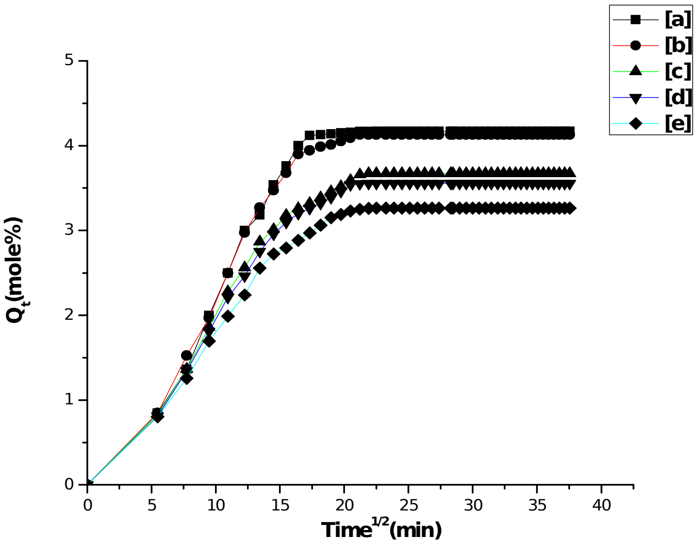

Figure 5.1 Mole % uptake of CCl_4 in dynamically vulcanized EPDM/PVC composites: [a]100/0 EPDM/PVC,[b] 100/2.5 EPDM/PVC,[c]100/5 EPDM/PVC , [d] 100/7.5 EPDM/PVC and [e] 100/10 EPDM/PVC.

5.2.2 Effect of Penetrants

Figure 5.2 shows the effect of penrtrant size on the sorption and diffusion of three chloromethanes through sulphur cured 100/5 EPDM/PVC composite It follows from the graph that the trend is in the order: carbon tetra chloride> chloroform>methylene chloride. ie., a steady increase insolvent uptake with increasing chlorine content is found .This anomalous results can be explained as follows:

The permeation through any matrix is a combination of sorption and diffusion. The kinetics of diffusion depends on the molecular mass of the solvent whereas sorption depends on the difference in the solubility parameter values. [12]. The highest uptake exhibited by carbon tetra chloride is due to the dominance of the solubility parameter over the molecular mass of the solvent during transport. The smaller the difference in solubility parameter, the greater is the affinity of polymer towards the solvent. The Qt value of methylene chloride is very low as solubility parameter value is far from EPDM. It exceeds size effect of methylene chloride on sorption. Between chloroform and carbon tetra chloride upto four hours, CCl_4 shows low Qt value due to the fact that the diffusion of the larger carbon tetrachloride has a retarding influence compared with chloroform[13] . When the sorption rate increases after that, the size effect is exceeded by solubility productie. ie., sorption increases with increasing number of chlorine atoms or molar volume, as it would be predicted from simple solubility parameter considerations. So in chlorinated hydrocarbons, the main deciding factor is solubility parameter. A similar trend has been observed for poly (ethylene-co-vinyl acetate) membranes [14] for aliphatic hydrocarbons.

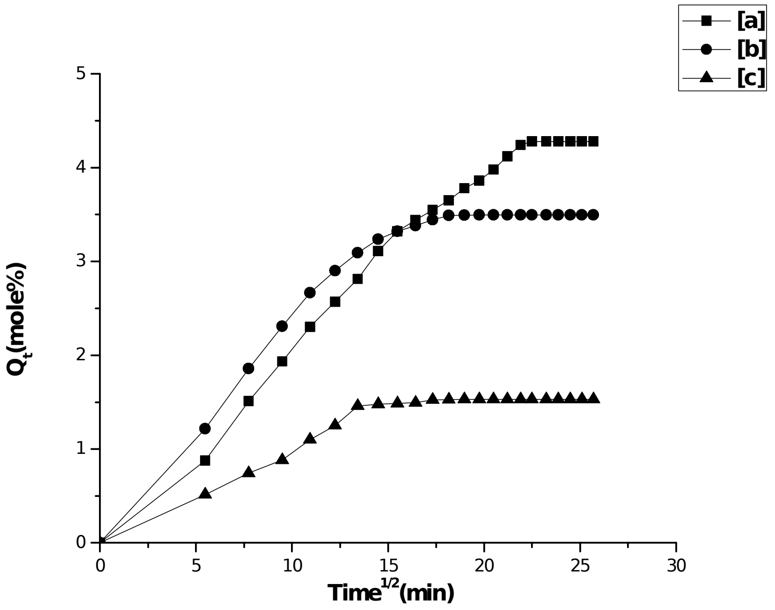

Figure 5.2 Mole % uptake of chloromethanes in (sulphur cured)dynamically vulcanised 100/5 EPDM/PVC composite.

5.2.3 Effect of Type of Vulcanization

Figure 5.3 shows the effect of the type of vulcanization techniques on the sorption behavior of EPDM/ PVC membranes, using carbon tetra chloride as penetrant. It is observed that dynamically vulcanized samples showed a lower swelling compared to the corresponding statically vulcanized one. The dynamic vulcanization produces a fine dispersion [15]of the rigid PVC particles in EPDM matrix.

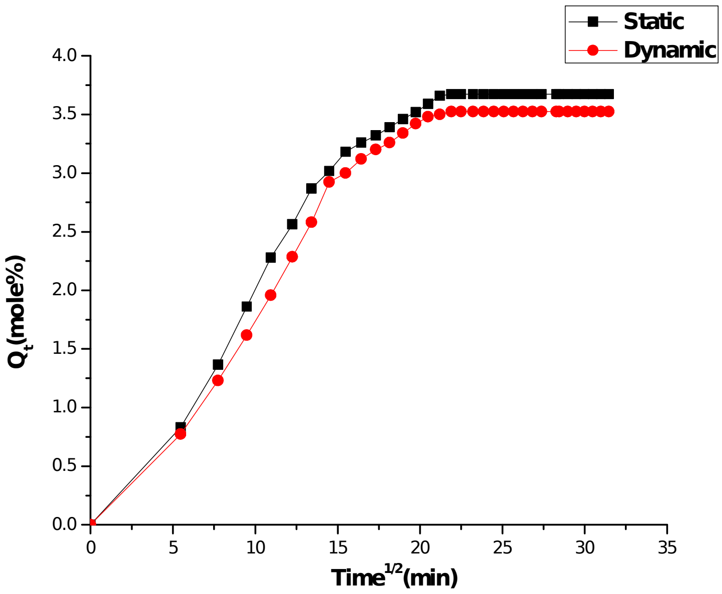

Figure 5.3 Effect of type of vulcanization on CCl_4 uptake in sulphur cured 100/5 EPDM/PVC composite.

5.2.4 Swelling mechanism

In order to investigate the type of transport mechanism, the sorption results were fitted to the following equation:

where Qt and Q∞ are the mole percent monomer uptake at time t and at equilibrium. k is a constant, which depends both on interaction between solvent and polymer and on the structure of the polymer. The value of n determines the mode of diffusion mechanisms [16]. The values of n and K are given in table 5.1 and 5.2. Plot of log (Qt/Q∞) versus log t showed that the values of n were between 0.5 and 1 and this suggested that the mechanism of transport slightly deviates from normal Fickian behavior observed for conventional elastomers. The values of 'K' at room temperature are given in table 5.3.

Table 5.1 Values of n and K at 28 °C for different PVC loading

EPDM/PVC	n	Kx10^2(g/g min^2)
100/0	0.661	2.32
100/2.5	0.697	1.99
100/5	0.613	3.04
100/7.5	0.636	2.76
100/10	0.578	3.65

Table 5.2 Values of n and K at 28 ^{o}C for different penetrants in 100/5 EPDM/PVCcomposite

Solvent	n	Kx10^2(g/g min^2)
Carbon tetra chloride	0.62	3.04
Chloroform	0.50	6.51
Methylene chloride	0.57	4.7

Table 5.3 Values of n (100/5 EPDM/PVC composite) at different temperatures

Temperature	n	K_sx10^2(g/g min^2)
28^{o}C	0.63	2.57
38^{o}C	0.54	4.96

5.2.5 Effect of concentration of sulphur

The Q_t decreases with increase in sulphur concentration. This is due to crosslinking of rubber phase and thereby exerting greater resistance to the flow of solvent. Figure 5.4 shows the effect of sulphur concentration on sorption values of EPDM/PVC composite. The crosslink density increases with increase in sulphur concentration.

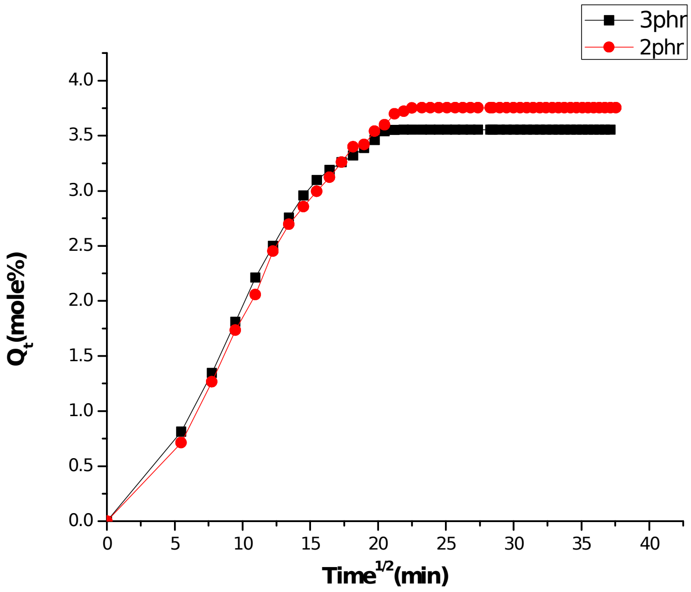

Figure 5.4 Effect of sulphur concentration on CCl_4 uptake in 100/5 EPDM/PVC composite

5.2.6 Effect of crosslinking system

Figure 5.5 shows the effect of crosslinking system on the sorption and diffusion of carbon tetra chloride in 100/5 EPDM/PVC composite. It can be seen that the solvent uptake is higher in sulphur vulcanized system. The nature of the cross link varies as can be seen from figure 3.4. It is evident from the SEM photograph given in Figure 3.13 that a fine and more uniform phase distribution is exhibited by the DCP vulcanized sample.

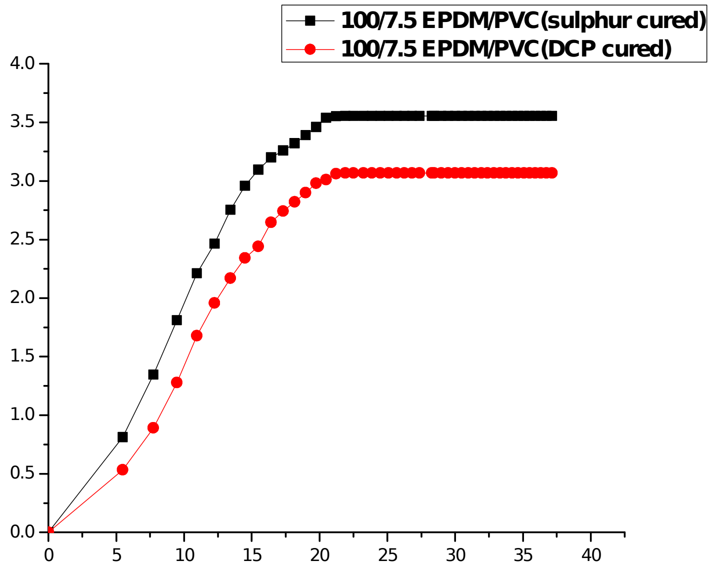

Figure 5.5 Effect of crosslinking system on CCl_4 uptake in 100/5 EPDM/PVC composite

5.2.7 Effect of temperature

To study the effect of temperature,sorption experiments at 38°C was conducted in addition to those at 28°C.Figure 5.6 shows the temperature dependence of of sulphur cured 100/5 EPDM/PVC composites in carbon tetra chloride.The rate of diffusion and the maximum uptake were found to increase with the temperature.

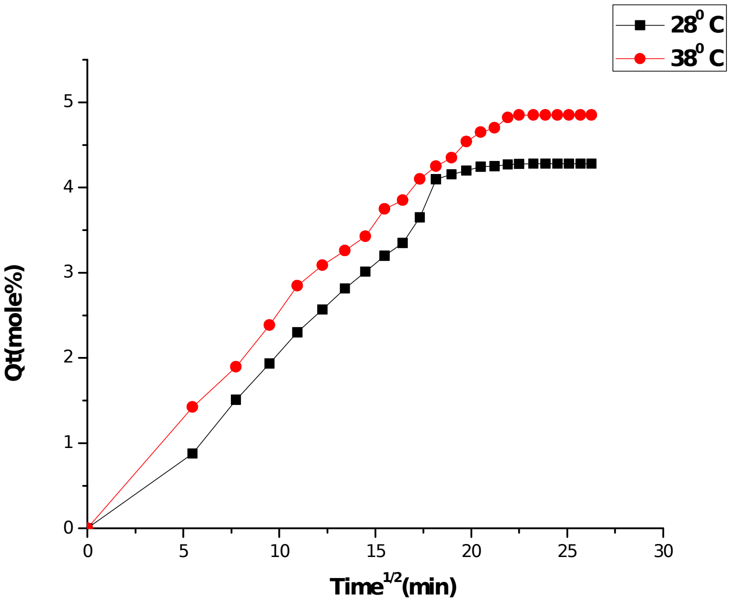

Figure 5.6 Effect of temperature on CCl_4 uptake in 100/5 EPDM/PVC composite;[a] 28°C and [b] 38°C

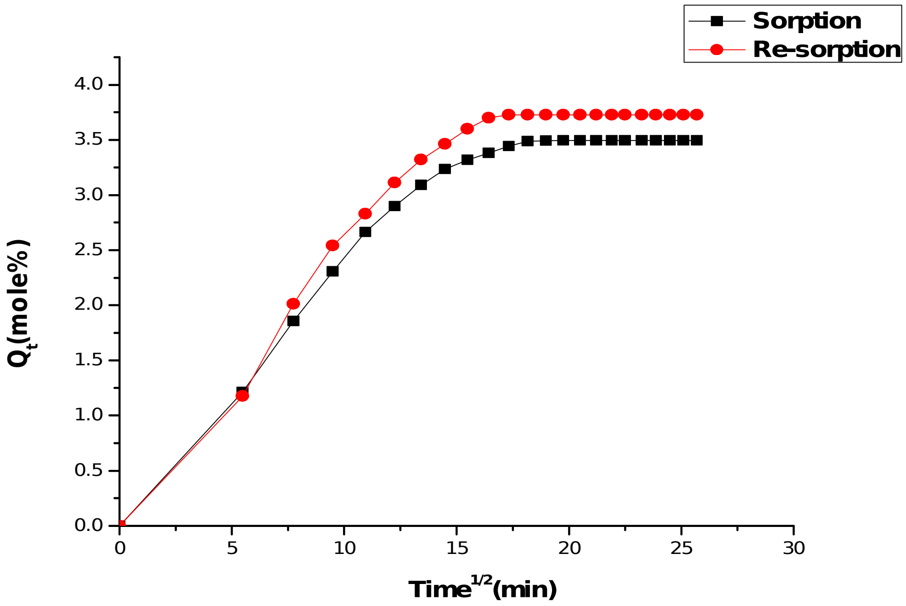

Figure 5.7 Sorption-resorption of $CHCl_3$ in sulphur cured 100/5 EPDM/PVC composites

The S-D-RS (sorption-desorption-resorption) testing of a polymer in presence of hazardous liquids is important to judge its suitability in field applications [17]. The physical changes associated with the diffusion of the penetrants through the composite have been analyzed by *S-D-RS* studies. The solvent saturated sample was desorbed completely, allowed to sorb the solvent again. The S-R-S curves of 100/7.5 EPDM/PVC composite vulcanized by sulphur in diesel are shown in Figure 5.7. The resorption curves show that the equilibrium uptake values and the time taken to attain equilibrium are higher compared to the first sorption process. This can be due to the leaching out of the ingredients and also the solvent stress which causes a small change in free volume.

5.3 Conclusion

The transport characteristics of EPDM/PVC composites were studied using carbon tetra chloride, chloroform and methylene chloride as penetrants in a temperature range of 28-38^{o}C, with special reference to filler loading, crosslinking systems, concentration of sulphur, penetrant's nature and temperature. The diffusion of halogenated hydrocarbon solvents through EPDM/PVC composites revealed that the diffusion was found to decrease with an increase in PVC content which was attributed to the rigid nature of PVC particles. The sample crosslinked by DCP showed the lowest equilibrium uptake compared to the sample with sulphur vulcanization mode. This can be explained in terms of the differences in the nature and distribution of crosslinks in the network. A peculiarity can be seen among the group of chloromethanes, i.e. methylene chloride, chloroform and carbon tetra chloride. Sorption increases with increasing number of chlorine atoms or molar volume, as it would be predicted from simple solubility parameter considerations. The polymer-solvent interaction The transport behavior of EPDM/PVC composites has been investigated using the three halogenated hydrocarbons; ethylene chloride, chloroform .The ‘n’ values suggest that the mechanism of transport is anomalous.

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Chapter 6

Interactions of some liquid fuels with EPDM/PVC composites

Summary

The interaction of EPDM /PVC composites with three liquid fuels viz; petrol, kerosene and diesel has been studied. The solvent transport was found to decrease with increase in PVC content in the composites. Diesel showed the lowest interaction with the composites compared to petrol and kerosene. The effect of crosslinking system and the type of vulcanization on the swelling behavior has also been analyzed. The observations have been explained in terms of their morphology, using scanning electron micrographs. The DCP system showed lower solvent uptake than sulphur system which can be explained by the difference in the nature of the cross chemical bonds introduced between the macromolecular chains during vulcanization. Dynamic vulcanized sample showed lower solvent uptake than static vulcanized one, due to the fine dispersion of the PVC particles in EPDM matrix. The observations have been supported by the thermodynamic sorption constant.

6.1 Introduction

Polymer and polymer composites are increasingly being used in a wide range of applications where long-term service in hostile environments is required. As a consequence, manufacturers of polymer-based materials are increasingly being asked for assurance of product lifetime, particularly for components, which cannot be easily inspected or may fail catastrophically in service. Understanding the mobility and distribution of penetrant molecules in polymeric systems is crucial for the success of a wide variety of applications of polymers. Swelling experiments of rubber composites are important for analyzing the service performance of these composites in such environments. Rubber articles come in contact with different liquids during service performance. This can happen either as a part of the service requirement as in the case of of oil seals or by accidental splashing of oils and greases that occurs with automobile components. The contact of rubbers with organic solvents can be well explained by absorption and diffusion phenomena . The amount of swelling at equilibrium was treated as a special case of Flory Rehner theory. The mass transport process through filled polymer systems is influenced by factors such as nature of fillers, the degree of adhesion, their compatibility with the polymer matrix, nature of components, crosslink density and nature of penetrants. Swelling experiments are important because they give valuable information about the service performance of composites in liquid environment and also to study the characteristics of rubber / fibre interface [1].Lowering of equilibrium swelling in filled samples generally indicate an excellent filler-matrix adhesion. For all practical purposes, liquids that attack crosslinked rubbers either degrade the rubber or cause swelling through absorption. A swollen elastomeric network is much weaker and more susceptible to damage, although in certain sealing applications, a small positive swell is beneficial for the retention of sealing force One sector where the use of polymer materials is still evolving is the automotive industry, where they are coming in contact with various industrial fuels, oils and lubricants. Petrol comprises a mixture of many thousands of different hydrocarbon compounds plus additives that may contain other elements.

There exist interesting reports on the molecular transport through different polymer membranes [2-4]. It has been reported that the permeation depends upon a number of factors like composition, method of formation, type of cross linking agents used, nature and size of the penetrants, temperature etc. For example, a decrease in diffusivity with an increase in the size of penetrant has been reported by many investigators [5, 6].Greenwood [7] studied the permeability of polymer pipework for underground use at petrol stations. It was observed that the permeability is not sensitive to the proportion of volume filled with fuel and a polyamide composite liner on the inside reduced the permeability to 0.15 g/m2 day. Diesel oil includes heavy gas oils, obtained from the lowest fraction from atmosphericdistillation of crude oil, while heavy gas oils are obtained by vacuum redistillation of the residual from atmospheric distillation. Sombatsompop et al.[8] investigated the oil resistance of acrylonitrile-butadiene rubber (NBR) filled with 60 phr carbon black (CB) and different amounts of silica from fly ash [fly ash silica (FASi)] and precipitated silica (PSi). The solvent resistance of NBR vulcanizates increased with CB and silica. The results in this work suggested that silica from fly ash particles could be used as an extender for cost savings in NBR compounds.K.J. Kallio etal [9] developed a new test method which enables to investigate the fuel permeation properties of polyamide-12 (PA-12) – based pipes. Fuel lines were exposed to circulating fuel with equal volume contents of toluene, isooctane and 0, 25 or 85 vol.% ethanol for up to 6 months at 60–110 °C. The pipes were either of a single PA12-layer or a multi-layer type, the latter having a poly(vinylidene fluoride) barrier layer between two PA12 sections. With a Thwing-Albert cup attached to the fuel line, it was possible to expose a pipe-section to surrounding air running in a separate pipe loop at a controlled flow-rate. Gas/vapour samples were collected from this loop using a syringe and, subsequently, analysed with a flame ionization detector. It was observed in the case of multi-layer pipes that the presence of ethanol increased the permeability (average values) of the “total” fuel as well as of the individual hydrocarbons. In addition, the 60 °C fuel permeability (85 vol. %

ethanol) increased after a high temperature (110 °C peak) cycle, whereas the ethanol-free fuel flux seemed to decrease.

In the present work Equilibrium sorption studies have been conducted using commercial fuels like petrol, diesel and kerosene in order to understand the interfacial adhesion and performance of PVC reinforced EPDM composites under these environments. Effect of curing temperature, PVC loading, penetrant size and crosslinking agent on the equilibrium swelling of EPDM/PVC composites have also reported.

6.2 Results And Discussion

6.2.1 Effect of PVC Loading

Figure 6.1 shows the amount of diesel sorbed throughs statically vulcanised pure EPDM and 100/2.5 EPDM/ PVC system. It has been observed from the figure that EPDM shows higher sorptrion than the PVC loaded system due to the flexible nature of the chains that creates more free volume in the matrix. Adding rigid PVC to EPDM phase improves the barrier property due to the reduction in free volume or microvoids.Increase in PVC content also restricts the macromolecular chain mobility resulting in a tortuous path for the diffusion of the penetrants.

6.2.2 Effect of Amount of PVC

Figure 6.2 shows the swelling behaviour of different statically vulcanised composites in diesel.The solvent uptake decreases from 100/0 EPDM/PVC to 100/10 EPDM/PVC.It implies the reduction in free volume or microvoids due to better filler reinforcement.Increase in filler content also restricts the macromolecular chain mobility resulting in a tortuous path for the diffusion of penetrants. At low filler loading,relatively large distances between the dispersed particles exist.In this case,the rubber chins are attached to one particle because of a single attachment or multiple attachment of chain segments of one rubber molecule.With the increase in the concentration of dispersed particle,a coherent gel can be formed and this gives rise to lesser chain flexibilty leading to lower sorption characteristics[10].

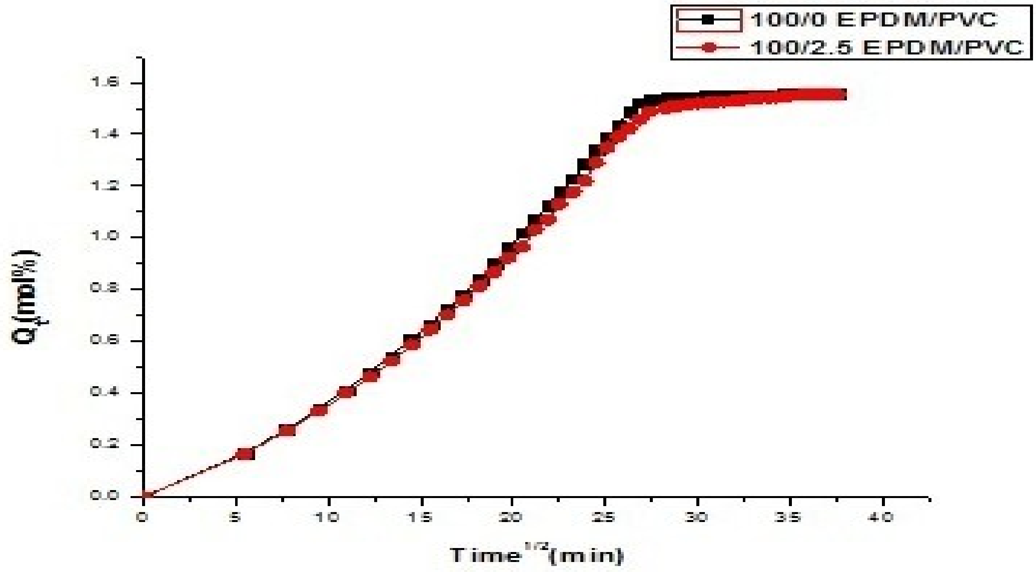

Figure.6.1 Effect of PVC loading on mole percentage diesel uptake by statically vulcanized pure EPDM and EPDM/PVC (2.5phr) composite.

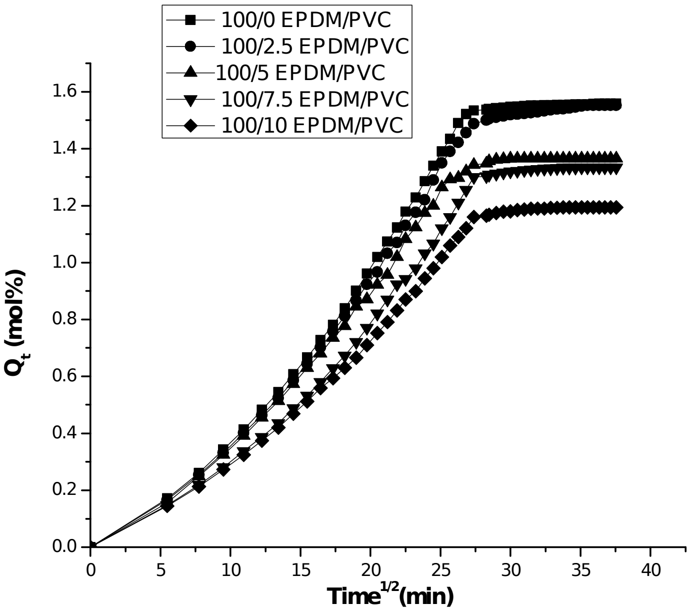

Figure 6.2 The mole percentage diesel uptake by statically vulcanized EPDM and EPDM/PVC composites

This can be better understood by determinig their swelling coefficient(α) values calculated using the equation[11]

$$\alpha = \frac{M_{\infty} - M_0}{M_0\,\rho}$$

Where M α is the mass of the swollen rubber sample at equilibrium saturation,Mo is the original mass of the cmposites and ρ is the solvent density.The swelling coefficient values of composites are give in table 6. 1.It has been found that the swelling coefficient value decreases with increase in PVC content,due to rigid nature of the PVC , supporting the solvent uptake behaviour.

Table 6.1. Swelling coefficient values (in diesel).

EPDM/PVC	**£**
100/0	0.0042
100/2.5	0.0039
100/5	0.0036
100/7.5	0.0028
100/10	0.0025

6.2.3 Crystallinity

Pure EPDM has been found to show the highest solvent uptake, in all penetrants, due to the complete amorphous nature of the matrix. The liquid uptake tendency decreases with an increase in PVC content in the blends. The macromolecular chains of EPDM undergo rearrangement readily to accommodate solvent molecules during sorption. The presence of the crystallites of PVC in the matrix generates a more tortuous path for the penetrants and subsequently, the rate of solvent ingression and equilibrium sorption values decrease. As the amount of PVC in the composites increases, the matrix becomes more crystalline. Figure 3.11shows the effect PVC loading on the crystallinity of the matrices under investigation. The reduction in the equilibrium solvent uptake is due to the modification of the amorphous component, EPDM, with the rigid phase of pure PVC.

6.2.4 Morphology

Morphology is a major determinant of properties of heterogeneous polymer systems The scanning electron micrographs of statically vulcanized EPDM/PVC and, EPDM/PVC composites using sulphur as the crosslinking system are shown in Figure 3.13(i). Particles are found to be randomly dispersed as domains in the continuous EPDM matrix. The particle size of the dispersed phase was found to be decreased and the composite attains a relatively uniform morphology for 100/7.5 EPDM/PVC samples. From the scanning electron micrographs, it can be concluded that the distribution of PVC domains becomes more uniform when the EVA content increases, which contributes to the observed decrease in the diffusion of solvents.

6.2.5 Effect of Penetrants

The size,shape and side chain of the penetrant molecule is found to influence its rate of diffusion through the polymer membrane[12]. The effect of molecular weight of the three solvents on the mole percentage uptake by the EPDM/PVC (7.5 phr) sample at 28°C is shown in Figure 6.3. There is a systematic trend in the sorption behaviour of liquids of different molecular weight. With an increase in molecular weight of the solvent molecules, there is a decrease in the values of Qt and $Q\infty$ for all the systems. Petrol shows the maximum value of $Q\infty$ and diesel the minimum, among the solvents used in the work. Kerosene takes an intermediate position. The low molecular weight hydrocarbons present in petrol can easily penetrate into the material. As the molecular size increases as in Kerosene and diesel, the uptake of solvent decreases. This may be due to the larger size of solvent molecule that hinders the molecule from entering into the solvent pockets present in the composite. An exactly similar trend is observed for all the compositions. This can be explained on the basis of free volume theory, according to which the diffusion rate of a molecule depends primarily on the ease with which the polymer chain segments exchange their positions with the penetrant molecules. As the penetrant size increases, the ease of exchange becomes less, particularly in the case of filled matrices.

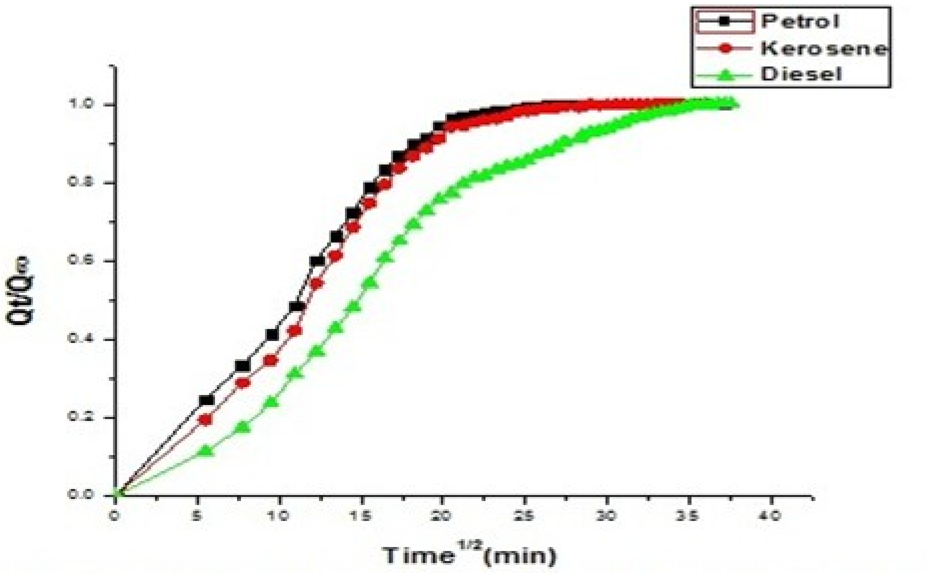

Figure 6.3 The mole percentage uptake by dynamically vulcanized 100/7.5 EPDM/PVC in petrol, kerosene and diesel

6.2.6 Effect of cross-linking

Figure 6.4 shows the effect of cross-linking system on the sorption behavior of EPDM/ PVC membranes, cross-linked by two vulcanizing modes, viz., sulphur and DCP with diesel as probe molecule. It is observed that the liquid sorption behavior decreases from sulphur to DCP. This can be explained by the nature of the cross chemical bonds introduced between the macromolecular chains during vulcanization. The sulphur vulcanization introduces mono sulphidic and poly sulphidic linkages between the chains. The polysulphidic linkages between the rubber chains give overall flexibility for the network and help to accommodate more solvent between the rubber chains. The DCP which introduces only C-C linkages, do not allow the chains to rearrange easily under solvent stress. This accounts for the lowest solvent uptake by DCP cured systems [13]. The values of Ø for 100/5 EPDM/PVC for sulphur and DCP crosslinked systems are 0.2813 and 0.2881 respectively, as diesel as the penetrant. The sulphur system shows the minimum value, which is exactly in compliance with the order noted for Q_t values. A schematic representation of the networks formed by different crosslinking systems has been given in Figure 3.4.

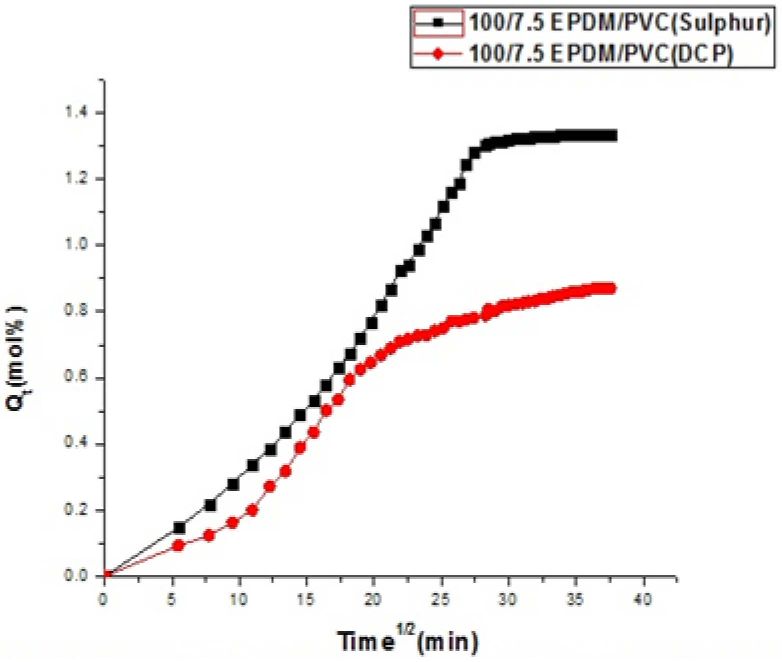

Figure 6.4 Mole percentage uptake of diesel by statically vulcanized 100/7.5 EPDM/PVC with different crosslinking systems

By means of accelerators and activators the sulphur cycle opening (1) occurs providing for an active sulfurizing complex. (2) The self destruction of this complex results in an active sulfur oligomer (3), which reacts with the ruber molecules crosslinking them (4).Due to the high vulcanization temperatures, thermo-oxidative degradation of the rubber molecules as well as the sulphidic bridges can take place. Maturation (5) is the separation of sulfur from the polysulfidic bridges. Reshuffling the crosslinks may form intramolecular bridges (cyclic structure).

The process of rubber peroxide crosslinking consists of three basic steps as follows:

(a) Homolytic cleavage

When a peroxide is heated to above its decomposition temperature, the oxygen-oxygen bond ruptures. The resulting molecular fragments are called free radicals, which are reactive species with high energy.

$$\mathrm{ROOR} \longrightarrow \mathrm{RO^*} + \mathrm{{}^*OR}$$

(b) Hydrogen abstraction

Those radicals that are generated from the peroxide decomposition are reactive to hydrogen atoms in the polymer chains. Hydrogen abstraction is a process that the radical removes a hydrogen atom from another nearby atom, through which radicals are transferred from the peroxide molecular fragments to the rubber backbone

$$\mathrm{RO^*} + \mathrm{P\text{-}H} \longrightarrow \mathrm{ROH} + \mathrm{P^*}$$

(c) Radical coupling

Rubber radicals are highly reactive species and when the two of these radicals come in contact, the unpaired electrons will couple and form a covalent bond or crosslink between the rubber chains.

$$\mathrm{P^*} + \mathrm{P^*} \longrightarrow \mathrm{P\text{-}P}\ \text{(crosslink)}$$

6.2.7 Effect of Type of Vulcanization

Figure 6.5 shows the effect of the type of vulcanization techniques on the sorption behavior of EPDM/ PVC membranes, using diesel as penetrant. It is observed that dynamically vulcanized samples showed a lower swelling compared to the corresponding statically vulcanized one.

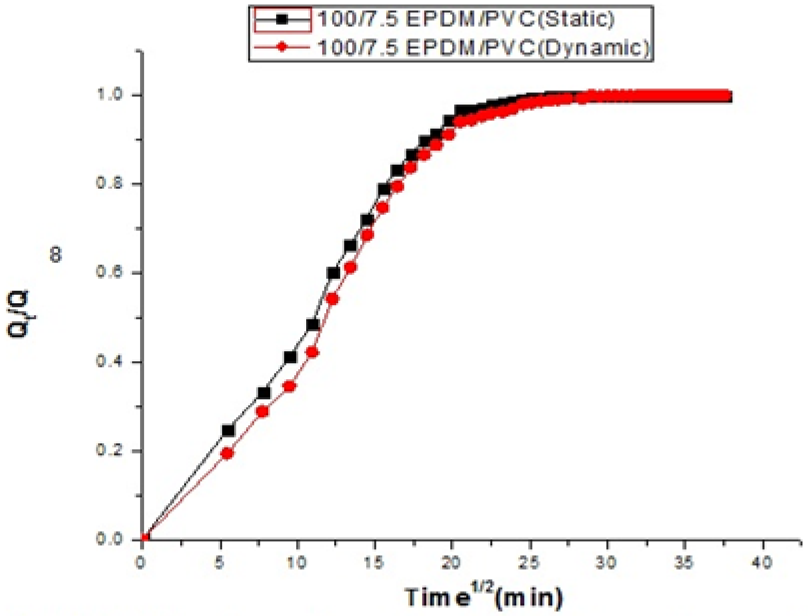

Figure 6.5 Effect of type of vulcanization techniques on the sorption behavior of 100/7.5 EPDM/PVC, using diesel as penetrant

The dynamic vulcanization produces a fine dispersion of the rigid PVC particles in EPDM matrix [14] as can be seen from FESEM of statcally and dynamically vulcanised 100/7.5 EPDM/PC compostes in figure 3.13. This generates a matrix with relatively lower free volume for sorption of solvent.

6.2.8 Sorption, Diffusion, and Permeation Coefficient

Sorption describes the initial penetration and dispersal of penetrant molecules into the polymer matrix. It is calculated using the equation,

$$S = \frac{M_\infty}{M_0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .6.1$$

where, M_∞ is the mass of the solvent at equilibrium swelling and M_0 is the initial polymer mass. The diffusivity,D,of the composite-solvent system has been calculated using the equation,

$$D = \pi\left(\frac{h\theta}{4Q_\infty}\right)^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .6.2$$

Where θ is the slope of the initial portion of the plots of Qt versus $t^{½}$.

The permeation coefficient for all the systems under investigation was calculated by using (1.9).

The values of S , D and P for sulphur cured samples are given in Table 6.2.The maximum value for 100/0 EPDM/PVC system is an indication of the better accommodation of solvent molecules in the highly flexible polymer chains.

Table 6.2 Values of Sorption (S) and Permeation constant (P)

System	100/0	100/2.5	100/5	100/7.5	100/10
S	3.7432	3.2513	3.1473	2.4940	2.1273
$DX10^4(cm^2/sec)$	1.64	1.47	1.23	0.821	0.748
$PX10^4(cm^2/sec)$	6.13	4.77	3.86	2.0	1.5

6.2.9 Thermodynamic Parameters

Thermodynamic sorption constant is a measure of the solvent uptake by the polymer. Thermodynamic constant K_s is defined as

$$K_s = \frac{\text{Number of moles of solvent srbed at equilibrium}}{\text{Mass of the polymer sample}} \quad \ldots\ 6.3$$

The values of K_s are placed in Table 6.3. The values of K_s are in the same order of equilibrium mol % uptake and are related to crosslinks.

Table 6.3 Thermodynamic Sorption Constants (K_s mol kg^{-1})

EPDM/PVC	**K_s**
100/0	22
100/2.5	19
100/5	18.5
100/7.5	14.6
100/10	12.5

6.2.10 Swelling mechanism

In order to investigate the type of transport mechanism, the sorption results were fitted to the following equation [5.1]

The value of n determines the mode of diffusion mechanisms. The values of n and K are given in table 6.4. Plot of log (Q_t/Q_{∞}) versus log t showed that the values of n were between 0.5 and 1 and this suggested that the mechanism of transport slightly deviates from normal Fickian behavior observed for conventional elastomers

Table 6.4 Values of n and K at 28 °C for different penetrants in 100/7.5 EPDM/PVCcomposite

Solvent	**Type of crosslinking**	**n**	**Kx10^{-2}(g/g min^2)**
Petrol	Sulphur	0.53	3.86
Kerosene	Sulphur	0.54	3.02
Diesel	Sulphur	0.71	0.942
Diesel	DCP	0.74	0.74

6.3 Conclusions

The transport characteristics of EPDM/PVC composites, vulcanized by DCP and sulphur have been studied. The solvent transport has been found to be decreased with an increase in PVC content in the composites. It implies the reduction in free volume or micro voids and also the restriction of the macromolecular chain mobility with increase in PVC content. The observations have been explained in terms of their morphology, using scanning electron micrographs. The DCP system showed lower solvent uptake than sulphur system which can be explained by the difference in the nature of the cross chemical bonds introduced between the macromolecular chains during vulcanization. Dynamic vulcanized sample showed lower solvent uptake than static vulcanized one, due to the fine dispersion of the PVC particles in EPDM matrix.

6.4 References

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Chapter 7

Ageing Behaviour of EPDM/PVC composites

Summary

The effect of thermal and weather ageing on observed properties of the EPDM/PVC composites was compared by measuring changes in modulus,tensile strength ,tear strength and elongation at break.The elongation at break and tensile strenght of all samples decreased due to weathering.*The morphology of the samples were studied to compliment the observations.The chemical resistance of the samples were also studied in acid and alkali solutions. In the case of chemical resistance behavior, it has been observed that resistance towards chemicals increases with the increase in PVC loading.This may be due to increase in PVC content in the composite which is not vulnerable to the chemical attack.It can be seen that the 100/10 sample has got the greatest resistance. The results indicate that incorporation of PVC hasimproved aging behavior significantly.*

7.1 Introduction

Many types of thermoplastic elastomers are used in outdoor applications and a common concern of these materials is the durability of the materials in enduse applications. During long periods of service, most of the polymer products gradually lose their properties due to the macromolecular chain degradation. Normally, polymers in the state of their end-use are not pure materials. In many cases there are added substances which alter the engineering and/or chemical properties of the polymer in a useful way. The polymer also may contain small amounts of monomer, entrapped during the polymerization process. Such additives and impurities may participate in the slow chemical degradation of the polymer and, of course, add to the general physical complexity of the polymer. If the polymer is attacked by the environment,the performance of the material in service will be adversely affected.Degardation of the performance of the polymer may lead to premature failure of the material,resulting in increased downtime for the system, and requiring costly maintenance procedures. The study of dimensional stability and mechanical properties of polymeric materials under different environmental conditions such as humidity changes or changes in temperature, solvent, mechanical load, radiation, deserves much importance. This is because materials with superior ageing resistance can be satisfactory durable. It has been reported that the short time ageing at high temperature improves the mechanical properties of thermoplastic composites. This can be explained by an additional process of annealing of the thermo pressed composites at the softening temperature [1]. Mechanical properties such as tensile strength, modulus, elongation are decreased by chain degradation while cross-linking enhance these properties. The long-term exposure of polymeric composite materials to extreme-use environments, such as pressure, temperature, moisture, and load cycles, results in changes in the original properties of the material. These changes in material properties translate to structural changes that can have a potentially catastrophic effect on load-bearing composite structures. Therefore the study and understanding of the long-term effect of exposure on the time-dependent viscoelastic properties of polymeric composite structures is crucial to their proper design, construction, and safe operation.

Since a polymer is a repeating chain of simple chemical functional groups linked together, the usual types of chemical reactions that the individual functional units undergo in small molecules also apply to a polymer of these groups. However, the rates at which these reactions take place are often altered because of morphological effects in the solid polymer which are not present in solutions and vapors of simple organic molecules. In general, because of the difficulty encountered with the penetration of chemical agents and, radiation (e.g., sunlight) into a solid polymer, chemical degradation rates are usually considerably slower for the polymer than for small organic molecules made from the same functional groups .Degradation may be initiated several ways. Absorption of ultraviolet radiation and/or thermal energy can lead to rupture of weak bonds. This is often followed by formation of new bonds to give an alteration of the original polymer structure.The presence of oxygen, water and atmospheric pollutants can alter these processes and lead to the formation of new types of chemical groups. Bond-breaking processes may occur in polymer backbone bonds to lower the average length of the polymer chains and/or in pendant group bonds leading to the emission of small molecules. Bond-making processes between chains give crosslinked material of increased molecular weight and rigidity. Two experimental options are used to characterize the viscoelastic properties of polymeric composites: the conventional and time-consuming method of directly measuring the response over long periods of time and the second method of using accelerated aging processes to obtain the properties during short term testing. During thermal ageing, cross link formation or cross link breakage can take place or an existing cross linkmay break and a stable linkage can be formed. In composites, bonding action of the resin also take place during ageing. All these reactions greatly influence the performance of the composites.

To reduce the time required to evaluate the durability of materials, accelerating ageing by artificial weathering is sometimes used.Such artificial weathering systems simulate temperature,humidity, and solar radiation but often the individual parameters are more intense than the average values under general exposure conditions.Following the ageing process,the material is tested and the results are compared with those obtained for control samples. If time admits, real exposure tests outdoors are still preferable.Measurements of the mechanical properties before and after the exposure will then give information about the weathering resistance of the polymers.

There exist a number of reports on ageing of polymers[2-6]. Harvey Alter examined [7] literature data for the effect of mineral fillers on the mechanical properties of polyethylene at two temperatures, styrene–butadiene rubber, and natural rubber were examined. The data for modulus, tensile strength, elongation at yield and ultimate elongation could be well represented by linear plots of the relative mechanical property (ratio of the values for the filled to the unfilled) as functions of the reciprocal of the filler particle size. A plot of one of these properties versus reciprocal filler size shows a family of lines, one line for each concentration of filler and independent from the chemical nature of the filler. The dependence of the mechanical properties on reciprocal particle size may express a dependence on the surface-to-volume ratio of the filler, a balance between the effective cross-linking due to the large surface area of the filler and the dilution of the polymer by the volume of filler present. Viveca Lonnberg & Paul Starck [8] compared the weather resistance of different thermoplastic elastomer blends by measuring the change in hardness, tensile modulus, tensile strength and elongation at break. hardness and modulus of the materials changed to a very small extent during the exposure period .The elongation of the partly cross linked PP/EPDM decreased drastically due to the migration of the plasticizing oil.Also tensile strength of all TPEs decreased.

The objective of this study is to compare the weather,thermaland solvent resistance of EPDM/PVC cmposites and to compare the properties to those of the control samples.Also accelerated ageing method and resistance to chemicals is also investigated.The ageing of the materials was studied by measuring the changes in different mechanical properties such as tensile modulus,tensile strenght,tear strenght and elongation at break and from the morphology.

7.2 Results and discussion

7.2.1 Effect of thermal ageing on mechanical properties

7.2.1.1 Effect of PVC loading

Figure 7.1 shows the tensile strenght of peroxide cured pure EPDM before and after thermal ageing at 100^{0}C for 3days .Figure 7.2 shows the variation in tensile strenght after thermal aging for the same period.It can be seen that PVC loaded sample has more aging resistance than pur EPDM.

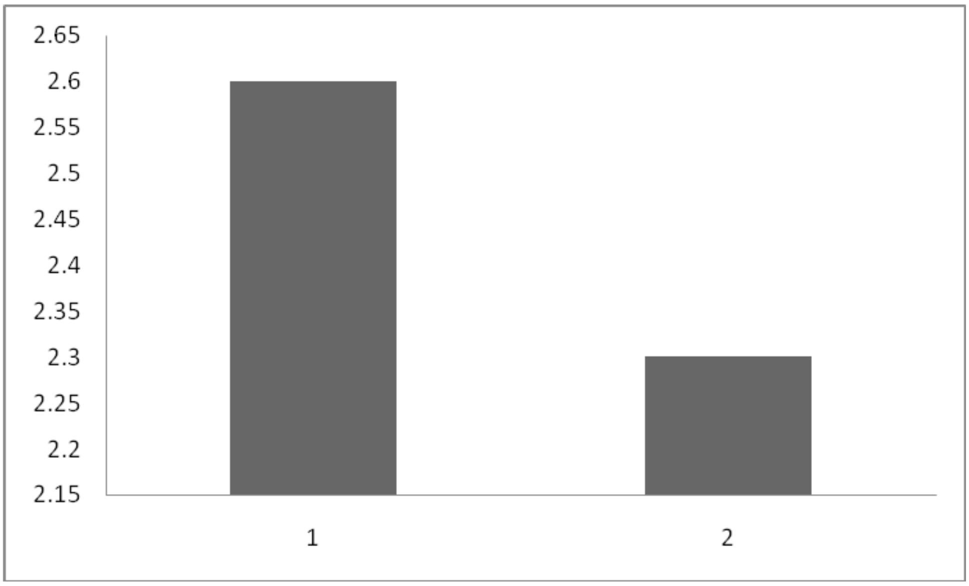


Figure 7.1 Tensile strenght of peroxide cured pure EPDM before and after thermal ageing; 1. unaged and 2. aged

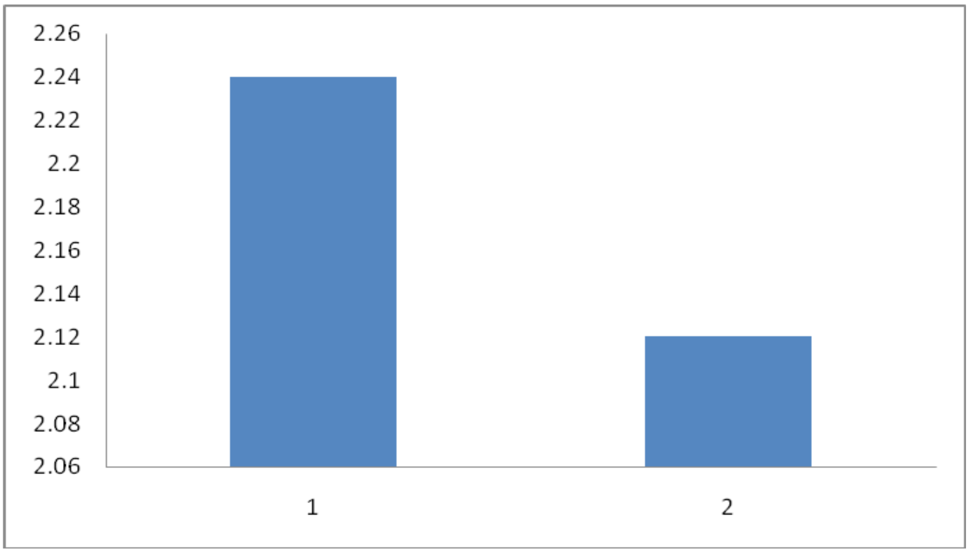


Figure 7.2 Tensile strenght of peroxide cured PVC loaded EPDM before and after thermal ageing;1.unaged and 2. Aged.

7.2.1.2 Effect of amount of PVC

Figures 7. 3 shows the tensile strenght of unaged and thermally aged peroxide cured EPDM/PVC composites as a function of PVC loading.Tensile strenght of all unaged samples incresese with PVC loading upto 7.5 phr and then decreases.Tensile strenght of all samples decreadses after aging at 100°C.This is due to the degradation of crosslinks at elevated temperature. It can be seen from the figure that 100/7.5 EPDM/PVC has maximum aging resistance among all the composites.

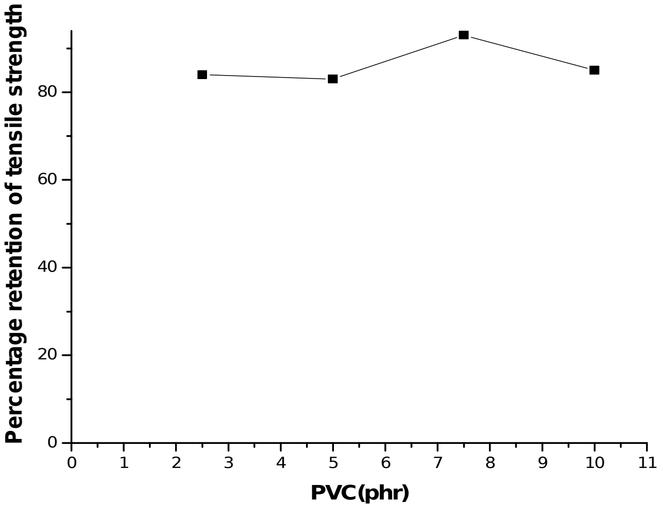


Figure 7.3 Percentage retention of tensile strenght of EPDM/PVC composites after 3 days thermal ageing at 100 °C

7.2.2 Effect of solvent swelling on mechanical properties

The retention of mechanical properties of the EPDM/PVC composites after immersing the samples in different solvents like aromatic,halogenated hydrocarbon and mixture of aliphatic hydrocarbons for 24 hours are given in the table 7.1.Among these solvents,the composite exhibits maximum aging resistance in Kerosene .

Table 7.1 Percentage retention of mechanical properties of 100/5 EPDM/PVC composite after immersion in solvents for 24 hours

Solvent	Tensile strenght	Young’s modulus
Toluene	84	58
Carbon tetra chloride	78	68
Kerosene	55	72

7.2.3 Swelling coefficient values

Swelling coefficient values of the 100/5 EPDM/PVC composite calculated using equation 2.2 in different solvents are given in table 7.2.

Table 7.2 Swelling coefficient values of sulphur cured 100/5 EPDM/PVC composite

Solvents	Swelling coefficient
Benzene	1.87
Carbon tetra chloride	2.9999
Diesel	0.0036

7.2.4 Effect of natural weathering on the mechanical properties

The effect of natural exposure of pure EPDM and 100/2.5 EPDM/PVC composite on tensile strenght are given in figures 7.4.The modulus of the tested samples has changed to a very small extent during the exposure period.The elongation of the composites decreased drastically in all the samples.Also tensile strenght of the composite samples decreased to some extent.

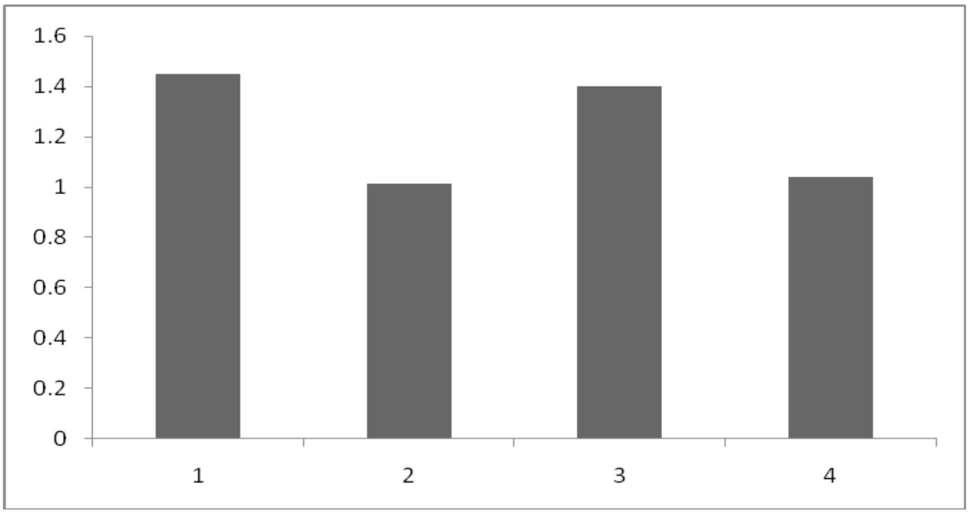
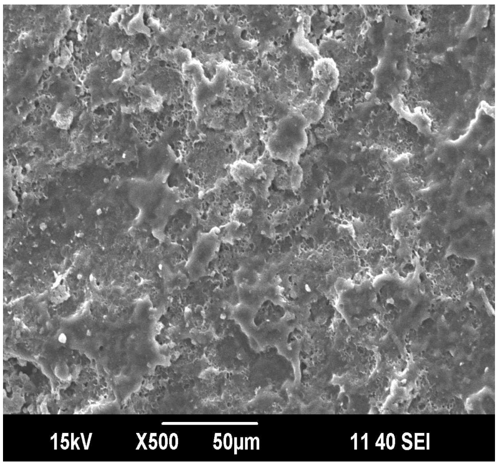


Figure 7.4 Tensile strenght of sulphur cured EPDM/PVC composite before and after natural weathering;1.unaged pure EPDM , 2. aged EPDM, 3.unaged 100/2.5 EPDM/PVC and 4.aged 100/2.5 EPDM/PVC composites.

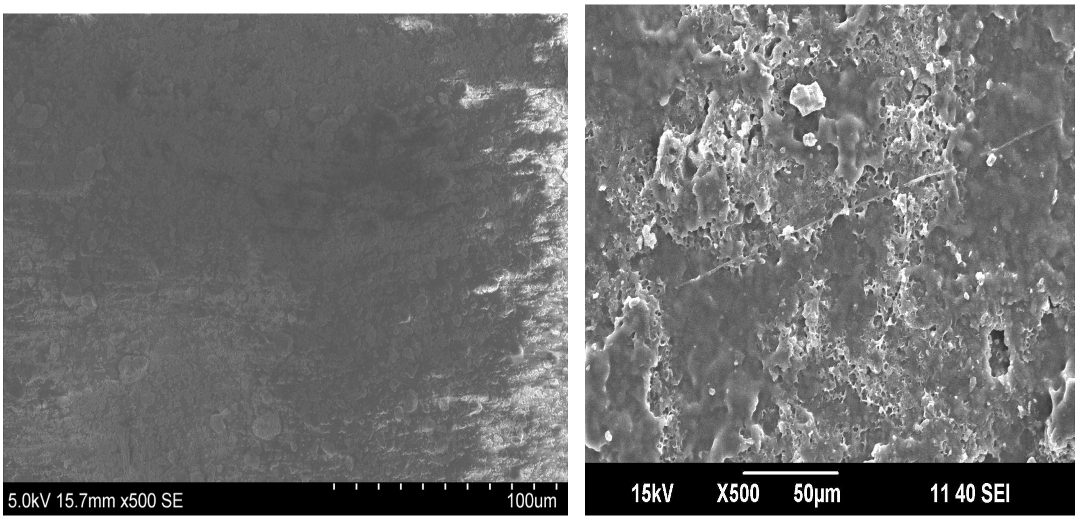
7.2.5 Effect of natural weathering on Morphology

Scanning Electron Micrograph is a reliable tool to monitor the surface changes during degradation of polymers. The presence of highly eroded surface with small cavities in the samples, indicates the higher degradation after 4 months exposure to natural weathering. Because at 2 days aging time, the vulcanization process was completed then the aging caused the degradation for the crosslink between EPDM vulcanizates with increase aging time**.** From the SEM pictures ,it is clear that the100/7.5 EPDM/PVC and 100/10 EPDM/PVC composites have less degradation.



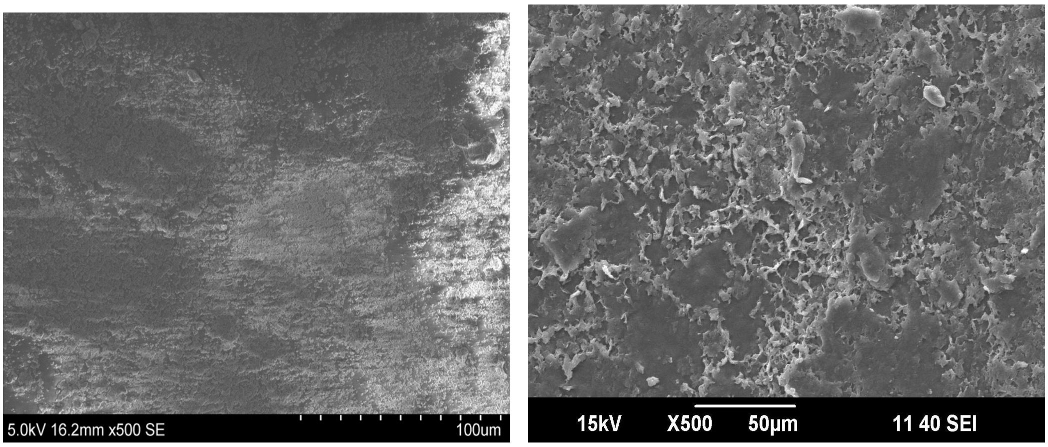
(a) **(b)**

Figure 7.5 (i)Natural weathering for four months of statically vulcanized sulphur cured 100/0 EPDM/PVC (a) before ageing (b) after ageing



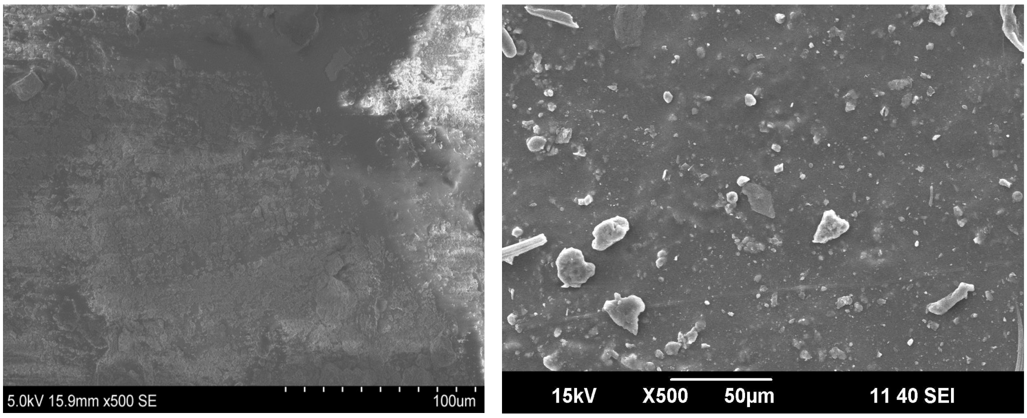
(a) before aging (b) after aging

Figure 7.5 (ii)SEM picture of statically vulcanized sulphur cured 100/2.5 EPDM/PVC after natural weathering for four months



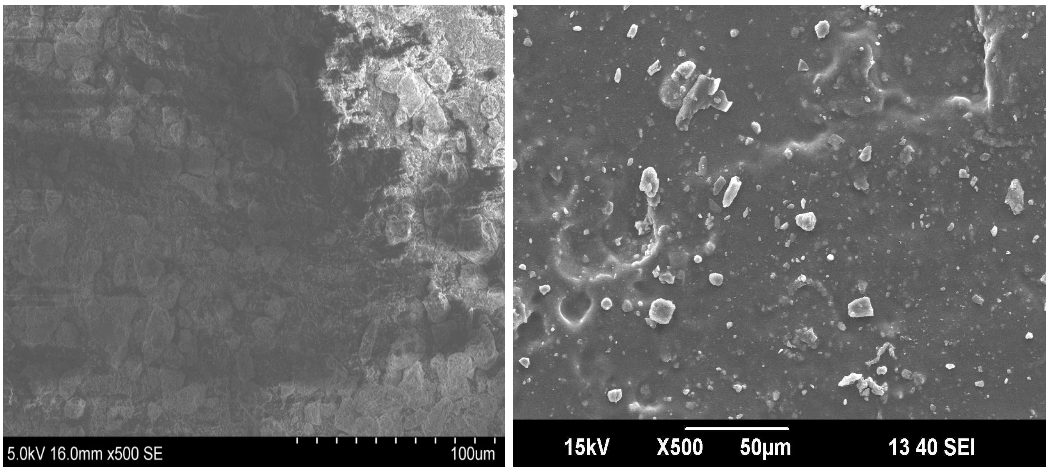
(a) before aging **(b)** after aging

Figure 7.5 (iii) SEM picture of statically vulcanized sulphur cured 100/5 EPDM/PVC after natural weathering for four months



(a) before aging (b) after aging

Figure 7.5 (iv) SEM picture of statically vulcanized sulphur cured 100/7.5 EPDM/PVC samples after natural weathering for four months



(a) before aging (b) after aging

Figure 7.5 (v) SEM picture of statically vulcanized sulphur cured 100/10 EPDM/PVC composites after natural weathering for four months.

7.2.6 Chemical resistance

The percentage chemical resistance (P_{cr}) of EPDM/PVC composites calculated by equation 2.11 in water, saline water, IN HCl and IN NaOH after 30 days of exposure are given in table 7.3 and 7.4.The results indicate that the composite has high resistance toewards water and saline water.Also,the chemical resistance increases with increase in PVC content due to the chemical resistance of PVC.

Table.7.3 Percentage chemical resistance of100/5 EPDM/PVC in water

Solvent	Pcr
Saline water	0.013
Water	0.017

Table 7.4 The percentage chemical resistance of EPDM/PVC composites in IN HCl and IN NaOH

Sample	P_{cr} in (HCl)	P_{cr} in (NaOH)
100/0 EPDM/PVC	0.761	1.393
100/2.5 EPDM/PVC	0.5884	1.617
100/5 EPDM/PVC	0.3180	1.6894
100/7.5 EPDM/PVC	0.3913	1.300
100/10 EPDM/PVC	0.2541	1.276

7.3 Conclusion

During long periods of service, most of the polymer products gradually lose their properties due to the macromolecular chain degradation. This is due to the action of degrading agents such as heat, oxygen, ozone and high energy radiation on them. The effect of these degrading agents depends mainly on the chemical structure of the polymer chain. The mechanical properties of polymers are also changed considerably by the action of these different degrading agents. This may be the result of either cross-linking or degradation of polymer chains.

The effecet of thermal and weather ageing on observed properties of the EPDM/PVC composites was compared by measuring changes in modulus,tensile strenght and elongation at break. The morphology of the samples were studied to compliment the observations.The chemical resistance of the samples were also studied in acid ,alkali ,water and saline water solutions.The results indicate that incorporation of PVC into EPDM matrix improved aging behaviour significantly.

PVC is a normal impact, high corrosion resistant polyvinyl chloride. Because of its exceptional corrosion resistance, it is ideally suited for applications where maximum chemical resistance is necessary.

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Chapter 8

Conclusions and Future Outlook

Summary

The major findings based on the present investigation have been summarized in this Chapter. The results of the various examinations like barrier property, cure characteristics, mechanical properties, dielectric properties, thermal features, X-ray analysis, morphology and ageing characteristics under different environmental conditions have been consolidated. The scope of future studies based on the results of the work has also been discussed.

8.1 Conclusions

It has been well- recognized that polymer composites offer a key option in solving many emerging materials' application requirements. It allows to overcome certain deficiencies of the parent material by incorporating other suitable component and also to develop new structural systems by mixing different polymers .The ability to combine existing polymers into new compositions with commercializable properties offers the advantage of reduced research and development expenses compared to the chemical synthesis of new polymers to yield a similar property profile. The addition of fillers to polymers is a fast and cheap method to modify the properties of the base materials. For this reason, particulate filled polymers have been, and continue to be, the subject of increasing interest in both industry and research. In this way, barrier property,strength, stiffness, electrical and thermal conductivity, hardness and dimensional stability, among other properties can be tailored to the required values. 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,fertilizers and pesticides. 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 system. This technology could revolutionise the biochemical, pharmaceutical and other chemical industries. Correct and energy advanced polymerization and catalyst technologies also provide the ability to design polymers to meet application and processing needs that are important to meet the ever increasing demands for product quality ,uniformity and performance.

Ethylene propylene diene monomer (EPDM) is a synthetic elastomer extremely useful in the automotive, electrical and construction industries, due to its unique mechanical and chemical properties. EPDM exhibits excellent resistance to weather, ozone, acids and alkalies while accommodating high volume fraction of fillers and liquid plasticizers and retaining desirable physical and mechanical properties. However, its performance is inferior in the presence of organic solvents and oils. Poly vinyl chloride (PVC), a rigid low cost material, offers excellent weather resistance, toughness, chemical resistance, solvent resistance and processability. By blending EPDM and PVC in suitable ratios, it is possible to develop materials with the attractive features of both of them. No systematic study has yet been carried out to evaluate the influence of mode of vulcanization on the transport properties of EPDM/PVC composite system with special reference to the effects of filler ratio and crosslinking systems. A systematic attempt has there for been done, through the present investigation, to develop and characterize crosslinked EPDM / PVC system.

The composites were prepared by static and dynamic vulcanization techniques, by using three different vulcanizing systems viz. sulphur, dicumyl peroxide and mixed. The transport characteristics of the blends were examined by using organic probe molecules. The evaluation of cure characteristics, mechanical features and thermal properties has also been done. The findings have been supported by morphological studies and X-ray analysis.

Initially, examinations on the transport, mechanical and thermal features of EPDM/PVC composites vulcanized by DCP, sulphur and a mixed system of sulphur and DCP have been carried out. The solvent transport has been found to be decreased with an increase in PVC content in the systems. The observations on the transport behavior through the blends have been explained in terms of their morphology, using scanning electron micrographs and X-ray diffraction studies. Mechanical studies revealed that sulphur and mixed systems showed almost similar stress-strain behaviour. To attain an impressive morphology, the blends were dynamically vulcanized in the next phase, and the sorption and permeation characteristics were compared with those of statically vulcanized blends. The influence of cross linking techniques, blend composition,cross-linking systems and nature of penetrants on transport through EPDM/PVC composites was analysed. Dynamically vulcanized composites showed enhanced transport resistant properties compared to the corresponding statically vulcanized blends. The sorption behaviour of dynamically and statically vulcanized composites was greatly correlated with the morphology of the composites. The followed the order sulphur> mixed> DCP for all the solvents used in the study. An increase in the mechanical properties, such as tensile strength and Young’s modulus was observed for the dynamically vulcanized blends. The studies clearly indicate that dynamic vulcanization can significantly modify the properties of EPDM/ PVC systems. Industrial solvents such as petrol, diesel and kerosene are considered as possible threats to polymers when they are used in automotive applications. The interactions of EPDM/PVC composites with these three penetrants have been studied with special reference to the effects of different filler loadings and penetrant size. Solvent uptake trend followed the order: petrol > kerosene > diesel for a given matrix. From the sorption-desorption-resorption cycles it has been found that the filled samples exhibited good mechanical stability after subjecting them to solvent interaction.

8.2 Future Scope of the Work

The present investigation opens up some new areas those require further attention.

i) Morphological studies

The morphological features of the dynamically and statically crosslinked EPDM/PVC systems can be further investigated by Transmission Electron Microscopy (TEM), since the structure- property relationships explored in this work strongly depend on the details of the phase segregation

ii) Sorption and diffusion studies using new probes

The performance of EPDM/PVC systems in the environment of aromatic hydrocarbons, aliphatic hydrocarbons and liquid fuels such as petrol, diesel and kerosene. has been examined in this work. The behaviour of these composites in alcohols, aldehydes, acids, industrial oils etc. can be investigated in future.

The barrier property of EPDM/PVC composite membranes has been investigated and the examination of their utility for the separation of liquid or gaseous mixtures is an emerging area in polymer science. This technology could revolutionize the biochemical, pharmaceutical and other chemical industries. It would be worth attempting to develop thin membranes from EPDM/PVC and to examine their efficiency for the separation of organic liquid mixtures, particularly by using permeation technique. Amorphous glassy polymers are the basic materials for the separation of many gases by membrane permeation. The solubility and diffusivity of gases in polymeric systems can be tuned by changes in the molecular architecture. Therefore, a detailed investigation on the gas separation efficiency of EPDM/PVC composites would be interesting.

iii) Modification with particulate fillers

The effect of incorporation of various other fillers such as calcium carbonate, surface modified nanosilica and clay on the morphology and properties of EPDM/PVC composites can be investigated. The study of the influence of filler geometry on the different physical properties could be a very interesting extension to the present research programme.

iv) Evaluation free volume

In the present work, the transport property has been explained based on the cure, morphology, X-ray analysis and mechanical properties of EPDM/PVC system in compliance with the earlier practices. More precise characterizations include the evaluation free volume of the composites by using Positron Annihilation Lifetime Spectroscopy (PALS).

v) Product development

Efforts can be made to produce transformer oil seals, gaskets, cable insulations etc, which require oil and solvent resistance, from suitably modified EPDM/PVC composites.

Although composite materials have certain advantages over conventional materials, they have some disadvantages also. PMC's and other composite materials tend to be anisotropic; that is, properties like strength, stiffness etc. are different in different directions depending on the orientation of composite constituent materials. These anisotropic properties pose a significant challenge for the designer who uses composite materials in structures that place multi-directional forces on structural members. Also formation of a strong connection between the components of the composite material is difficult. The broader use of advanced composites is inhibited by high manufacturing costs. Development of advanced composite materials having superior mechanical properties opened up new horizons in the engineering field. The advantages such as corrosion resistance, electrical insulation, low thermal expansion, higher stiffness, strength and fatigue resistance make them preferred candidates for many applications

APPENDICES

Appendix 1

EPDM/PVC	Qt (mol %)	H	Dx10^{-5} (cm^2/sec)	Ø
100/0	2.06	0.201	16.4	0.2588
100/2.5	1.91	0.192	14.7	0.2834
100/5	1.74	0.188	12.3	0.2980
100/7.5	1.36	0.193	8.21	0.3096
100/10	1.25	0.192	7.48	0.3155

Appendix 2

EPDM/PVC	ρ_p	Mc	χ
100/0	0.86	0.3246	0.61
100/2.5	0.88	0.2918	0.62
100/5	0.91	0.2677	0.63
100/7.5	0.94	0.2650	0.636
100/10	0.97	0.2504	0.639

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