EFFECT OF CROSSLINKED POLYMER ON DRYING OF BINARY POLYMERIC COATINGS

M.Tech. Dissertation

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by

AMAN PATHANIA

(Roll No. 601511001)

Under the supervision of

Dr. Raj Kumar Arya

DEPARTMENT OF CHEMICAL ENGINEERING
THAPAR UNIVERSITY, PATIALA, PUNJAB, INDIA

AUGUST 2017

Certificate

This is to certify that the dissertation work entitled "**EFFECT OF CROSSLINKED POLYMER ON DRYING OF BINARY POLYMERIC COATINGS"** submitted by **Aman Pathania (Roll. No. 601511001)** in partial fulfillment for the award of degree of Master of Technology in Chemical Engineering from Thapar University, Patiala, Punjab, has been carried out under my supervision. This work has not been submitted partially or wholly to any other university or institute for the award of this or any other degree or diploma.

21-8-17

Dr. Raj Kumar Arya
Assistant Professor
Department of Chemical Engineering
Thapar University, Patiala

Declaration

I hereby declare that the work being presented in the dissertation report entitled "**EFFECT OF CROSSLINKED POLYMER ON DRYING OF BINARY POLYMERIC COATINGS"** by me in the partial fulfillment of the requirements for the award of degree of Master of Technology in Chemical Engineering from Thapar University, Patiala, Punjab, is an authentic record of my work carried under the supervision of Dr. Raj Kumar Arya, Assistant Professor, Department of Chemical Engineering, Thapar University, Patiala. The matter presented in this dissertation has not been submitted in any other University/ Institute for the award of any degree / diploma.

Dated: 21-08-2017

Aman Pathania
(Roll. No. 601511001)

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Aman Pathania
(Roll. No. 601511001)

Abstract

Coating of poly(styrene) in p-xylene and ethyl benzene has been prepared using solvent casting method. Effect of initial coating thicknesses on residual solvent, average concentration of polymer, average concentration of solvent, and change in coating thickness has been studied for poly(styrene) – p-xylene and poly(styrene) – ethyl benzene coatings. The drying of these coatings was externally controlled: evaporation of solvent, for sufficiently long time followed by a slow diffusion controlled mechanism. The time taken in diffusion controlled regime was very much higher as compared to externally controlled regime.

Effect of Crosslinked poly(styrene-co-divinylbenzene) content on drying behavior was studied in binary poly(styrene) – p-xylene and poly(styrene) – ethyl benzene systems. Crosslinked content has increased the drying time in both the polymer – solvent systems. The residual solvent content was high in coatings having crosslinked content as compared to linear polymer – solvent coatings. This high amount of solvent is nearly permanently trapped in these coatings and may give high solvent losses.

The surface morphology study of coating having crosslinked content is not uniform. The crossslinked particles are highly densed near the edges of coating. The particles were in regular shape of rod and sphere in p-xylene system. However, there was no such observation in ethyl benzene system.

Key words: Crosslinked, Residual solvent, Coating thickness

Contents

List of Tables

List of Figures

Chapter 1

Introduction

1.1 Polymeric Coatings

The surface of an object is basically covered with the different types of coatings. The main purpose of the coatings is to increase the life of the object, prevent the object from moisture, corrosion, cracking, blisters etc. The coating covers the substrate in a very homogenized manner. The substrate can be fully or partially coated depending on the requirement.

Polymeric coatings are prepared by several methods with or without solvent. The Polymers can be rubbery, crosslinked, or glassy in nature in the start of coating preparation. The crosslinked polymer films are used in various applications like protective coatings, paintings, barrier for separations of liquid and gases, storage media, semiconductors, micro fluidic devices, optical devices, fluorescent devices, surface acoustic wave devices drug release and encapsulation , and biomedical applications [1-11]. Multilayers and hybrid multilayers have attracted a lot of research due to their excellent properties like electrical, chemical, optical along with chemical and mechanical stability [12] .

Crosslinking hardens the coatings and reduces the penetration of external molecules into the coatings [13]. Crosslinking also improves the surface coverage and enhances electrophoretic separations [14]. Crosslinking improves mechanical strength, chemical resistance, thermal stability, separation characteristics, biomedical properties, and other functional properties [15]. Crosslinking can be done by various ways like UV irradiation, chemical crosslinking, and hyperthermal hydrogen induced crosslinking. Hyperthermal hydrogen induced crosslinking is an unique technique because it does not require any co-agents or solvents and it is able to crosslink the material upto several microns. The depth of crosslinked material is very important to find the material properties.

During crosslinking, linear polymer chains join together at a common junction point [16]. Crosslinking agents attach themselves to at least two chains. These agents are low molecular weight species. The properties of the polymer network are controlled by the degree of crosslinking. In case of a very high degree of crosslinking, the network will be very hard, brittle and solvent resistant [16]. Fluorescent devices require controlled deposition of crosslinked polymer based sensors [6]. The crosslinking degree can be manipulated to get the desired properties. This can be achieved by controlling curing temperature and crosslinking agent to monomer ratio.

All coatings degrade when they get exposed to UV radiations due to the complex photochemical process. The weather conditions like moisture, temperature, and pollutants, etc. enhance this degradation process. The coating will degrade when it absorbs UV radiations and that is sufficient enough to break the bonds of polymer. The pure polymers do not degrade because they do not absorb sufficient energy of radiations greater than $295\,nm$ wavelength, however the coatings will undergo degradation [2]. This shows that coatings have something other than the polymer. Improper drying and polymerization with other reacting species or ingredients are the main causes of degradation.

Durability of organic coatings can be enhanced by the addition of low molecular weight stabilizers [17]. These stabilizers absorb UV radiations which fall on the coating and hence, stop the photooxidation of the coating since it does not allow UV radiations to react with the binder used in the coating. These UV absorbers also protect the subsequent layers of the polymer film. A few light stabilizer compounds scavenge the free radical produced during the oxidation process and, hence, slow down the oxidation process. UV absorbers and free radical scavengers are chemically destroyed during the weathering process [17]. Due to the weathering process, the concentration of UV absorber at the surface decreases as compared to the deep inside the coating.

The transport of solvent in polymers or polymer films is affected by unsaturation, degree of crystallinity, crosslinks density, and glass transition temperature [5]. The glass transition temperature increases with the solvent evaporation. For instance, an addition of 20% toluene in poly(styrene) makes the glass transition equal to the ambient temperature [3]. The diffusion coefficient decreases linearly with crosslink density and levels off at high values. The type of crosslinking governs the solvent uptake by the polymer.

1.2 Coating Preparation Methods

Initial, polymer melt or solution is being prepared. The melt can prepared by heating the pure or mixture of polymers. The melt may be spinned or sprayed over the substrate to get the film. This method is being using to coat the larger size objects. In dry casting, the hot object is being passed through the block of polymer to get the desired coating on the surface. The multifunctional and high quality thin films are generally being prepared by solution casting technique. In this technique, the polymer(s) are dissolved into the solvent(s) to get the homogeneous solution. The required amount of the solution is being spreaded on the substrate or may be poured into the geometry to be coated. Coating can be prepared in layer by layer , single layer, or simultaneous multilayer fashion to get the desired coating. The solution casting technique has following advantages:

- High temperature resistant films are prepared from non- thermoplastic soluble raw materials.
- Processed at low temperatures, which is valuable for incorporating temperature-sensitive active ingredients or thermally activated films.
- Simplified incorporation of fillers and additives.
- A huge range of material solutions can be casted into the film

Linear polymer(s) are generally being used to prepare the coating solution. However, the polymer(s) having low degree of crosslinking may also be used to prepare the coating solutions. These coating solutions may take very long time to get the homogeneity. The schematic representation of the crosslinked solution coating is shown in Figure 1.3.

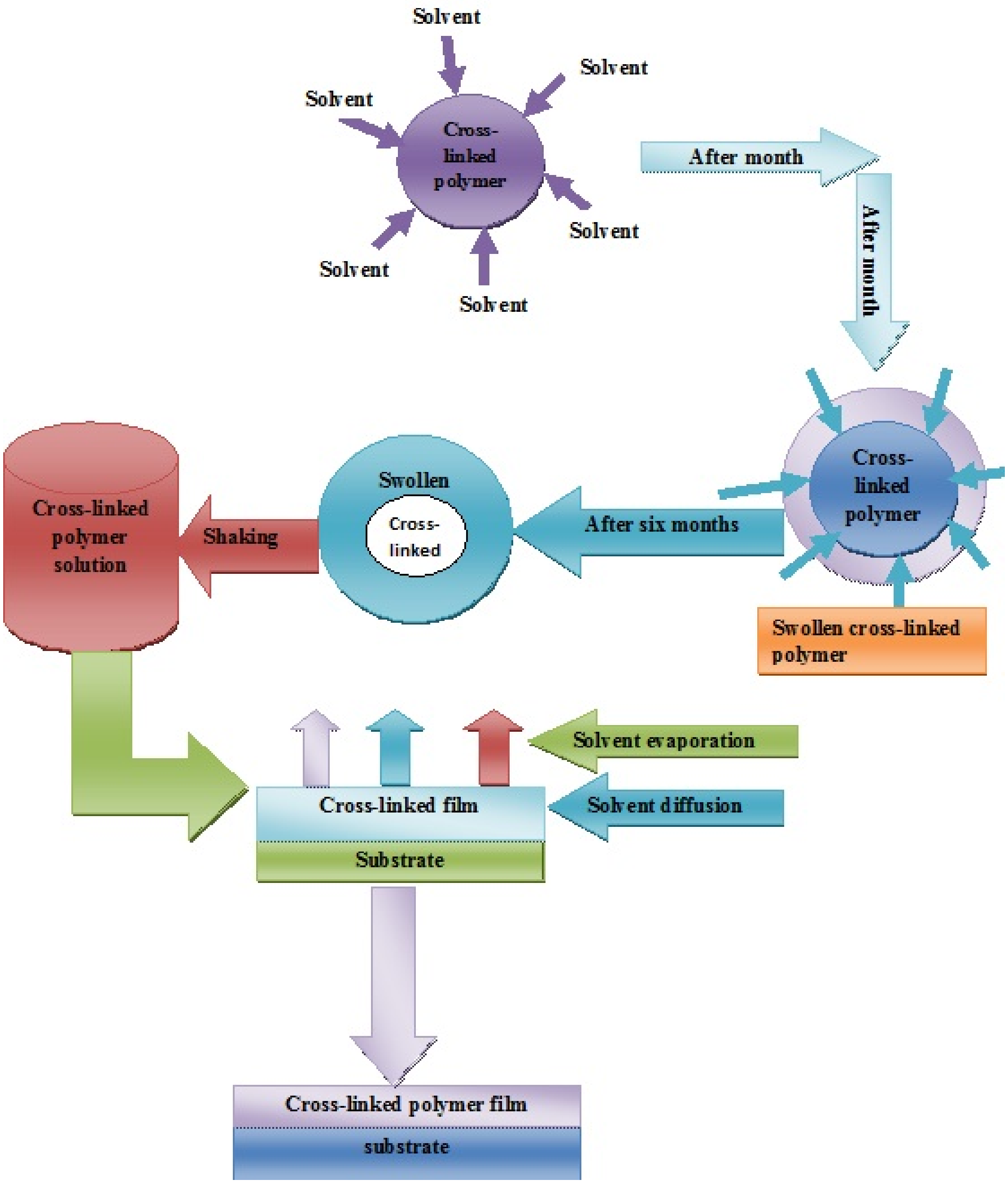


Figure 1.1: Schematic of crosslinked solution coating preparation.

1.3 Classification of Coatings

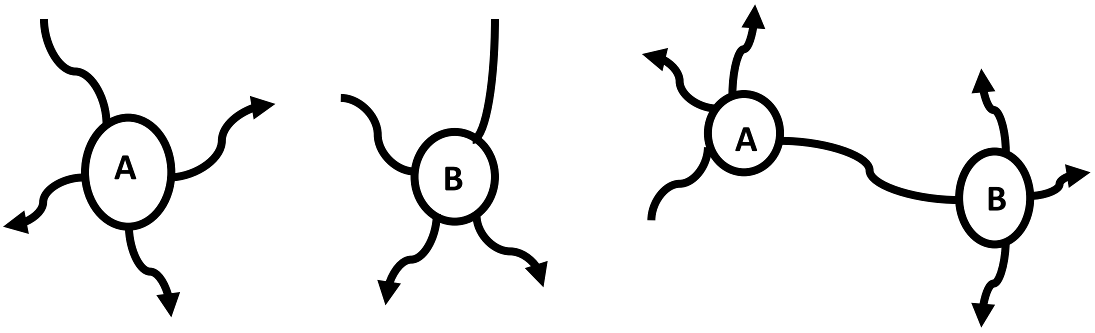
Broadly coatings are classified as crosslinked and uncrosslinked. These can be further classified as binary and multicomponent coating. In binary coating one polymer and one solvent is used however in multicomponent coatings more one polymer or solvents are used.In uncrosslinked polymers, there is lot of free volume available due to the flexibility of monomer chains. However, in the case of crosslinked polymers monomers chain are tightly packed and very less free volume is available. Polymer chains are joined at common junction point by the use of low molecular weight of crosslinking agents.

The coatings can be further classified into organic coatings and inorganic coatings. In organic coatings, organic solvents are used which are toxic and costly in nature. Therefore these coatings need to be dried completely in order to remove the entire solvent to avoid production losses and defects. In green coatings, inorganic solvents generally water. However, the water soluble polymers are very costly and these coatings require lot of energy in order to get the dried films.

1.4 Crosslinking

The lateral attachment of the polymer chains is called crosslinking or curing. The entire bulk of the polymer is converted into a three dimensional network structure. This makes the polymer harder and the mobility of the molecular chains decreases. The increase in degree of crosslinking enhances the molecular weight and glass transition temperature.Physical properties like density, viscosity, melting point, mechanical strength, elastomeric properties, etc. progressively improve with the increase in crosslink density. Oxygen permeability, water permeability, solubility, chemical resistance, etc. decrease with the increase in crosslink density. A highly crosslinked polymer behaves as a hard glassy material that is not recyclable. Thus, an initially thermoplastic polymer is converted to a thermosetting polymer as a result of curing. The thermosetting polymer does not show melting behaviour and instead burns or degrades upon heating [18].

Polymer crosslinking can be achieved by the application of heat, pressure, change in pH, and radiation. In the radiation method, the polymer is exposed to electron beam, gamma rays, ultra-violet, or visible light [19]. The typical wavelength range for the UV method is 200-400 *nm* and for the visible light the range is 380-450 *nm*. The radiation curing can take place via either free radical or cationic mechanism and follows initiation, propagation and termination steps. Commonly, 2-hydroxy-2-methyl-1-phenyl-propan-1-one and 1-hydroxycyclohexyl phenyl ketone are used as free radical photoinitiators and sulphonium salts are used as cationic photoinitiators. Adding a specific curing agent to a partially polymerized resin also facilitates crosslinking. If the curing agent is activated through UV radiations the process is called UV curing. The crosslinking of a polymer can be hastened by the addition of catalysts and accelerators to the curing agents. The accelerators increase the curing rate by catalyzing the reaction of the polymer chains with the curing agent [20]. Figure 1.2 shows various types of crosslinking.



Trifunctional crosslink

Bifunctional crosslink

Tetrafunctinal and trifunctional crosslink

Figure 1.2: Various types of crosslinks.

1.5 Drying of Coatings

All solvents based coatings are subjected to drying. The solvent present in the coating is removed during the course of drying. The coatings may be heated or dried at room temperature depending on the requirement. The mass of the coating changes with time due to the loss of solvent from the coating into the surrounding medium. The thickness of the coatings shrinks in longitudinal direction towards the substrate. Initially drying is externally controlled due to presence of high amount of solvent on the top surface. During this period the rate of drying is nearly constant. As the time passes, the amount of solvent on the top decreases and drying rate starts falling due to slow diffusion of solvent from the coating to the coating air - interface. Figure1.1 shows the various drying process of polymeric coating.

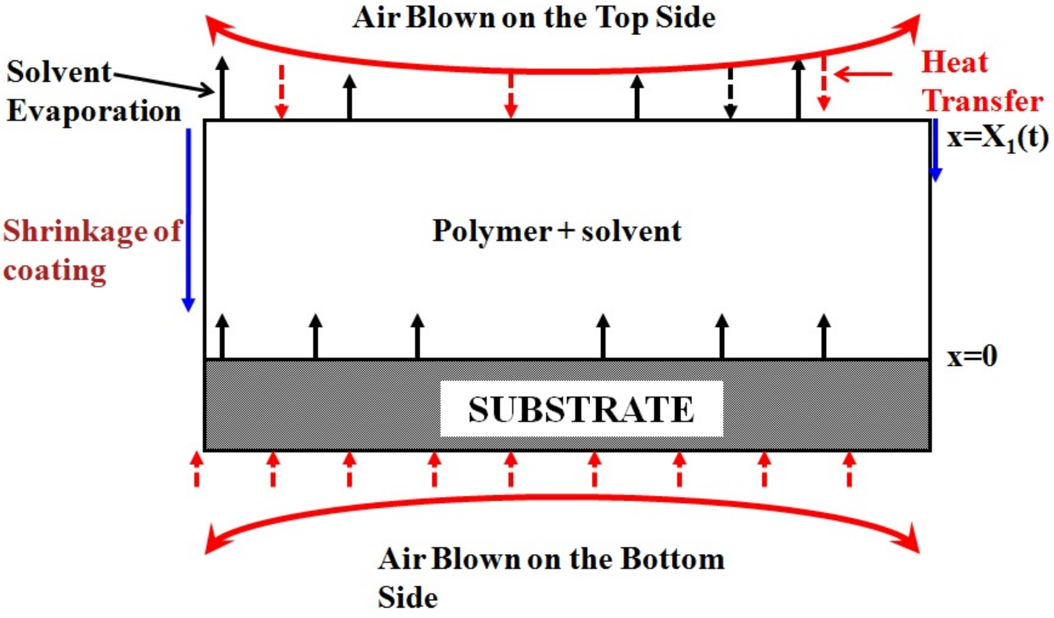


Figure 1.3: Schematic of drying of polymeric coating.

1.6 Objective

Based on the literature review and the gaps identified in chapter 2, the objective of the present work have been set as follows

To study the effect of crosslinked polymer on drying of binary polymeric coating.

1.7 Dissertation Outlines

Chapter 1: A brief introduction about cross-linked coating, preparation of crosslinked coating, application of cross-linked coating, classification of coating, cross-linking and drying of coating.

Chapter 2: Literature review regarding preparation, characterization, diffusion and application in cross-linked coating and their importance have been summarized.

Chapter 3: Materials and methods has been explained in details

Chapter 4: Results and discussions of various observations has been given.

Chapter 5: Conclusions of present study are documented.

Chapter 2

Literature Review

In this chapter the literature review of the cross-linked coating has been provided. The chapter is divided in several sections: preparations and characterization of cross-linked coatings, diffusion in cross-linked coating, and limitations and future scope of Study.

2.1 Preparations and Characterization of Crosslinked Coatings

Martin and Mandelkern [21] studied the glass transition behavior during the vulcanization of natural rubber. The glass transition and the temperature of application are important parameters to define the nature of polymer, i.e., whether it is rubber like or brittle. The free volume available in polymer is a measure of the ease of molecular rearrangement. They found that the specific volume of the vulcanized rubber keeps on decreasing with increase in the sulfur content. Hence, the glass transition temperature of the vulcanized rubber will increase with the sulfur content. They assumed a linear relationship of free volume with glass transition temperature as given by

$$\phi(T) = \phi_g + \Delta\alpha\left(T - T_g\right) \tag{1}$$

where, ϕ_g: free volume at glass transition temperature, T_g, $\Delta\alpha$: rate of change of free volume with temperature.

Various types of crosslinks are shown in Figure 1.2 [22]. The degree of crosslinking relates to the number of groups that interconnect monomer and crosslinking species. The degree of crosslinking is generally expressed in mole percent. The degree of cross linking can be determined using chemical and physical methods [23]. In the chemical method, the calibration curves are prepared to calculate the percentage of crosslinked bonds. In the physical method, the crosslinked material is put in the solvent for a sufficiently long time so that no change is observed in solution concentration. After that, unswollen material is filtered and dried and its mass is recorded. The physical degree of crosslinked can be calculated as follows

$$\text{Physical Degree of Crosslinking} = \frac{\begin{bmatrix}\text{Initial Mass of} \\ \text{Material}\end{bmatrix} - \begin{bmatrix}\text{Final Mass of} \\ \text{Unswollen Material}\end{bmatrix}}{\text{Initial Mass of Material}} \times 100 \quad \textbf{(2)}$$

Mullins [24] determined the crosslinking degree in vulcanizates of natural rubber. The polymers of different molecular weights were taken to prepare seven samples having same crosslinking degree. Di-tert-butyl peroxide and sulfur vulcanization agents were used to prepare two types of vulcanizates. n-decane was used as a swelling agent. Volume of swelling and stress-strain properties were determined. He used the Flory-Huggin's equation to correlate network structure and equilibrium swelling degree. Several equations were developed to see the effect of initial molecular weights on the swelling volume. The average molecular weight of the rubber molecules between crosslinks (M_C) was given by

$$-\ln(1-v_r) - v_r - \mu v_r^2 = \rho v_0 M_c^{-1} v_r^{1/3} \tag{3}$$

The force (f) required to extend the rubber was given by

$$f = 2A_0 v_r^{\frac{-1}{3}} (\lambda - \lambda^{-2})(C_1 + \lambda^{-1} C_2) \tag{4}$$

$C_1(swollen) = \frac{1}{2}\rho RT M_c^{-1}$ From Flory theory was corrected for the chains ends because the chain ends are not contributing to the network, by replacing M_c^{-1} with $M_C^{-1}(1 - 2M_c M^{-1})$ which gave the following

$$C_1\left(swollen\right) = \frac{1}{2}\rho RT M_c^{-1} - \rho RT M^{-1} \tag{5}$$

The swelling volume was given by

$$-\ln(1-v_r) - v_r - \mu v_r^2 = 2V_0 C_1(swollen) R^{-1} T^{-1} v_r^{1/3} \tag{6}$$

where v_r:volume fraction of rubber in the swollen material, μ:interaction constant characteristic of the rubber and the swelling liquid, v_0: molar volume of the swelling liquid, $\boldsymbol{\lambda}$: extension ratio, R: gas constant, T: absolute temperature, M_c: average molecular weight of the rubber molecules between crosslinks, A_0: unstrained area of cross section, C_1, C_2: constants

Moore and Watson [23] also measured the crosslinking degree in vulcanizates of natural rubber by using chemical and physical methods. Di-tert-butyl peroxide was used as crosslinking agent. During the process, peroxide decomposed into tert-butanol, methane, and ethane. The crosslinked rubber prepared by this method was used in chemical method for determination of crosslinking degree. They found that the degree of crosslinking by chemical method was greater than the physical method.

Mullins [25] has further measured the crosslinking degree of vulcaniztes of rubber. During simple extension of vulcanizated rubber, he used statistical theory and gave the following expression:

$$f = A_0 \rho k T (\lambda - \lambda^{-2}) \tag{7}$$

where, A_0: unstrained cross-sectional area, T : absolute temperature, $\boldsymbol{\lambda}$: extension ratio, k : Boltzmann constant. f: force required to extend a sample of rubber.

He further studied deviations from the statistical theory for low and moderate extension, which was given by

$$f = 2A_O(\lambda - \lambda^{-2})(C_1 + \lambda^{-1}C_2), \quad C_1 = \frac{1}{2}\rho RTM_C^{-1} \tag{8}$$

where, ρ: density of the rubber, M_C: the number average molecular weight of the chain segents of rubber between adjacent crosslinks, R: gas constant.

He [25] developed two parameter relationship for stress-strain behavior using C_1 and C_2. Swelling reduced the number of network chains and the effect of this on finite extensibility was theoretically correlated. Finite extensibility swelling departure at low elongation was also considered in highly swollen rubber. He used the linear portion in stress-strain curves to determine parameters C_1 and C_2 . The linear portion becomes very limited because of very high degree of swelling departures. They found degree of crosslink using λ and network flaws in a simple extension stress-strain curve. They also used this technique for the degradation studies of vulcanized rubbers.

The dependence of C_1 and C_2 on the swelling degree was given by

$$\frac{1}{2} fA_O(\lambda - \lambda^{-2})^{-1} v_r^{\frac{1}{3}} = C_1(dry) v_r^{\frac{1}{3}} + \lambda^{-1} C_2(dry) v_r^{4/3} \tag{9}$$

where, v_r:volume fraction of rubber in the swollen material, R: gas constant, T: absolute temperature, A_0: unstrained area of cross section, C_1, C_2: constants, $\boldsymbol{\lambda}$: extension ratio, f: force required to extend a sample of rubber.

Moore and Scanlan [26] determined the crosslinking degree of vulcanizates of natural rubber. Scissions of chains were observed during crosslinking using organic peroxide at 140^oC. They studied crosslinking kinetics and peroxide decomposition. They measured the stress relaxation in an extended sheet of rubber that was vulcanized. This was further crosslinked using di-cumyl peroxide in the presence of nitrogen. All the previous methods of crosslinking determination were not sensitive to chain scission. They found that the primary networks degraded during the secondary network formation which results in only 10% new crosslinks formation.

Mullins and Thomas [22] determined the crosslinking degree in natural rubber vulcanizates and its dependence on network flaws. The network flaws were observed due to free chain ends. They considered Flory's and Tobolsky's approaches in this work. According to Flory's approach, $(n-1)$crosslinks were required to link n molecules for taking network flaws into account. The chain density was given by $= 2(v-n+1) - 2(v-n)$. They got correct gel point and its molecular weight dependence using this approach. However, the assumption used in Flory theory was unrealistic. Flory had assumed that each crosslink added two network chains.

Tobolsky's approach introduced cuts into the network which initially did not contain any free ends. Each cut produced two free chain ends that increased the value of n by 1 and reduced network chains by1. In this approach, the chain density was given by

$c = 2v - n$. Mullins and Thomas [22] addressed the discrepancy between the above two approaches by making allowance for the differing functionality of crosslinks.

Mullins [27] modified the previous physical method for determination of degree of crosslinking [23] and used it to improve the stress-strain properties method for vulcanized rubber. He modified this method of determination by developing a relationship between elastic constant C_1 , and swelling rubber free volume (v_r). He again compared the physical and chemical methods of measurements and made empirical corrections to incorporate network flaws and chain entanglements and found that the measured degrees of crosslinking from both the methods were nearly same.

Barie et al. [11] developed new material for surface acoustic wave devices using UV crosslinking of poly(siloxanes). The uncrosslinked sensor device showed significant sensitivity decrement in the first few days. The total decrease in sensitivity was 50% in six weeks time, however, in the case of the crosslinked ones the fall was only 8% in the first few days and 0.2% per day thereafter. Sensor stability and reproducibility of siloxanes were very high over a long period of time as these were greatly enhanced by crosslinking.

Esser et al. [28] studied waterbased crosslinkable surface coatings. These coating were prepared by simple crosslinking and are generally used in furniture applications. Coatings were prepared from the mixture of monomer and water by using emulsion polymerization. Monomers used were methacrylic acid, butyl acrylate, acetoacctoxyethyl methacrylate and methyl methylacrylate in the ratio of 12:37:30:21 by weight. The coatings were dried under ambient conditions. Their results showed that crosslinked coatings had excellent hardness and resistance to chemicals, heating, and wetting.

Hu et al. [7] used crosslinked coatings for electrophoretic separations in poly(dimethylsiloxane) microchannels. They used three different monomers of poly(ethylene glycol), acrylic acid ,and diacrylate poly(ethylene glycol) and then polymerized them with the help of ultraviolet light on the surface of poly(dimethylsiloxane) microdevice. They used three different surface coatings: the first one was single poly(ethylene glycol), the second one was a mixture of acrylic acid and poly(ethylene glycol) and the third one was a mixture of three poly(ethylene glycol), acrylic acid, and diacrylate poly(ethylene glycol). In this mixture, diacrylate poly(ethylene glycol) worked as a crosslinking agent. They measured monomer ratio, graft density, and contact angle. They used these coatings for separations and have found the best separations in case of crosslinked coatings. Low cost and disposable microfluidic devices can easily be fabricated using poly(methyl methacrylate) and poly(dimethylsiloxane). The electroosmotic fluid flow in microchannels can be controlled by using multilayers of poly(allylamine hydrochloride) and poly(styrene sulfonate).

Peters et al. [17] studied the mobility of UV light absorber in crosslinked coatings. They used tinuvin 900 UV absorber. Their results showed that the UV absorber was moving into the deeper side of the coating from the coating surface. These UV absorbers did not allow the UV radiations to reach the binder of coating by absorbing the UV radiations. These UV absorbers were chemically consumed during the weathering process. The glass transition temperature and cross linked density were very much affected by the UV exposure time. The glass transition temperature can increase or decrease with the crosslink density depending on the coating chemistry.

Ramaraj [29] studied the composite films of starch and crosslinked poly(vinyl alcohol). He studied the physicomechanical, thermal, and swelling properties of these films. He prepared and compared uncrosslinked and crosslinked films. In uncrosslinked films, the poly(vinyl alcohol) was blended with starch having different wt% of starch up to 50% in an increament of 10% starting with 10%. The crosslinked film was prepared by using glutaraldehyde as a crosslinking agent. Glutaraldehyde gave the crosslinked solution of poly(vinyl alcohol) that was spread on a glass substrate at room temperature for 48 hours to get a dried crosslinked film of poly(vinyl alcohol). He found that the crosslinked films had high tensile modulus, tensile strength, burst strength, tear resistance, and solubility resistance as compared to the uncrosslinked ones due to the crosslinked network formation. However, uncrosslinked films had a high moisture content, tensile elongation, swelling content, and moisture absorption as compared to the crosslinked films.

Al Akhrass et al. [3] studied the influence of progressive crosslinking on poly(styrene) dewetting. The behavior of partially crosslinked films and thickness get affected by the dewetting nature of the film. They found that 100% conversion of azide was not enough for the complete dewetting in 20 *nm* film. They also found that the nucleated holes diameter grew with time when dewetting of poly(styrene) thin film was done on poly(dimethylsiloxane) coated substrate. They found that crosslinking lead to macromolecular network which inhibited the dewetting and stopped residual stress relaxation. They also suggested that the films with long polymer chains can be successfully stabilized by crosslinking.

Akhrass et al. [12] designed several multilayer crosslinked hybrid thin films using poly(styrene) and platinum nanoparticles. They prepared these films using sequential spin coating followed by UV crosslinking. They studied the neutron reflectivity of these hybrid films and found that UV crosslinking at the room temperature is enough to stabilize the layers prior to the segregation of platinum nanoparticles.

Campos et al. [8] prepared chitoson cross-linked films that are used for drug delivery applications. They used acetic acid solution to dissolve the chitoson. Hexamethylene 1,6-bis was the cross-linking agent. They used the solvent evaporation technique to prepare three chitosan films: 30% crosslinked, 50% crosslinked, and un-crosslinked films. They characterized these films by Fourier transform infrared spectroscopy and found that the crosslinked films and their resolution were better than the uncrosslinked films. They found 0°contact angle for both the crosslinked films which shows that crosslinking enhances the hydrophobic characteristic of the crosslinked films. They also studied the swelling behavior and found that the films without crosslinking are more susceptible to swelling as compared to the crosslinked films. They suggested that the crosslinked films are more suitable as compared to the un-crosslinked films for drug delivery process.

Liang et al. [30] used selective crosslinking method to prepare single and double network films of chitosan and poly(vinyl alcohol). In the first method, they used borate as a crosslinking agent and the crosslinking depends on di-diol interaction between poly(vinyl alcohol) / chitosan and borate. Di-diol interaction is an interaction of two hydroxyl groups. In the second method, they have used tripolyphosphate as the crosslinking agent and the crosslinking depends on electrostatic interaction between poly(vinyl alcohol)/chitosan and tripolyphosphate. They prepared four films one was uncrosslinked while the remaining three were crosslinked using borate, tripolyphosphate, and a mixture of borate and tripolyphosphate. They found that crosslinking decreased the permeation value, improved the mechanical strength and elastic modulus. Their atomic force microscopy results showed different size particles and aggregates, however the original particles were nanoparticles of same size. This showed variation in the behavior of different types of crosslinking processes.

Bossi et al. [6] synthesized polymeric crosslinked coating using initiator, transfer agent, and terminator technique. The polymerization was initiated using UV irradiation. They were able to control the crosslinked thickness by changing the concentration of chain termination agent ($N, N-N', N'-$tetraethyl thiuram disulphide) between 5 and 130 *nm* crosslinked thickness and this effect plateaus off at higher concentration of the terminator. Their study showed greater variability with the irradiation time. The crosslinked films thickness increased with irradiation time but the increase was not very significant as the thicknesses were 5 *nm* and 6 *nm* for the irradiation times of 20 min and 40 min respectively. They also studied the effect of polymerization atmosphere on the crosslinked film thickness. They recorded 6 *nm* and 20 *nm* thicknesses when the atmosphere was purged with argon and atmosbag, respectively. Furthermore, they studied the effect of polymerization time on film thickness and recorded 70 *nm* and 100 *nm* for 40 min and 80 min polymerization respectively.

Das et al. [31] studied crosslinked starch/poly(vinyl alcohol) films. They prepared four crosslinked films and one simple film. The crosslinking agents used by them were borax, formaldehyde, epichlorohydrin, and ZnO. They used gelatinization by solution casting method to get the films. Their scanning electron microscopy results show that starch granules did not fully collapse during gelatinization process specially in the case of un-crosslinked film and ZnO film. They concluded that zinc oxide particles act as fillers and did not take part in chemical crosslinking reaction. They found that tensile stress and tensile modulus were higher in the case of borax crosslinker due to formation of tough network. The tough network was formed between three hydroxyl groups of the poly(vinyl alcohol), starch, and borax. They found that the storage modulus of all the crosslinked films were much greater than the uncrosslinked films due to the addition of crosslinker between poly(vinyl alcohol) and starch molecules. Their thermo gravimetric analysis showed low thermal degradation and high char yield in the case of crosslinked films with high degree of crosslinking. They found significant fall in moisture absorption in the crosslinked films as compared to the uncrosslinked one due to less number of hydroxyl groups.

Telford et al. [9] studied antifouling activities of thermally crosslinked poly(n-vinylpyrrolidone) films in biomedical applications. The crosslinked films were prepared by thermal annealing technique at temperature of 200℃ for 3 hours. Thermal gravimetric analysis was done to determine the mass loss density during thermal annealing. It was noticed that there was no significant decomposition of the polymer. Their atomic force microscopy results showed that there was no change in the surface morphology during annealing. During annealing process, oxygen content increased by 30%, carbon content decreased by 5% and nitrogen remained unchanged as recorded by X-ray photoelectron spectroscopy. Their results showed that mass density and X-ray scattering length density increased during annealing process. They found that an insoluble network was formed due to $C-C$ interaction bonds of different radicals.

They [9] also checked the stability of coatings in different solvents like water, ethanol, and solution of peroxide in concentrated sulphuric acid and found no effect of these solvents on the films. They also studied the protein adsorption on poly(n-vinylpyrrolidone) coating. They used two type of proteins: fibrinogen (FGN) and IgG (Immunoglobulin G) having different structures. They used quartz crystal microbalance to find the adsorbed mass of IgG and FGN, which were 21 and 34 ng/cm^2 respectively. These findings show the improved biocompatibility of the crosslinked films in vivo devices.

Lu et al. [32] studied the crosslinkable poly(vinyl acetate) emulsions for furniture applications. They prepared the crosslinked films by the mixture of acetoacetoxyethyl methylacrylate and diamine solution using emulsion polymerization. They used vinyl acetate and veova 10(vinyl decanote) as copolymers. Enamine structures were formed by the reaction of acetoacetoxyethyl methylacrylate and diamines. The prepared films were characterized using Fourier transform infrared resonance and nuclear magnetic resonance. Glass transition temperature was measured using dynamic mechanical thermal analysis. They found that in the crosslinked films, the glass transition temperature and viscosity increased with increase in the amount of acetoacetoxyethyl methylacrylate. However, the trend was reversed in the case of uncrosslinked films.

Nguyen et al. [2] extensively studied the degradation modes of crosslinked coatings that were exposed to the photolytic environment. They found that the crosslinked coatings exposed to the UV environment underwent degradation. This degradation was very inhomogeneous. The degradation started with nanoscale pits that deepen and grew in size with exposure time. They gave a conceptual model to explain the degradation. They found that the degradation started at the hydrophilic sites that were randomly distributed in the densely crosslinked films. These hydrophilic sites were the unreacted and partially polymerized molecules and other additives. They found that the morphological changes were related to the gloss of the coatings. The coating gloss changed due non-uniform degradation of the films otherwise only films thickness would have changed without affecting the glossiness of the film. They found that degradation of an acrylic melamine film in the humid environment was much faster as compared to the dry UV degradation.

Carias et al. [4] have studied phototunable swelling in poly(N-isopropylacrylamide crosslinked coatings. They synthesized and characterized the crosslinked terpolymer coating. Terpolymer is a copolymer of three distinct monomers. The three monomers used were N-isopropylacrylamide (NIPAAm), methacryloxybenzophenone (MaBP), and phenacyl methacrylate (PHEm). NIPAAm (N-isopropylacrylamide) swelled and collapsed when the temperature was increased. MaBP is a photo-crosslinking agent that activates at 365*nm* wavelength. PHEm is a photolabile protected carboxyl group which can be deprotected at 254*nm* wavelength. They prepared the coating surfaces using different compositions of PHEm from 7.1% to 17%, but MaBP remained constant at 3%. They found that swelling increased with time. They also studied the effect of pH on swelling and found that swelling ratio increases with pH. They also studied the photocleavage properties by UV-VIS absorbance and found that the deprotection follows the first order kinetics. Photocleavage reaction starts at a lower wavelength that controls the transition temperature and swelling due to the production of free carboxylic groups, which depends on the exposure time. They found that phenacryl methacrylate loading is very important to control the swelling.

Kusuma et al. [10] studied cell growth media and membrane gas separation using crosslinked films. Thiol-functionalized polysiloxane films were crosslinked with poly(ethylene glycol) diacrylate (PEGDA) in the presence of poly(ethylene oxide) as a crosslinker. They checked biocompatibility of the films with the help of human adult mesenchymal stem cells. They also studied the viability and differentiation. Viability and differentiation were measured through experiments performed on polymer films in which the cell was put in polymer film. They found that 33% SH (ratio of 1 thiol to 4 acrylate) was highly viable as compared to 20% SH and 40% SH. In the membrane separation study, they found high gas permeability and $\frac{CO_2}{N_2}$ selectivity. Based on their results, they suggested that these films can be used in a variety of materials due to their potential in stem cell carrier materials in transplantation and performance in gas separation.

Guo et al. [15] characterized the crosslinked depth of polymeric films using atomic force microscopy. The films were crosslinked using hyperthermal hydrogen bombardment technique. They found that the presence of carbon nanotubes in the poly(isoprene) lowers the depth of crosslinking. Due to a shortage of double bonds in the therban and poly(acrylonitrile), the crosslinked depth came out to be 2.1 and 1.1 microns respectively. On the contrary, the carbon nanotubes have abundant double bonds but these were not helpful in deeper depth of crosslinking due to the formation of a large stable conjugate system that cannot help the carbon free radical propagation.

Birck et al. [33] studied the antimicrobial citric acid/poly(vinyl alcohol) crosslinked films. The poly(vinyl alcohol) films were prepared by solvent casting technique which were crosslinked by the mixture of citric acid and with or without hydroxypropyl-β-cyclodextrin. They found that the effect of citric acid and hydroxypropyl-β-cyclodextrin were not able to change the barrier properties of poly(vinyl alcohol). Their investigations showed that a high amount of sodium benzoate (NaBz) was released in the case of low citric acid content and low crosslinking time due to smaller network density. They also noticed an increase in the diffusion activity with crosslinking time with hydroxypropyl-β-cyclodextrin.

de Dicastillo et al. [34] studied the antioxidant activities, polymer flexibility, swelling characteristics and mechanical properties of crosslinked films. The films were prepared using methyl cellulose polymer and maqui berry as an antioxidant. The films were crosslinked using glutaraldehyde as crosslinking agent. They found that the polymer flexibility and degree of swelling reduced due to glutaradehyde. However, maqui berry decreased the crosslinking degree and increased the swelling degree of material as the ratio of glutaraldehyde was increased from 2.5 to 5%. They found that the crosslinked films improved the water vapor permeability properties and it was the highest when glutaraldehyde concentration was the highest. They found that the use of plasticizer increased the thermal stability between 360 to 380℃. However, the thermal stability decreased with the addition of glutaraldehyde. They found that the addition of maqui berry protected the film from thermal degradation. The film prepared using maqui berry was transparent and little pink in color. However, the addition of glutaraldehyde made the color yellowish. Tensile strength, elongation at break (%), and Young's modulus decreased as the percentage of glutaraldehyde increased from 2.5 to 7.5%. The release of active agents such as poly(phenols) on stimulant was higher when the concentration of glutaraldehyde was higher due to a higher antioxidant from the natural extract that acts as crosslinking agent. This film is environmentally friendly in nature.

2.2 Diffusion in Crosslinked Films

Hayes and Park [35] obtained diffusion coefficients of benzene in rubber by sorption-desorption technique. Samples of deproteinized crepe rubber that were crosslinked by peroxide process and sulphur crosslinking were used for experiments. It was observed that the diffusion coefficients obtained were unexpectedly high and were not significant in many systems while the concentrations were changed. It was noticed that the benzene diffusion coefficient at zero concentration decreased with the increase in crosslink density. The diffusion coefficient also became more dependent on the concentration of benzene with increasing crosslink density. The linearity of the diffusion coefficients with concentration of benzene was observed irrespective of the density of crosslinking. This indicated the absence of time-dependence complications of the process. The average diffusion coefficient of benzene was given by

$$D_{av} = D_0(1+\alpha c) \tag{10}$$

Polymer swelling was incorporated into above expression to get the intrinsic diffusion coefficient as following

$$D = D_0(1+2\alpha c)/(1-v)^3 \tag{11}$$

where D_{av}: Diffusion coefficient averaged out over the concentration of benzene from zero to the equilibrium concentration after the sorption stage, D_o: diffusion coefficient at zero concentration of benzene, c: mass of penetrant per unit mass of polymer, and V: volume fraction of the penetrant.

Aitken and Barrer [36] studied diffusion in crosslinked rubbers. In this work, they used pentanes and isomeric butanes as solvents. The rubber membranes were crosslinked using *tert*-butyl peroxide. They investigated the effect of crosslinking, concentration, temperature, and size and shape of molecules. The extent of crosslinking was estimated using average molecular weight between the crosslinks. The diffusion coefficient inversely varied almost linearly with the molecular weight between the crosslinks and, hence, decreased as the crosslinking increases. There was linear increament in diffusion coefficient with solvent at low solvent concentration. This observation was in agreement with the preceding study [35]. The diffusion coefficients at zero concentration was shown to decrease in the order of *n*-C_4H_{10} > *n*-C_5H_{12} > *iso*-C_4H_{10} > *iso*-C_5H_{12} > *neo*-C_5H_{12}. Branching of CH_3 – groups decreased the magnitude of diffusion coefficient much higher as compared to the diffusion in the case of increased chain length by CH_3 – groups.

DiMarzio [37] exhibited how the glass transition for a crosslinked rubber has a thermodynamic basis. A relationship between the elevation in the glass transition temperature with the number of crosslinks was derived. Theoretical results were validated with the available experimental data for natural rubber, styrene-divinyl benzene copolymer, and methyl methacrylate-ethylene glycol dimethacrylate copolymer.

Chen and Ferry [38] studied the diffusion of *n*-hexadecane and *n*-dodecane solvents styrene-butadiene random , poly-isobutylene , several poly-butadienes, several styrene-butadiene block copolymers, poly-dimethylsiloxane, and natural rubber. The samples were crosslinked using tetramethylthiuram disulfide dicumyl peroxide, sulfur, and high-energy electrons. The diffusion coefficients for the two solvents were evaluated and found to be inversely proportional to their molecular length. The diffusion coefficient diminished slightly on increasing the crosslinking.

Dicumyl peroxide decreased the free volume in the crosslinked natural rubber. The diffusion of *n*-hexadecane was governed by the following expression:

$$\log D = A_d - \frac{1}{2.303} f \tag{12}$$

where, A_d: constant that depends on the nature of the solvent only and f: fractional free volume derived from the temperature dependence of viscoelastic relaxation.

Flisi and Crespi [39] studied the effect of crosslinking on polymer – solvent interaction parameters. They found that crosslinking efficiency in ethylene propylene copolymer is highly dependent on organic peroxides. Crosslinking efficiency of α,α'-di(tert-butylperoxy)diisopropylbenzene during of propylene - ethylene vulcanization was studied at variable composition of propylene from 27 wt% to 66.3 wt%. They found that degree of crosslinking and swelling was independent of the composition. Their result showed the 100% degree of crosslinking whereas the earlier researcher [40] found only 65% crosslinking for the same sample. Their calculation method over predicted the crosslink efficiency in high concentrated samples. They were also not able to find any relationship of interaction parameter with the composition. They calculated the degree of crosslinking using the following relation

$$\sigma = \nu_e RT\left(\lambda - \frac{1}{\lambda^2}\right)\nu_r^{-1/2},\ \nu = \nu_e + \frac{2\rho}{\bar{M}_n} \tag{13}$$

where, σ:elastic force per unit cross section of unstretched and unswollen test piece, R: gas constant, T: absolute temperature, λ: extension ratio, ν_r:volume fraction of polymer, ν_e:degree of crosslinking, ρ:specific gravity of material, $\bar{M}_n$: average molecular weight of polymer before crosslinking, ν:crosslinking efficiency.

Arkhangelsky et al. [41] developed a method to calculate the molecular weight of the crosslinked chain using sorption data when the polymer – solvent interaction parameter was concentration dependent. They did the sorption study of hexane in crosslinked poly(methylphenylhydrosiloxane). The following equations were given by them

$$\frac{\left[\ln\left(\frac{a_1}{\phi_{1a}}\right)-\phi_{2a}\right]}{\phi_{2a}^2}=\chi+\left(\frac{\rho\overline{V}_1}{M_c^{cr}}\right)\phi_{2a}^{-5/3} \tag{14}$$

$$\frac{\left[\ln\left(\frac{a_1}{\phi_{1a}}\right)-\phi_{2a}\right]}{\phi_{2a}^2}=\chi+\left(\frac{\rho\overline{V}_1}{M_c}\right)\left[\phi_{2a}^{\frac{1}{3}}-\frac{2}{f}\phi_{2a}\right]\phi_{2a}^2 \tag{15}$$

ϕ_{1a}: volume fraction of solvent absorbed, ϕ_{2a}: volume fraction of the polymer, M_c:molecular mass of chain section between the cross links, χ: polymer – solvent interaction parameter, $a_1=\frac{p}{p_0}$: relative vapor pressure, ρ: density of polymer, $\overline{V}_1$: molar volume of polymer, M_c^{cr}: average molecular mass of chain element between crystallites, f: functionality of crosslink, M_c: molecular mass of chain section between the crosslinks.

Kulkarni and Mashelkar [42] developed a mathematical model to correlate diffusivity and structure in crosslinked polymers. The model was based on a Maxwell model and considered diffusion in a two-phase system consisting of a crosslinked discrete phase dispersed in a continuous uncrosslinked matrix. This model was used to explain the effect of the crosslinking degree (f_c) on diffusion of Chlorazol Sky Blue FF dye and chrysophenine G dye in cellophane crosslinked with bishydroxyethyl sulphone and dimethylol ethylene urea. The equilibrium dye absorption as well as the rate of dyeing decreased considerably with increased crosslinking in the limiting conditions. This was attributed to the decrease in diffusivity. The molecular size and affinity of dye governed the diffusion of the dye under consideration. Increment in the crosslink density decreased interaction sites and free volume for dye diffusion. The diffusion of chlorazol Sky Blue FF was much sensitive to crosslink density as compared to Chrysophenine G. Other practical inferences from the developed model had also been drawn in this work. The following equation was given for the diffusivity:

$$D=D^*\left(\frac{1}{1+\frac{f_c}{2}}\right)+D_0 \tag{16}$$

where f_c: fraction of the dispersed crosslinked phase, and D^* and D_o are constants characteristic of the polymer-solvent system.

Peppas and Reinhart [43] developed a theoretical model for predicting diffusion coefficients of solute in swollen membranes and polymeric network. The theoretical model was satisfactorily verified with experimental results of cellulose-based semi-crystalline membranes. The model is described as under:

$$\frac{D_{2,13}}{D_{2,1}} = f\left(\frac{\overline{M_C} - \overline{M_C^*}}{\overline{M_n} - \overline{M_C^*}}\right)\exp\left(\frac{\pi r_s^2 l}{V_1(Q_m - 1)}\right) \tag{17}$$

Peppas and Moynihan [44] extended the above model for moderately swollen networks and given following model equations:

$$\frac{D_{2,13}}{D_{2,1}} = f\left(v_{3,s}^{-\frac{3}{4}}\right)\exp\left[k_3\left(\bar{M}_c - \bar{M}_n\right) - \pi r_s^2 l_s \phi(V)\right] \tag{18}$$

$$\phi(V) = \frac{V_1 - V_3}{(Q-1)V_1^2 + V_1 V_3} \qquad k_3 = \frac{-2\Delta E}{\overline{M}_n R T_F} \tag{19}$$

where $D_{2,13}$: diffusion coefficient for solute through water swollen polymeric membrane, $D_{2,1}$: diffusion coefficient for solute through water, M_c: number average molecular weight between crosslinks, M_n: upper limit of M_c, number average molecular weight of the uncrosslinked polymer, M_c^*: lower limit of M_c below which no diffusion of a specific solute occurs, r_s: stokes hydrodynamic radius of the solute, l: characteristic length, equal to or less than the translational jump length, V_1: free volume of the pure diluent (water), and Q_m: ratio of the voumes of the swollen gel to the dry polymer, *Q***:**quilibrium degree of swelling, *Q***, *r* :** the hydrodynamic radius of the solute, *M***:** number average molecular weight between crosslinks, $f(\xi)$ *:* a function of the mesh size ξ, $v_{3,s}$: polymer volume fraction at isothermal swelling equilibrium, $\Phi(V)$: free volume contribution , V_1 and V_3: free volumes of the pure diluent (water) and polymer, and constant k_3 **,** ΔE: internal energy, R: universal gas constant, and T_f: forming temperature of the polymer.

Smith and Peppas [45] studied the effect of crosslinking degree on penetrant transport in crosslinked poly(styrene). In this study, they used the cyclohexane as penetrant. Anomalous behavior of penetrant in crosslinked poly(styrene) was observed. The volume fraction of cyclo-hexane deceased as the degree of crosslinking increased. This behavior was observed due to the coupling of diffusion and relaxation mechanisms. The thickness of solvent penetration into the polymer was very low in highly crosslinked systems as compared to the loosely crosslinked ones. Average molecular weight of the crosslinked polymer was calculated using following expression:

$$\frac{1}{M_C} = \frac{1}{M_n} - \frac{v\left[\ln(1-v_2) + v_2 + \chi v_2^2\right]\left[1 - \frac{v_2^{2/3}}{N}\right]^3}{V_1\left[v_2^{1/3} - 0.5v_2\right]\left[1 + \frac{v_2^{1/3}}{N}\right]^2}, \quad \frac{M_c}{M_R} = N \tag{20}$$

$$\chi = 0.4433v_2^2 + 0.2308v_2 + 0.507, \quad v_2 = Q^{-1} = \frac{W_a^{'} - W_W^{'}}{\rho_w} \tag{21}$$

M_c: average molecular weight of crosslinked polymer, M_n : average molecular weight of uncrosslinked polymer, $W_a^{'}$: weight of sample in air, $W_W^{'}$: weight of sample in water , V_1 : volume fraction of polymer

Vrentas and Vrentas [46] developed the model to predict the self diffusion in crosslinked polymer by modifying earlier free volume theory [47, 48]. They made several assumptions while modifying the free volume theory of amorphous polymers. The assumptions were D_0, E, solvent properties: $\hat{V}_1^*, M_{j1}, \hat{V}_{FH1}$, polymer properties: γ, M_{j2}, thermal expansion coefficient, specific volume of polymer, and interstitial free volume were assumed to be independent of the crosslinking degree. These assumptions forced that self–diffusion coefficient can be affected by $\hat{V}_{FH2}$ and temperature only. The $\hat{V}_{FH2}$ was related to the pure polymer free volume and was calculated using density data. The calculations were simpler because they did not require the nature of crosslinking, rather the volumetric properties of crosslinked polymer. They found the decrement in diffusion coefficient with increment in crosslink density. They tested their model for natural rubber and found very good agreement with the volumetric expansion data. They gave the following self–diffusion equation:

$$D_1 = D_0 \exp\left(-\frac{E}{RT}\right)\exp\left[-\frac{w_1\hat{V}_1^* + w_2\xi\hat{V}_2^*}{w_1\frac{\hat{V}_{FH1}}{\gamma} + w_2\frac{\hat{V}_{FH2}}{\gamma}\delta}\right],\ \xi = \frac{\hat{V}_1^* M_{j1}}{\hat{V}_2^* M_{j2}} \tag{22}$$

$$\delta = \frac{\hat{V}_{FH2(T,X)}}{\hat{V}_{FH2(T,0)}} = \frac{\hat{V}_{2(0,X)}}{\hat{V}^0_{2(0,0)}} = \frac{\hat{V}^0_{2(T,X)}}{\hat{V}^0_{2(T,0)}} = \frac{\hat{V}^0_{2(T_1,X)}}{\hat{V}^0_{FH2(T_1,0)}} \tag{23}$$

where, w_i: mass fraction of species i, $\hat{V}_i^*$:specific hole free volume of component i, ξ: ratio of critical molar volume of solvent jumping unit to the polymer jumping unit, M_{ji}: molecular weight of jumping unit of species i, E: activation energy for diffusion, D_0: preexponential factor, γ: overlapping factor

Best and Moylan [49] studied the diffusion of water into a photopolymer film. They prepared the crosslinked film of dimethacrylate UV-cured polymer. They performed a sorption experiment to determine the diffusion coefficient and solubility in water vapor at 21°C and 19 torr. Sorption of water vapor was measured by quartz crystal microbalance. They also measured the diffusion coefficient for liquid water sorption by gravimetrical and spectroscopic techniques. After that, they compared the diffusion coefficients and water uptake from all the three techniques. They found that the quartz crystal microbalance data were much more accurate than the remaining techniques. From their results, they concluded that this photopolymer could not prevent the water sorption to films for a long period of time under ambient conditions for polymer thickness less than 1 cm.

Liyina and Sillescu [50] measured the self–diffusion coefficient of toluene in linear and crosslinked poly(styrene). In the linear poly(styrene), they found that self diffusion data follows the Arrhenius law in the beginning up to 230 K. They suggested that activation energy for diffusion is a function of temperature and concentration due to which deviations were observed beyond 230K. They considered two step diffusion of toluene in poly(styrene) to explain this deviation. They found higher value of self diffusion of toluene in crosslinked poly(styrene) as compared to linear poly(styrene). Their results showed that self–diffusion coefficient was not much affected by the crosslinks at high polymer concentrations. It was just same as that for uncrosslinked poly(styrene) at same concentration.

Mateo et al. [51] prepared crosslinked block copolymer of styrene-butadiene-styrene by exposing to UV radiations using photo-initiators. Weight gain experiments were conducted to study the sorption and diffusion of chloroform and toluene. The results conformed to the Fickian model up to nearly 60% of reaching the equilibrium swelling value. A higher crosslinking density and higher molecular size of the solvent expectedly yielded smaller equilibrium swelling value. The observed deviation from the Fickian model was due to di-phasic morphology of the SBS copolymer diffusion in more swollen part. Micro-phase separation was decreased by increasing crosslinking temperature which changed the diffusion behavior to nearly Fickian. The diffusivity was determined from the following relation:

$$D = \pi \left(\frac{h.\theta}{4.Q_{eq}} \right)^2 \tag{24}$$

where Q_{eq}: moles of liquid sorbed per 100 g of the polymer at equilibrium, y: slope of the linear part of the sorption curves before attainment of 50% equilibrium, and h: the initial sample thickness.

The interaction parameters for the crosslinked styrene-butadiene-styrene block copolymer-solvent χ and the crosslinking density v were correlated from Flory-Rehner equation [51].

$$\left[\ln\left(1 - v_r\right) + v_r + \chi v_r^2 \right] = v V_s A_\phi \left(v_r^{\frac{1}{3}} - 2\frac{v_r}{f} \right) \tag{25}$$

where v_r: volume fraction of polymer in the swollen sample, v: number of effective network chains/cm^3 of crosslinked polymer (chain density or network density), V_s: the molar volume of the solvent, f: crosslink functionality, number of chains emanating from each crosslink (generally 4), and A_f: structure factor which depends on how much the deformation deviates from the affine limit, in which the displacements of the crosslinks are a simple linear function of the macroscopic strain.

The molar mass between crosslinks was given by

$$M_C = -\frac{d_p V_S A_\phi (v_r^{1/3} - v_r / 2)}{\ln(1 - v_r) + v_r + \chi v_r^2} \tag{26}$$

where, d: the polymer density (0.94), and $A_\Phi = (1 - 2/f)$ for these highly swelling systems.

There was strong interaction between polymer and solvent as supported by calculated values of χ interaction parameters 0.41 and 0.40 for toluene and chloroform respectively. The densities of crosslinking were relatively low as indicated by the M_c values which ranged from 23000 to 5000 for 30 min to 120 min irradiation time respectively for the irradiated styrene-butadiene-styrene block copolymer [51].

Zhao et al. [52] measured the infinite dilution diffusion coefficients of *n*-decane, *n*-hexane, and *n*-heptane in crosslinked silicone rubber using inverse gas chromatography. They used several crosslinking agents in varying amount to crosslink the silicone rubber. Solvent, crosslinking agent and prepolymer polydimethylsiloxane (PDMS) were dissolved to get the crosslinked silicone rubber. The effects of small molecule solvent and crosslinking agent concentrations on the diffusion coefficient were studied. The enhancement in CH_2 group in solvent alkane series decreased the diffusion coefficient in infinite dilution. Higher amount of crosslinking agent concentration decreased the infinite dilution diffusion coefficient. The log of diffusion coefficient increased linearly with an increase in the free volume. The diffusion coefficients were determined according to the following Van Deemter equation:

$$D^\infty = \frac{8 d_p^{\,2}}{\pi^2 C} \cdot \frac{k}{(1+k)^2} \tag{27}$$

where d_p: thickness of the polymer coated on the column material, k: partition ratio, and C is related to the column characteristics and depends on probe diffusion in the liquid phase. d_p was determined from the equation:

$$d_p = \frac{w_p \rho_d d_d}{6 \rho_p w_d} \tag{28}$$

where w_p: the mass of the silicone rubber inside the carrier, w_d: the mass of carrier, ρ_p: silicone rubber density, ρ_d: carrier density, and d_d: carrier average diameter.

Krongauz [1] studied the diffusion in polymer and its dependence on the crosslink density. They studied the evaporation of N-methyl pyrrolidone from the photo crosslinked poly(acrylate). The degradation of polymer was controlled by controlling the diffusion of volatile and oxygen into the film. He found that the swelling of the polymer depends on the chain length and crosslinked density. He calculated molar concentration of crosslinks, glass transition temperature, and average number of atoms in crosslinks to explain the crosslinking. He found that the rate of diffusion increased with the temperature. The increment in crosslinked density decreased the activation energy. However, the increased chain length enhanced the activation energy for water diffusion in monolayer.

2.3 Limitations and Future Scope of Study

The literature on crosslinked polymeric coatings can be summarized in the following noteworthy points which can be helpful for further studies:

- The literature reported so far is limited mainly to the methods of crosslinking and the characterization of the crosslinked thickness [2-4, 6-12, 15-17, 21, 22, 24-34, 53].
- Sufficient literature is available to show the importance of the crosslinked polymers and coatings and their applications in the emerging areas like biosensors, biomedical, optics, physical and chemical separations, and control drug delivery [1-12].
- Very limited studies and data are available regarding the diffusion of solvent with the crosslinked polymer – solvent coatings. The literature available is limited to the sorption and that is fully developed i.e. mathematical model to explain the penetration fronts etc [1, 35-39, 41-47, 49-52]
- Neither experimental nor computational study is reported regarding the residual solvent analysis in the crosslinked polymeric coatings which plays

very important role related to stability of coatings, production defects like phase separation, blister formation, cracking, etc.

- Only one diffusion model is available to predict the self-diffusion coefficient in crosslinked polymeric coatings [46]. There were several assumptions in this model. Hence, there is an urgent need to validate this model with experimental diffusion coefficient data. The model can be further expanded to calculate the mutual diffusion coefficient which will require the activity coefficient model for crosslinked polymer – solvent systems and this too is not available in the literature.
- Vrentas and Vrentas [46] is based on free volume theory. The free volume, swelling and solvent absorption can be greatly reduced by crosslinking the coating. The crosslinking also reduces the rate of solvent evaporation from the film [1] due to decrease in free volume. Hence, crosslinked coatings will retain large amount of solvent in it, which will give rise to the production defects like phase separation, blister formation, cracking, etc. Therefore, a parameter study of free volume theory parameters is required to study the effect of variation of these parameters on the diffusion coefficient and hence the residual solvent remaining.
- The diffusion model should also be validated with depth profiling data using confocal Raman spectroscopy.
- Morphological study should be performed during the course of drying. The top layer will be highly dense as compared to the bottom layer due more amount of solvent retained. This could be an easy way to produce high mechanical strength asymmetric membranes.

Chapter 3

Materials and Methods

3.1 Chemicals Used

Poly(styrene) was provided by Sigma Aldrich, Germany (density: 1.04 g.cm^{-3}, molecular weight: 192000), *p*-xylene was provided by Spectrochem, India (density: 0.861 g.cm^{-3} , molecular weight: 106.16), Ethyl benzene was provided by Spectrochem, India (density: 0.866 g.cm^{-3} , molecular weight: 106.17), Poly(styrene-co-divinylbenzene) was provided by Sigma Aldrich, Germany (density: 0.29 g.cm^{-3}) and its chemical structure are shown in Figure 3.1. All chemicals were utilized as provided with no further purification.

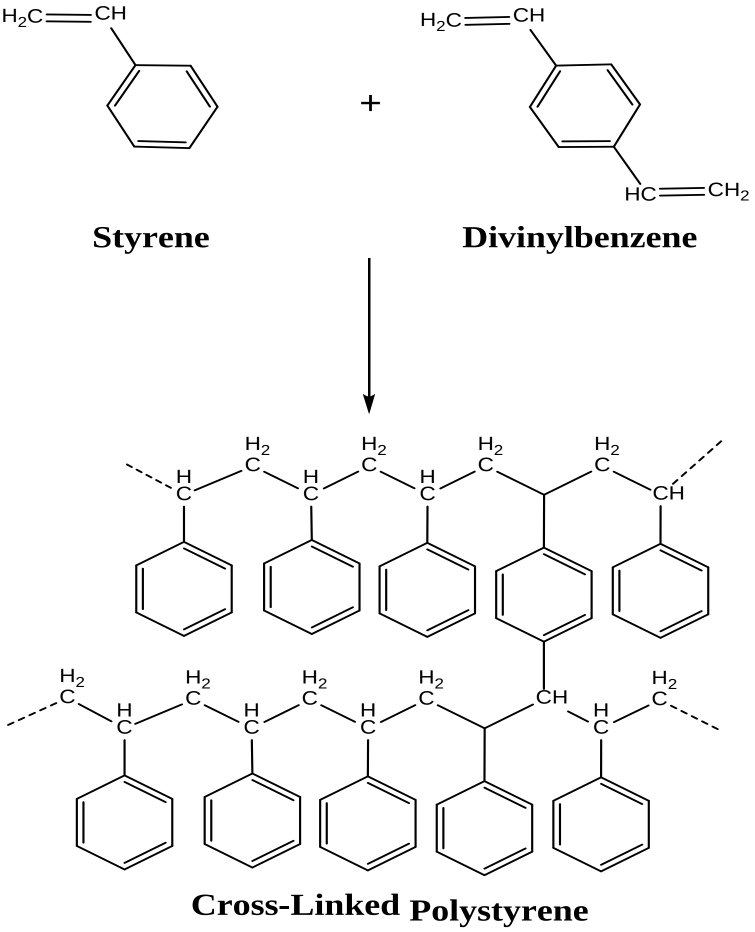


Figure 3.1: Poly(styrene) crosslinked with divinylbenzene.

3.2 Methodology

As described in Chapter 1, the solution casting technique was followed for the preparation of coatings in the present work. A predecided amount of polymer solution was poured into the sample holder to get the desired initial coating thickness. In this work, the coatings of poly(styrene) and crosslinked poly(styrene-co-divinylbenzene) were prepared in *p*-xylene and ethylbenzene. Crosslinked poly(styrene-co-divinylbenzene) mass fraction was varied in poly(styrene) solution to see the effect of the proportion of crosslinked poly(styrene-co-divinylbenzene) on the residual solvent.

Two solutions of poly(styrene) were prepared in *p*-xylene and ethylbenzene having 10.12% and 9.93% poly(styrene) by weight respectively. Another two solution of poly(styrene), Poly(styrene-co-divinylbenzene) and *p*-xylene were prepared having their weight percentage (9.94% , 0.98% , and 89.08%) and (2.01%, 10.07% , and 87.92%) respectively. Another two solution of poly(styrene), Poly(styrene-co-divinylbenzene) and ethylbenzene were prepared having their weight percentage (10.01% , 0.99%, and 89%) and (2.08%, 9.98% and 87.94%) respectively. These solutions were prepared by taking the required quantity of solvent and polymer(s) in reagent bottles. These solutions were shaken mechanically for 24 hours and left for swelling of crosslinked polymer around 3 months to swell the uncrosslinked polymer. Manual shaking was done every day for around 30 minutes to get the homogeneous solutions.

Several coatings of different initial thicknesses were prepared by pouring varied quantity of polymer solutions by using micropipette in the circular sample holder having 12.24mm diameter and1000 µm depth of sample holder is shown in Figure 3.2. Solvent evaporates from the coating immediately after pouring, resulting the loss in weight of the coating solution. The sample weight was recorded as a function of time by using Sartorius Analytical weighing balance (ES225SM-DR) having accuracy of ± 0.0001 g. The weight data with time were recorded until no further change in two consecutive weight data to make sure that drying process has been stopped for practical purpose. Coatings were dried under natural convection. All the experiments were conducted at 25±1°C or as stated.

3.3 Calculations of Various Coating Parameters

Let the mass of solution in any time is “m” of polymer solution having 10.16% polymer and 89.84% solvent respectively.

Mass of polymer, $M_p = m \times \frac{10.16}{100}$

Initial mass of solvent, $M_S = m \times \frac{89.84}{100}$

Volume of coating, $V_{\text{Coating}} = \frac{M_p}{\text{density of polymer}} + \frac{M_S}{\text{density of solvent}}$

% Residual Solvent = $\frac{\text{Instantaneous coating mass} - m}{M_s} \times 100$

Thickness of coating, L = $\frac{V_{\text{Coating}}}{\text{Cross - sectional area of sample holder}}$

Concentration of polymer = $\frac{m \times 10.16}{V_{\text{coating}}}$

Concentration of solvent = $\frac{\text{Instantaneous coating mass} - M_P}{V_{\text{Coating}}}$

Figure 3.2: Circular sample holder.

Chapter 4

Results and Discussions

The effect of cross-linked polymer content on the drying behavior of polymeric coatings was studied. Poly(styrene)–ethylbenzene and poly(styrene)–*p*-xylene systems have chosen for the present study. Poly(styrene-co-divinylbenzene) has been chosen as the crosslink polymer having 1% crosslinking. The effect of crosslink content in the poly(styrene) – ethylbenzene and poly(styrene) – *p*-xylene systems has been studied and reported in this chapter.

4.1 Drying of Poly(styrene) – *p*-xylene Coating having 0.98% Poly(styrene-co-divinylbenzene)

Two solutions of poly(styrene), one having linear poly(styrene) and the other having linear poly(styrene) and poly(styrene-co-divinylbenzene) were prepared in *p*-xylene. The *p*-xylene weight percentages in linear and crosslinked solutions were 89.88% and 89.08% respectively. These solutions are named as type 1 and type 2. Several coatings of each type have been prepared to study the effect of crosslink content on residual solvent, coating thickness, concentrations of poly(styrene) and solvent, and the drying time.

Type 1: 10.12% poly(styrene) and 89.88% p-xylene

Type 2: 9.94% poly(styrene), 89.08% p-xylene and 0.98% poly(styrene-co-divinyl-benzene)

4.1.1 Percentage of Residual Solvent

The change of residual *p*-xylene content with time is shown in Figure 4.1. It shows that the percentage of residual *p*-xylene is decreasing with time. In type 1, the residual *p*-xylene linearly decreases up to 110 min 43 s, 141 min 10 s, and 185 min 52 s respectively in the cases of coatings having initial thicknesses 408 µm, 654 µm, 816 µm respectively, Up to 98.28%, 97.13%, and 96.8% *p*-xylene has been removed in, and the remaining 1.72%, 2.87% and 3.2% *p*-xylene is permanently trapped in the coatings respectively. The coatings of Type 2 solution have followed the same trend and the residual *p*-xylene is also decreasing linearly up to 110 min 34 s, 121 min 50 s, and 163 min 14 s in the cases of coatings having initial thickness 387 µm, 566 µm, and 752 µm respectively. Up to 91.93%, 90.45% and 89.02% *p*-xylene has been removed, in and the remaining 8.07%, 9.55% and 10.98% *p*-xylene is permanently trapped in the coatings respectively. With the increase in time, the percentage of residual *p*-xylene is decreasing at extremely slow rate due to poor diffusion of *p*-xylene at later stages of drying. In the beginning, the percentage of residual *p*-xylene decreases at a very fast rate, due to fast evaporation of *p*-xylene from the top surface and huge amount of *p*-xylene was present in the coating in the beginning and drying process is externally controlled. It was observed that type 2 takes more time for drying because of the presence of nearly 1% crosslinked polymer, due to which there is very less availability of free volume and the solvent cannot diffuse easily as compared to the uncrosslinked polymer, i.e., type1.

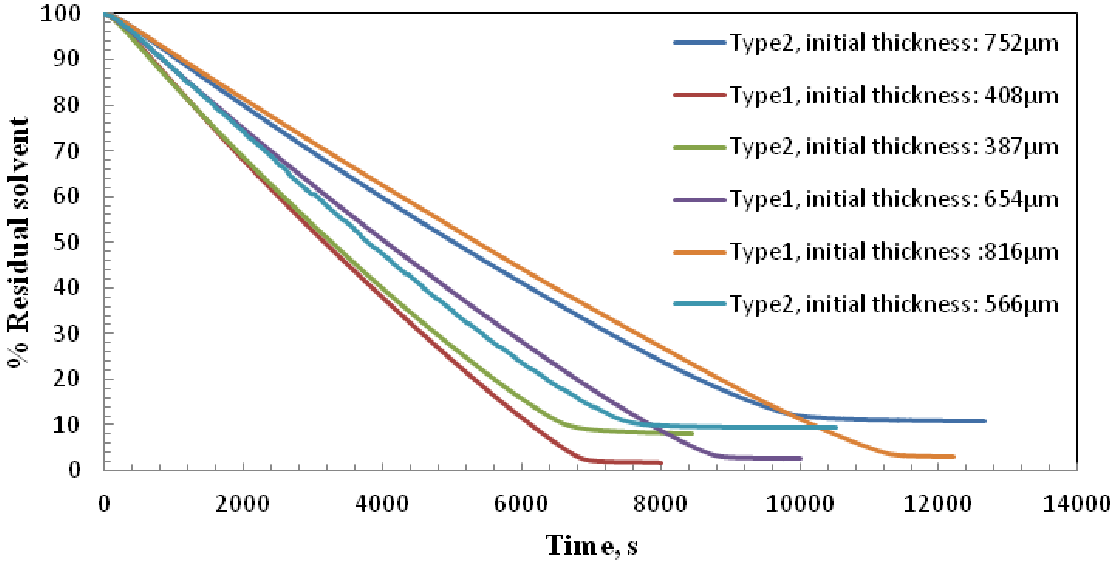


Figure 4.1: Residual solvent as a function of time in poly(styrene) – *p*-xylene system with and without crosslinked poly(styrene-co-divinylbenzene) at 18°C.

4.1.2 Coating Thickness

Figure 4.2 shows the variation of coating thickness with time. It shows that the thickness starts decreasing with time due to evaporation of *p*-xylene from the coating into surrounding. In the beginning, the thicknesses of type 1 coatings were 408 µm, 654 µm, and 816 µm respectively, and decreases linearly up to 114 min 18 s, 144 min 14 s and 185 min 18 s respectively and then it plateaus off. The Thickness of type 2 coatings in the beginning were 387 µm, 566 µm and 752 µm respectively, and also decreases linearly up to 110 min 53 s, 123 min 17 s and 159 min 38 s respectively and then it plateaus off. The coatings having very small amount of crosslinked poly(styrene-co-divinylbenzene) (0.98%) are left thicker at the end of drying process. It is due to the more amount of *p*-xylene has been trapped in these coatings since, the poly(styrene) content in type 1 and type 2 coatings are 10.12% and 9.94% respectively. For an instance, initial coatings thickness: 408 µm and 387 µm of type 1 and type 2 solution respectively are giving the dried coating thickness of 25 µm and 58 µm respectively at the end of 133 min 31 s and 140 min 56 s.

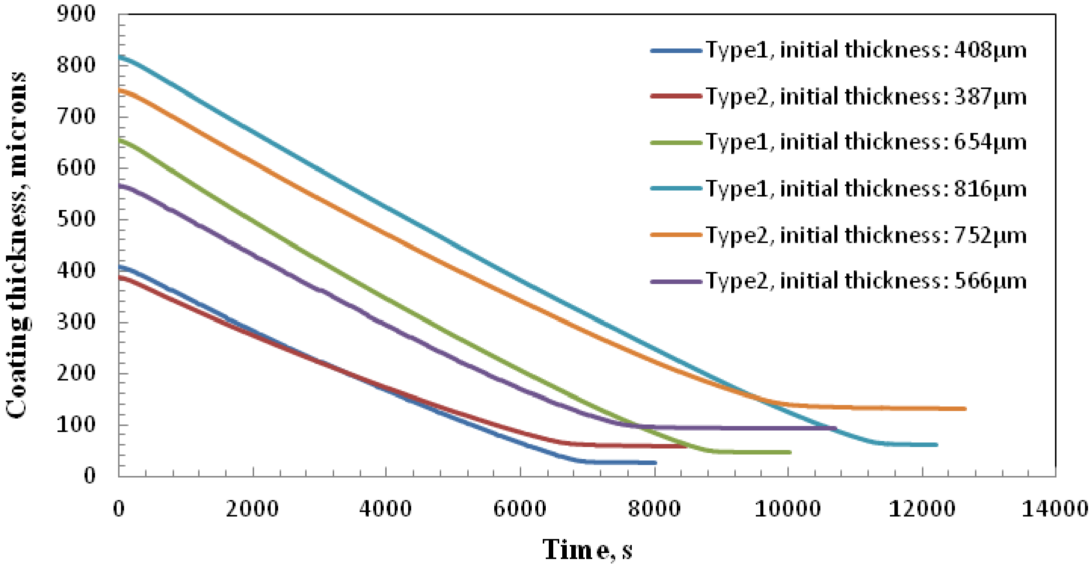


Figure 4.2: Thickness as a function of time in poly(styrene) – *p*-xylene system having crosslinked and uncrosslinked poly(styrene-co-divinylbenzene) at 18°C.

4.1.3 Average Concentration of p-xylene

The average concentration of *p*-xylene with time is shown in Figure 4.3. It describes that the *p*-xylene is evaporating from the coating and its concentration start decreasing with time. In type 1, the concentration of *p*-xylene decreases exponentially up to 118 min 21 s, 147 min 52 s and 189 min 17 s in the cases of the coatings having initial thicknesses of 408 µm, 654 µm, and 816 µm respectively, and then it leveled off. Type 2 coatings follows the same trend, the *p*-xylene concentration decreases exponentially at slow rate up to 109 min 22 s, 123 min 20 s and 162 min 52 s in the cases of coatings having initial thicknesses 387 µm, 566 µm, and 752 µm respectively, and then it leveled off. The final concentration of *p*-xylene in type 1 coating were 0.237 g.cm^{-3}, 0.334 g.cm^{-3} and 0.356 g.cm^{-3} for coatings having initial concentration 0.823 g.cm^{-3}, 0.823 g.cm^{-3} and 0.823 g.cm^{-3}, and thicknesses 408 µm, 654 µm, and 816 µm respectively. The final concentration of *p*-xylene in type 2 coating were 0.434 g.cm^{-3}, 0.470 g.cm^{-3} and 0.499 g.cm^{-3}, for coatings having initial concentration 0.797 g.cm^{-3}, 0.797 g.cm^{-3} and 0.797 g.cm^{-3}, thicknesses 387 µm, 566 µm, and 752 µm respectively.

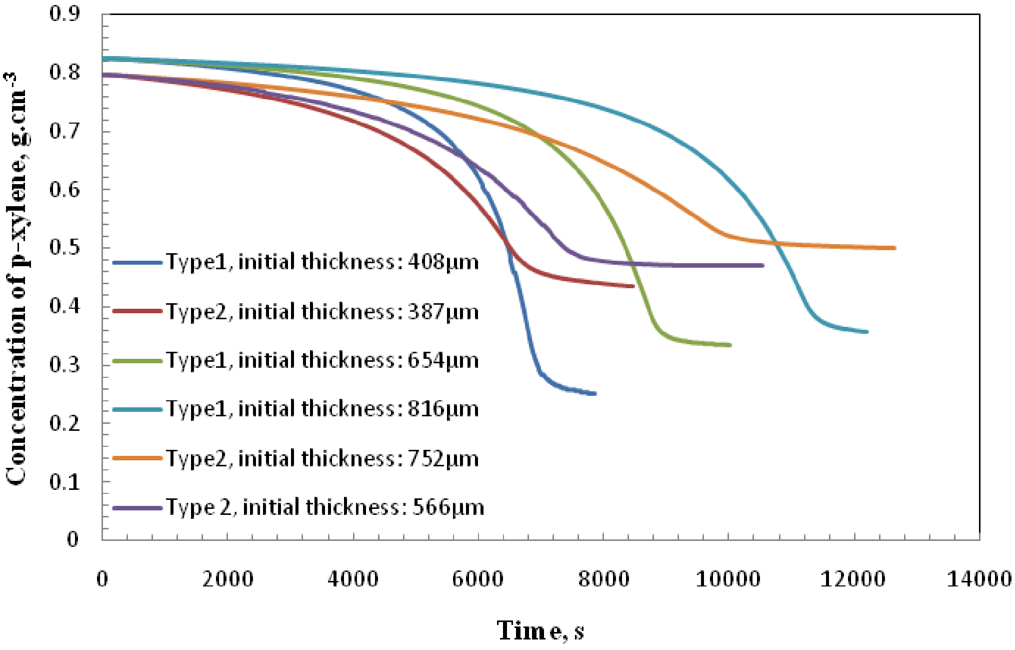


Figure 4.3: Concentration of *p*-xylene as a function of time in poly(styrene) – *p*-xylene system having crosslinked and uncrosslinked poly(styrene-co-divinylbenzene) at 18°C.

4.1.4 Average Concentration of Polymer

Figure 4.4 depicts the average concentration of polymer (poly(styrene) and poly(styrene-co-divinylbenzene)) with time. It represents that the polymer concentration start increasing with time due to evaporation of *p*-xylene from coating. In type1, coatings the concentration of the polymer increases exponentially up to 116 min 54 s, 148 min 17 s and 188 min 50 s respectively in cases of coatings having initial thickness of 408 µm, 654 µm, and 816 µm respectively and then plateaus off. Type 2 coatings also follow the same trend, the polymer concentration increases exponentially at slow rate up to 113 min 50 s, 123 min 44 s and 163 min 44 s in the cases of coatings having initial thicknesses of 387 µm, 566 µm, and 752 µm respectively and then plateaus off. With the increase in drying time, there is increase in the concentration of the polymer due to more solvent removal from the coating.

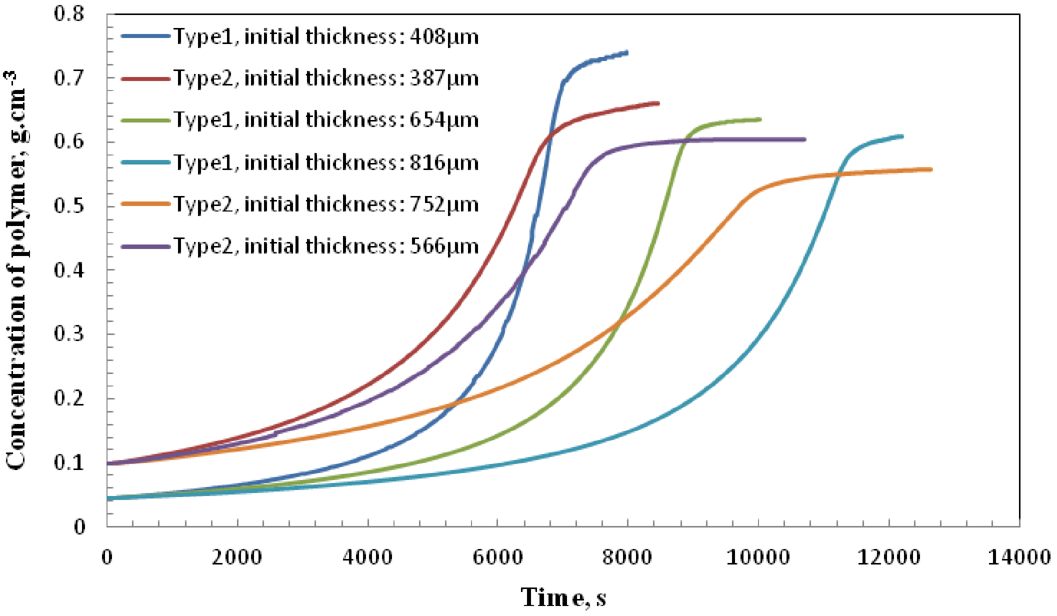


Figure 4.4: Concentration of polymer as a function of time in poly(styrene) – *p*-xylene system with and without crosslinked poly(styrene-co-divinylbenzene) at 18°C.

4.2 Drying of Poly(styrene) – *p*-xylene Coating having 2.01% Poly(styrene-co-divinylbenzene)

Two solutions of poly(styrene) one having linear poly(styrene) and the other having linear poly(styrene) and poly(styrene-co-divinylbenzene) were prepared in *p*-xylene. The *p*-xylene weight percentages were 89.88% and 87.92% respectively. These solutions are named as type 1 and type 3. Several coatings of each type have been prepared to study the effect of crosslink content on residual solvent, coating thickness, concentrations of poly(styrene) and solvent, and the drying time.

Type 1: 10.12% poly(styrene) and 89.88% *p*-xylene

Type 3: 10.07% poly(styrene), 87.92% *p*-xylene, and 2.01% poly(styrene-co-divinylbenzene)

4.2.1 Percentage of Residual Solvent

The change of residual *p*-xylene content with time is shown in Figure 4.5. It shows that the percentage of residual *p*-xylene decreasing with time. In type 1, the residual solvent linearly decreases up to 62 min 35 s, 97 min 20 s, and 110 min 35 s respectively in the cases of coatings having initial thicknesses of 446 µm, 632 µm, and 872 µm respectively. Up to 94.17%, 96.41%, and 93.61% *p*-xylene has been removed, and the remaining 5.83%, 3.59% and 6.39% solvent permanently trapped in the coatings respectively. The coatings of Type 3 solution have followed the same trend and the residual *p*-xylene is also decreasing linearly up to 56 min 55 s, 96 min 10 s, and 101 min 10 s in the cases of coatings having initial thicknesses of 331 µm, 603 µm, and 683 µm respectively. Up to 89.56%, 87.62% and 87.6% *p*-xylene has been removed, and the remaining 10.44%, 12.38% and 12.40% *p*-xylene is permanently trapped in the coatings respectively. With the increase in time, the percentage of residual *p*-xylene is decreasing at extremely slow rate due to poor diffusion of *p*-xylene at later stages of drying. In the beginning, the percentage of residual *p*-xylene decreases at a very fast rate, due to fast evaporation of *p*-xylene from the top surface and huge amount of *p*-xylene was present in the coating in the beginning and drying process is externally controlled. It was observed that type 3 takes more time for drying because of the presence of nearly 2% crosslinked polymer, due to which there is very less availability of free volume and the solvent cannot diffuse easily as compared to the uncrosslinked polymer, i.e., type1.

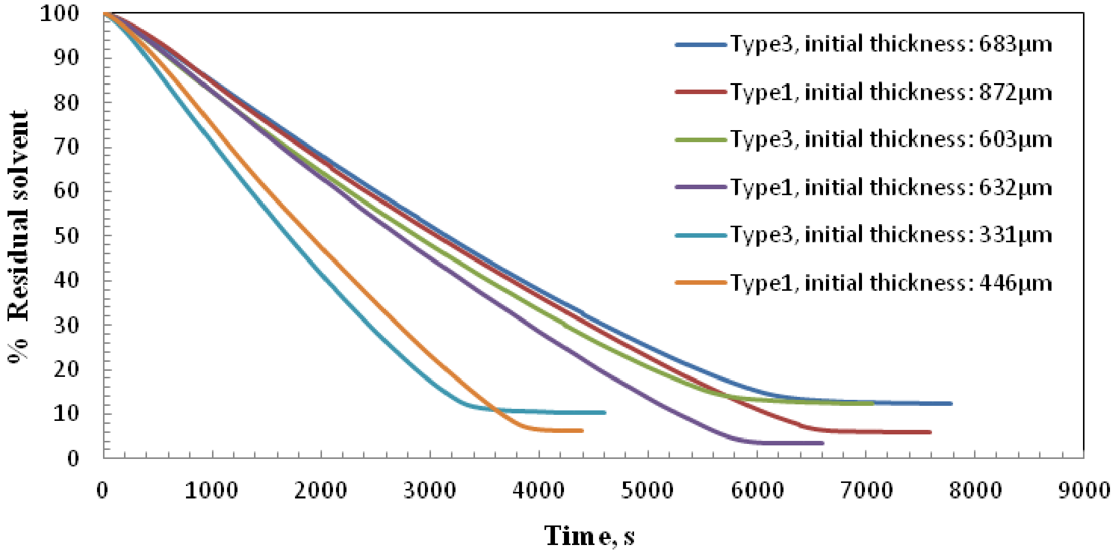


Figure 4.5: Residual solvent as a function of time in poly(styrene) – *p*-xylene system with and without crosslinked poly(styrene-co-divinylbenzene) at 25°C.

4.2.2 Coating Thickness

Figure 4.6 shows the variation of coating thickness with time. It shows that the thickness starts decreasing with time due to evaporation of *p*-xylene from the coating into surrounding. In the beginning, the thicknesses of type 1 coatings were 446 µm, 632 µm, and 872 µm respectively and decreases linearly up to 61min 45 s, 97 min 25 s and 107 min 20 s respectively and then it plateaus off. The thickness of type 3 coatings in the beginning were 331 µm, 603 µm and 683 µm respectively and also decreases linearly up to 54 min 10 s, 95 min 25 s and 102 min 10 s respectively and then it plateaus off. The coatings having very small amount of crosslinked poly(styrene-co-divinylbenzene) (2.01%) are left thicker at the end of drying process. It is due to the more amount of *p*-xylene has been trapped in these coatings since, the poly(styrene) content in type 1 and type 3 coatings are 10.12% and 10.07% respectively. For an instance, initial coatings thickness: 632 µm and 603 µm of type 1 and type 3 solution respectively are giving the dried coating thickness of 50 µm and 118 µm respectively at the end of 110 min 5 s and 117 min 35 s.

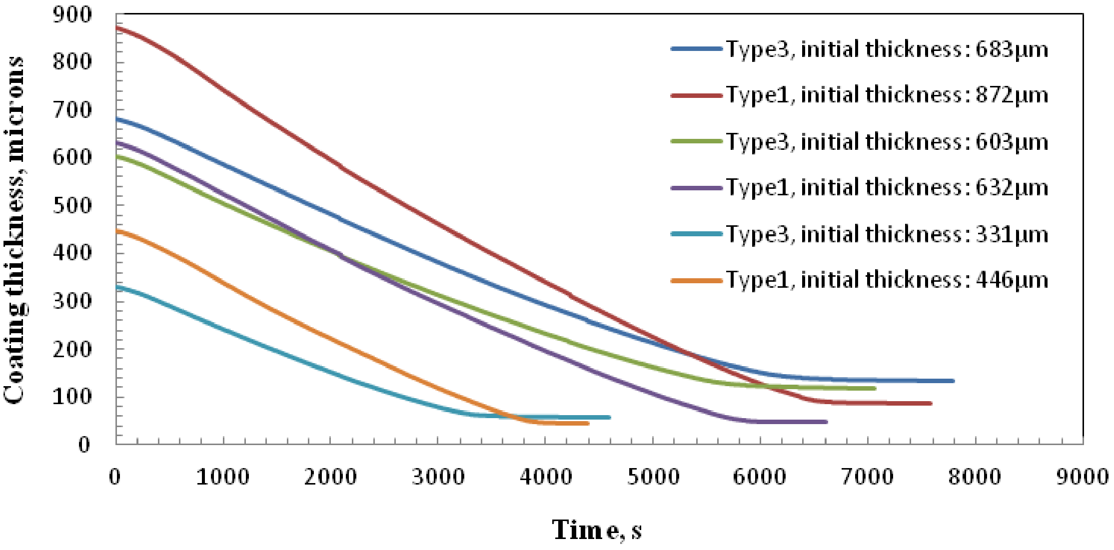


Figure 4.6: Thickness as a function of time in poly(styrene) – *p*-xylene system having crosslinked and uncrosslinked poly(styrene-co-divinylbenzene) at 25°C.

4.2.3 Average Concentration of *p*-xylene

The average concentration of *p*-xylene with time is shown in Figure 4.7. It describes that the solvent is evaporating from the coating and its concentration start decreasing with time. In type 1, coatings the concentration of *p*-xylene decreases exponentially up to 66 min 20 s, 91 min 10 s and 111 min 40 s in the cases of the coatings having initial thicknesses of 446 µm, 632 µm, and 872 µm respectively and then it leveled off. Type 3 coatings follows the same trend, the *p*-xylene concentration decreases exponentially up to 55 min 10 s, 97 min 35 s and 98 min 50 s in the cases of coatings having initial thicknesses 331 µm, 603 µm, and 683 µm respectively and then it leveled off. The final concentration of *p*-xylene in type 1 coatings were 0.504 g.cm^{-3}, 0.381 g.cm^{-3}, and 0.485 g.cm^{-3}, for coatings having initial concentration 0.823 g.cm^{-3}, 0.823 g.cm^{-3} and 0.823 g.cm^{-3}, and thicknesses 446 µm, 632 µm, and 872 µm respectively. The final concentration of *p*-xylene in type 3 coatings were 0.464 g.cm^{-3}, 0.501 g.cm^{-3}, and 0.501 g.cm^{-3}, for coatings having initial concentration 0.790 g.cm^{-3}, 0. 7906 g.cm^{-3} and 0.790 g.cm^{-3}, and thicknesses 331 µm, 603 µm, and 683 µm respectively.

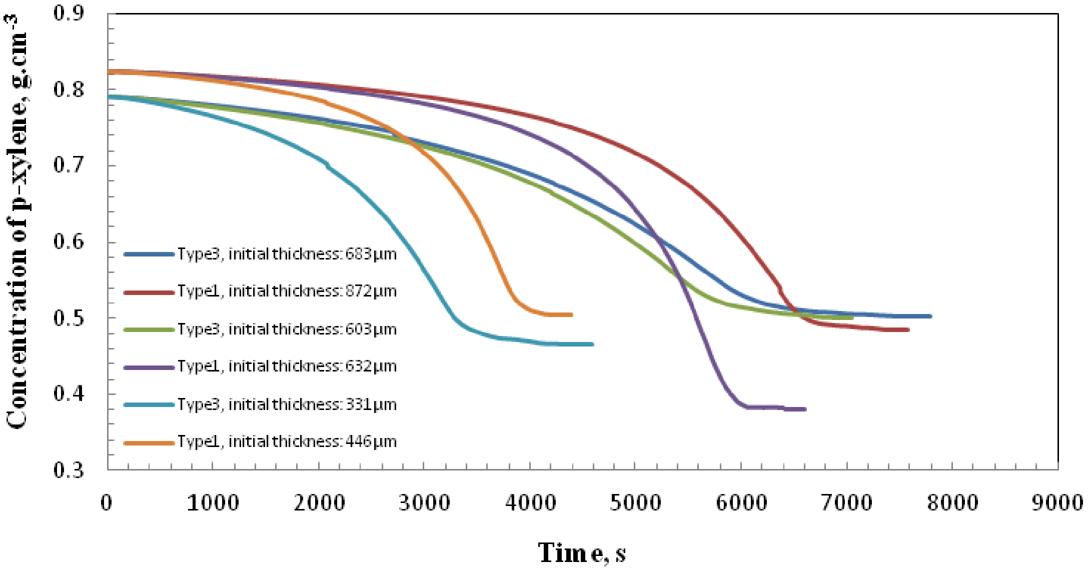


Figure 4.7: Concentration of p-xylene as a function of time in poly(styrene) – *p*-xylene system having crosslinked and uncrosslinked poly(styrene-co-divinylbenzene) at 25°C.

4.2.4 Average Concentration of Polymer

Figure 4.8 depicts the average concentration of polymer (poly(styrene) and poly(styrene-co-divinylbenzene)) with time. It represents that the polymer concentration start increasing with time due to evaporation of *p*-xylene from coating. In type 1, coatings the concentration of polymer increases exponentially up to 64 min, 99 min 55 s and 109 min 10 s respectively in cases of coatings having initial thicknesses of 446 µm, 632 µm, and 872 µm respectively and then plateaus off. Type 3 coatings also follow the same trend, the polymer concentration increases exponentially at slow rate up to 55 min 10 s, 95 min 55 s and 105 min 20 s in the cases of coatings having initial thicknesses 331 µm, 603 µm, and 683 µm respectively and then plateaus off. With the increase in time, there is increase in the concentration of the polymer due to more solvent removal from the coating.

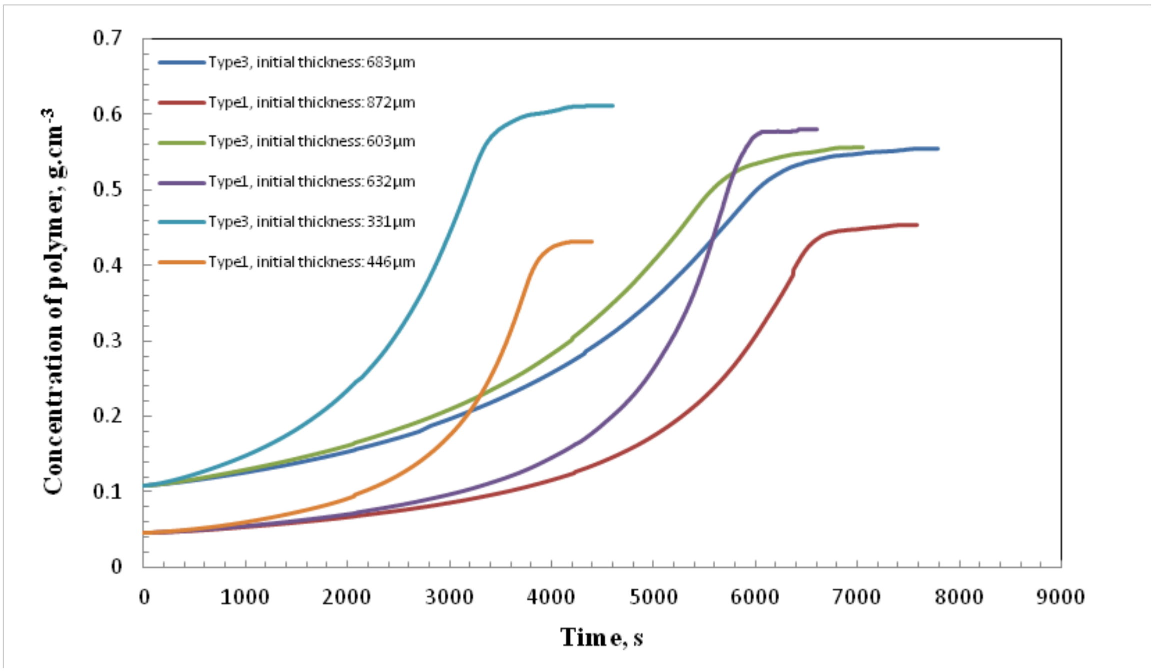


Figure 4.8: Concentration of polymer as a function of time in poly(styrene) – *p*-xylene system with and without crosslinked poly(styrene-co-divinylbenzene) at 25°C.

4.3 Drying of Poly(styrene) – ethylbenzene Coating having 0.99% Poly(styrene-co-divinylbenzene)

Two solutions of poly(styrene) one having linear poly(styrene) and the other having linear poly(styrene) and poly(styrene-co-divinylbenzene) were prepared in ethylbenzene. The ethylbenzene weight percentages were 90.07% and 89% respectively. These solutions are named as type 4 and type 5. Several coatings of each type have been prepared to study the effect of crosslink content on residual solvent, coating thickness, concentrations of poly(styrene) and solvent, and the drying time.

Type 4: 9.93% poly(styrene) and 90.07% ethylbenzene

Type 5: 10.01% poly(styrene), 89% ethylbenzene, and 0.99% poly(styrene-co-divinyl-benzene)

4.3.1 Percentage of Residual Solvent

The change of residual ethylbenzene content with time is shown in Figure 4.9. It shows that the percentage of residual ethylbenzene decreasing with time. In type 4, the residual ethylbenzene linearly decreases up to 54 min 10 s, 69 min 20 s, and 95 min 45 s respectively in the cases of coatings having initial thicknesses 399 µm, 518 µm, and 751 µm respectively. Up to 95.25%, 94.43%, and 94.61% ethylbenzene has been removed, and the remaining 4.75%, 5.57% and 5.39% ethylbenzene permanently trapped in the coatings respectively. The coatings of type 5 solutions have followed the same trend and the residual ethylbenzene is also decreasing linearly up to 60 min 25 s, 64 min 35 s, and 106 min in the cases of coatings having initial thicknesses 423 µm, 472 µm, and 755 µm respectively. Up to 86.5%, 88.96% and 87.55% ethylbenzene has been removed, and the remaining 13.50%, 11.04% and 12.45% ethylbenzene is permanently trapped in the coatings respectively. With the increase in time, the percentage of residual ethylbenzene is decreasing at extremely slow rate due to poor diffusion of ethylbenzene at later stages of drying. In the beginning, the percentage of residual ethylbenzene decreases at a very fast rate, due to fast evaporation of ethylbenzene from the top surface and huge amount of ethylbenzene was present in the coating in the beginning and drying process is externally controlled. It was observed that type 5 takes more time for drying because of the presence of nearly 1% crosslinked polymer, due to which there is very less availability of free volume and the solvent cannot diffuse easily as compared to the uncrosslinked polymer, i.e., type 4.

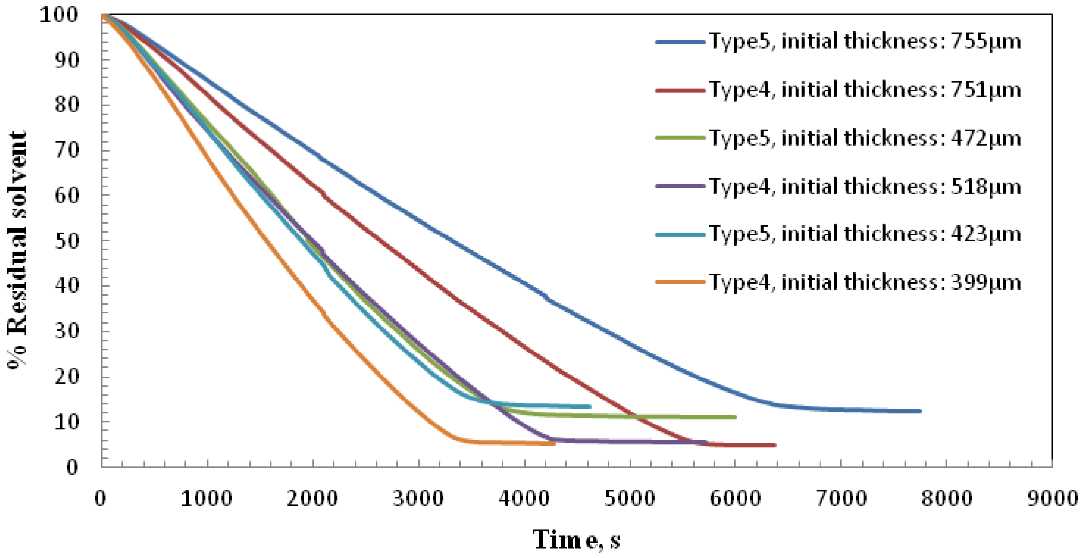


Figure 4.9: Residual solvent as a function of time in poly(styrene) – ethylbenzene system with and without crosslinked poly(styrene-co-divinylbenzene) at 25°C.

4.3.2 Coating Thickness

Figure 4.10 shows the variation of coating thickness with time. It shows that the thickness starts decreasing with time due to evaporation of ethylbenzene from the coating into surrounding. In the beginning, the thicknesses of type 4 coatings were 399 µm, 518 µm, and 751 µm respectively and decreases linearly up to 54 min 55 s, 70 min 20 s and 91 min 55 s respectively and then it plateaus off. The thickness of type 5 coatings in the beginning were 423 µm, 472 µm and 755 µm respectively and also decreases linearly up to 57 min 30 s, 60 min 40 s and 105 min 35 s respectively and then it plateaus off. The coatings having very small amount of crosslinked poly(styrene-co-divinylbenzene) (0.99%) are left thicker at the end of drying process. It is due to the more amount of ethylbenzene has been trapped in these coatings since, the poly(styrene) content in type 4 and type 5 coatings are 9.93% and 10.01% respectively. For an instance, initial coatings thickness: 399 µm and 423 µm of type 4 and type 5 solution respectively are giving the dried coating thickness of 38 µm and 85 µm respectively at the end of 71 min 15 s and 76 min 55 s.

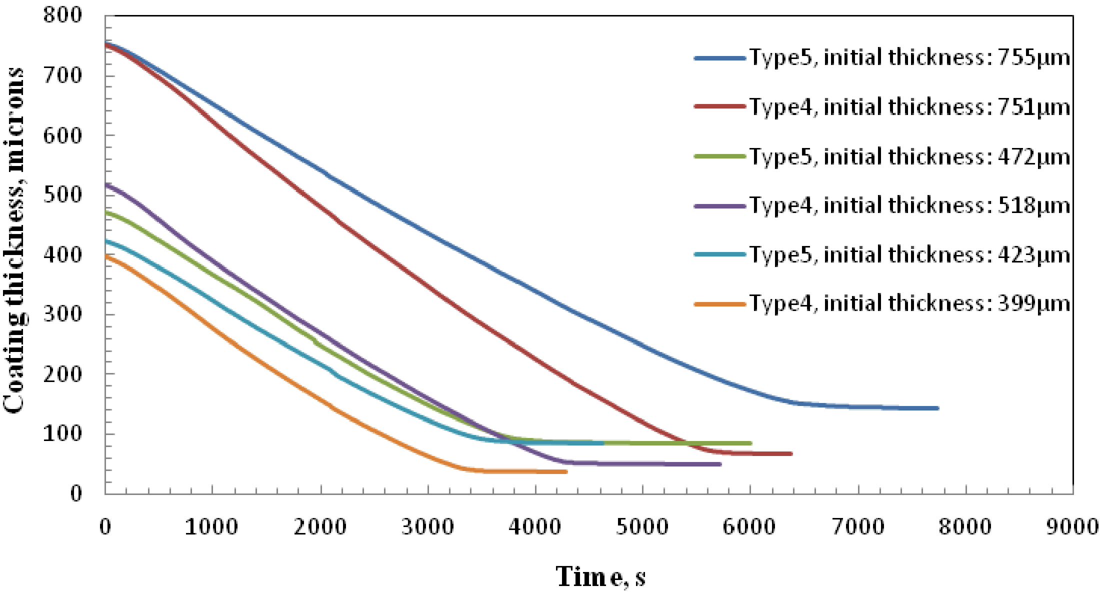


Figure 4.10: Thickness as a function of time in poly(styrene) – ethylbenzene system having crosslinked and uncrosslinked poly(styrene-co-divinylbenzene) at 25°C.

4.3.3 Average Concentration of Ethylbenzene

The average concentration of ethylbenzene with time is shown in Figure 4.11. It describes that the ethylbenzene is evaporating from the coating and its concentration start decreasing with time. In type 4, the concentration of ethylbenzene decreases exponentially up to 56 min 45 s, 72 min 25 s and 93 min 10 s in the cases of the coatings having initial thicknesses 399 µm, 518 µm, and 751 µm respectively, and then it leveled off. Type 5 coatings follows the same trend, the ethylbenzene concentration decreases exponentially at slow rate up to 49 min, 66 min 45 s and 107 min 30 s in the cases of coatings having initial thicknesses 423 µm, 472 µm, and 755 µm respectively, and then it leveled off. The final concentration of ethylbenzene in type 4 coatings were 0.476 $g.cm^{-3}$, 0.484 $g.cm^{-3}$, and 0.449 $g.cm^{-3}$, for coatings having initial concentration 0.829 $g.cm^{-3}$, 0.829 $g.cm^{-3}$and 0.829 $g.cm^{-3}$, and thicknesses 399 µm, 518 µm, and 751 µm respectively. The final concentration of ethylbenzene in type 5 coatings were 0.542 $g.cm^{-3}$, 0.500 $g.cm^{-3}$, and 0.525 $g.cm^{-3}$, for coatings having initial concentration 0.801 $g.cm^{-3}$, 0.801 $g.cm^{-3}$ and 0.801 $g.cm^{-3}$, and thicknesses 423 µm, 472 µm, and 755 µm respectively.

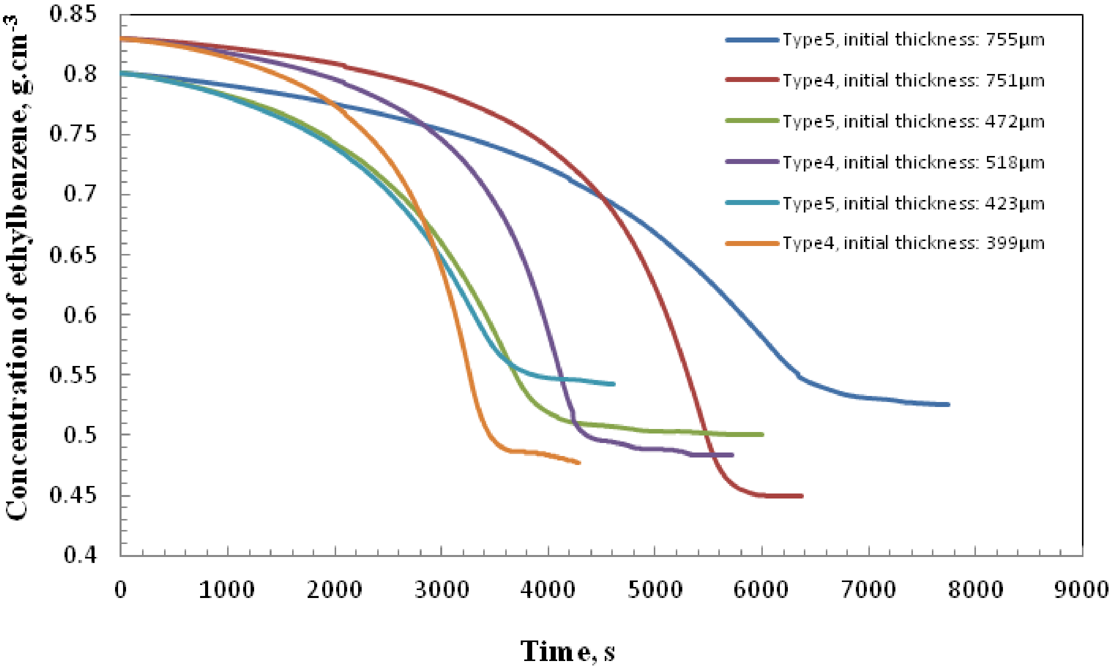


Figure 4.11: Concentration of ethyl benzene as a function of time in poly(styrene) – ethylbenzene system having crosslinked and uncrosslinked poly(styrene-co-divinyl-benzene) at 25°C.

4.3.4 Average Concentration of Polymer

Figure 4.12 depicts the average concentration of polymer (poly(styrene) and poly(styrene-co-divinylbenzene)) with time. It represents that the polymer concentration start increasing with time due evaporation of ethylbenzene from coating. In type 4, coatings the concentration of the polymer increases exponentially up to 57 min 30 s, 70 min 45 s and 94 min 50 s in the cases of coatings having initial thicknesses 399 µm, 518 µm, and 751 µm respectively, and then plateaus off. Type 5 coatings also follow the same trend, the polymer concentration increases exponentially at slow rate up to 60 min 20 s, 65 min 40 s and 109 min 30 s in the cases of coatings having initial thicknesses 423 µm, 472 µm, and 755 µm respectively, and then plateaus off. With the increase in drying time, there is increase in the concentration of the polymer due to more solvent removal from the coating.

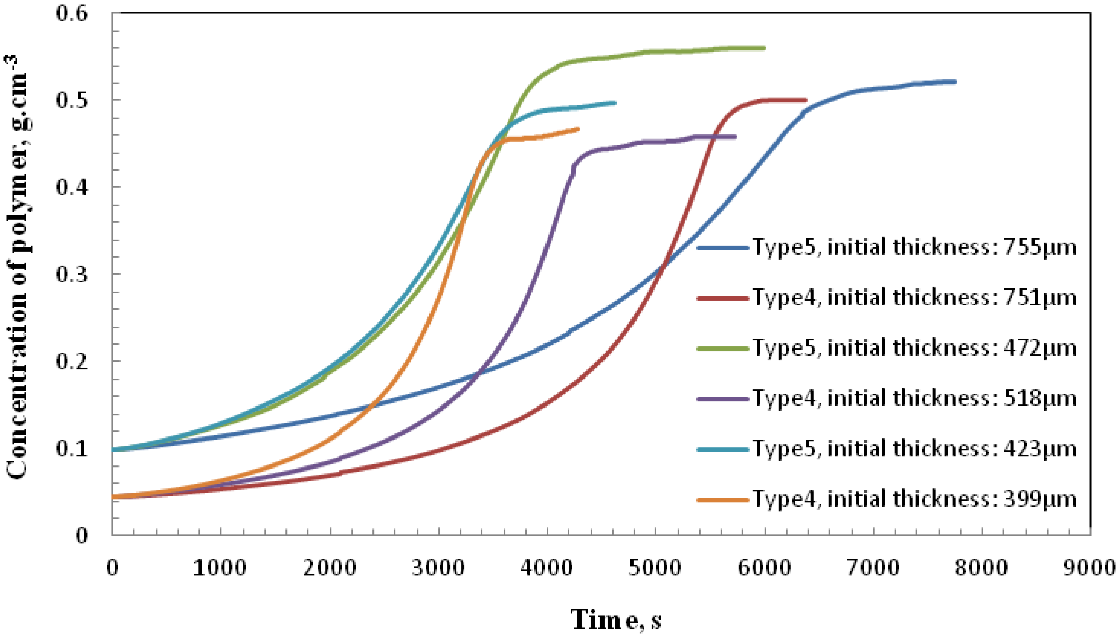


Figure 4.12: Concentration of polymer as a function of time in poly(styrene) – ethylbenzene system with and without crosslinked poly(styrene-co-divinylbenzene) at 25°C.

4.4 Drying of Poly(styrene) – ethylbenzene Coating having 2.08% Poly(styrene-co-divinylbenzene)

Two solutions of poly(styrene) one having linear poly(styrene) and the other having linear poly(styrene) and poly(styrene-co-divinylbenzene) were prepared in ethyl benzene. The ethylbenzene weight percentages were 90.07% and 87.94% respectively. These solutions are named as type 4 and type 6. Several coatings of each type have been prepared to study the effect of crosslink content on residual solvent, coating thickness, concentrations of poly(styrene) and solvent, and the drying time.

Type 4: 9.93% poly(styrene) and 90.07% ethylbenzene

Type 6: 9.98% poly(styrene), 87.94% ethylbenzene, and 2.08% poly(styrene-co-divinyl-benzene)

4.4.1 Percentage of Residual Solvent

The change of residual ethylbenzene content with time is shown in Figure 4.13. It shows that the percentage of residual ethylbenzene decreasing with time. In type 4, the residual ethylbenzene linearly decreases up to 54 min 10 s, 69 min 20 s, and 95 min 45 s respectively, in the cases of coatings having initial thicknesses 399 µm, 518 µm, and 751 µm respectively. Up to 95.25%, 94.43%, and 94.61% ethylbenzene has been removed, and the remaining 4.75%, 5.57% and 5.39% ethylbenzene permanently trapped in the coatings respectively. The coatings of type 6 solutions have followed the same trend and the residual ethylbenzene is also decreasing linearly up to 48 min 39 s, 83 min 40 s, and 91 min 40 s in the cases of coatings having initial thicknesses of 361 µm, 640 µm, and 779 µm respectively. Up to 83.66%, 88.13% and 87.26% ethylbenzene has been removed, and the remaining 16.34%, 11.87% and 12.74% ethyl benzene permanently trapped in the coatings respectively. With the increase in time, the percentage of residual ethylbenzene is decreasing at extremely slow rate due to poor diffusion of ethylbenzene at later stages of drying. In the beginning, the percentage of residual ethylbenzene decreases at a very fast rate, due to fast evaporation of ethylbenzene from the top surface and huge amount of ethylbenzene was present in the coating in the beginning and drying process is externally controlled. It was observed that type 6 takes more time for drying because of the presence of nearly 2% crosslinked polymer, due to which there is very less availability of free volume and the solvent cannot diffuse easily as compared to the uncrosslinked polymer, i.e., type 4.

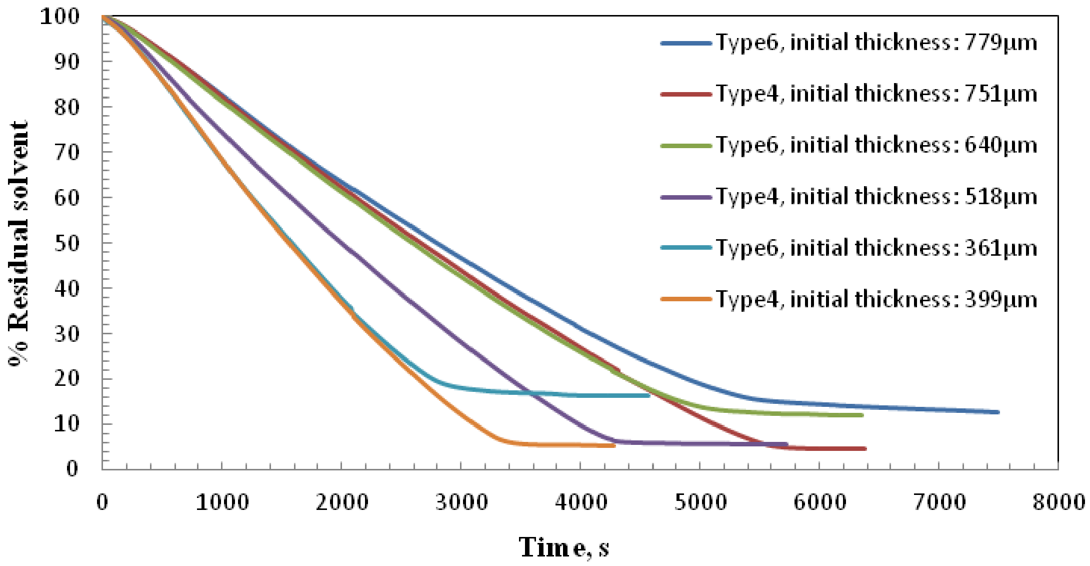


Figure 4.13: Residual solvent as a function of time in poly(styrene) – ethylbenzene system with and without crosslinked poly(styrene-co-divinylbenzene) at 25°C.

4.4.2 Coating Thickness

Figure 4.14 shows the variation of coating thickness with time. It shows that the thickness starts decreasing with time due to evaporation of ethylbenzene from the coating into surrounding. In the beginning, the thicknesses of type 4 coatings were 399 µm, 518 µm, and 751 µm respectively and decreases linearly up to 54 min 55 s, 70 min 20 s and 91 min 55 s respectively and then it plateaus off. The thickness of type 6 coatings in the beginning were 361 µm, 640 µm and 779 µm respectively and also decreases linearly up to 47 min 30 s, 80 min 10 s and 90 min 25 s respectively and then it plateaus off. The coatings having very small amount of crosslinked poly(styrene-co-divinylbenzene) (2.08%) are left thicker at the end of drying process. It is due to the more amount of ethylbenzene has been trapped in these coatings since, the poly(styrene) content in type 4 and type 6 coatings are 9.93% and 9.98% respectively. For an instance, initial coatings thickness: 399 µm and 361 µm of type 4 and type 6 solution respectively are giving the dried coating thickness of 38 µm and 84 µm respectively at the end of 71 min 15 s and 76 min 10 s.

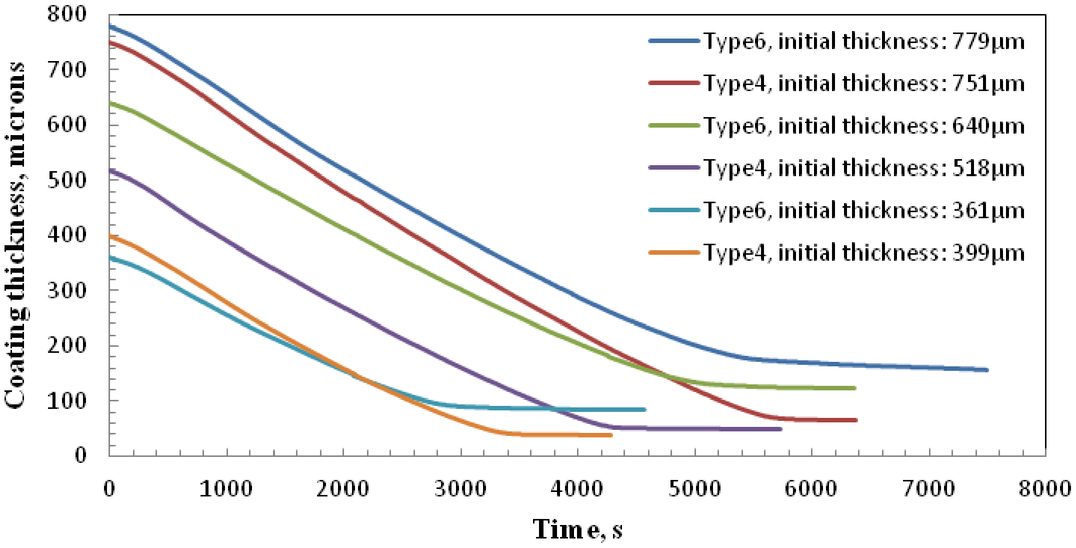


Figure 4.14: Thickness as a function of time in poly(styrene) – ethylbenzene system having crosslinked and uncrosslinked poly(styrene-co-divinylbenzene) at 25°C.

4.4.3 Average Concentration of Ethylbenzene

The average concentration of ethyl benzene with time is shown in Figure 4.15. It describes that the solvent is evaporating from the coating and its concentration start decreasing with time. In type 4, the concentration of solvent decreases exponentially up to 56 min 45 s, 72 min 25 s and 93 min 10 s in the cases of coatings having initial thicknesses 399 µm, 518 µm, and 751 µm respectively, and then it leveled off. Type 6 coatings follows the same trend, the ethylbenzene concentration decreases exponentially at slow rate up to 49 min 10 s, 85 min 25 s and 87 min 5 s in the cases of coatings having initial thicknesses 361 µm, 640 µm, and 779 µm respectively, and then it leveled off. The final concentration of ethylbenzene in type 4 coatings were 0.476 $g.cm^{-3}$, 0.484 $g.cm^{-3}$, and 0.449 $g.cm^{-3}$, for coatings having initial concentration 0.829 $g.cm^{-3}$, 0.829 $g.cm^{-3}$and 0.829 $g.cm^{-3}$, and thicknesses 399 µm, 518 µm, and 751 µm respectively. The final concentration of ethylbenzene in type 6 coatings were 0.559 $g.cm^{-3}$, 0.494 $g.cm^{-3}$, and 0.508 $g.cm^{-3}$, for coatings having initial concentration 0.794 $g.cm^{-3}$, 0.794 $g.cm^{-3}$ and 0.794 $g.cm^{-3}$, and thicknesses 361 µm, 640 µm, and 779 µm respectively.

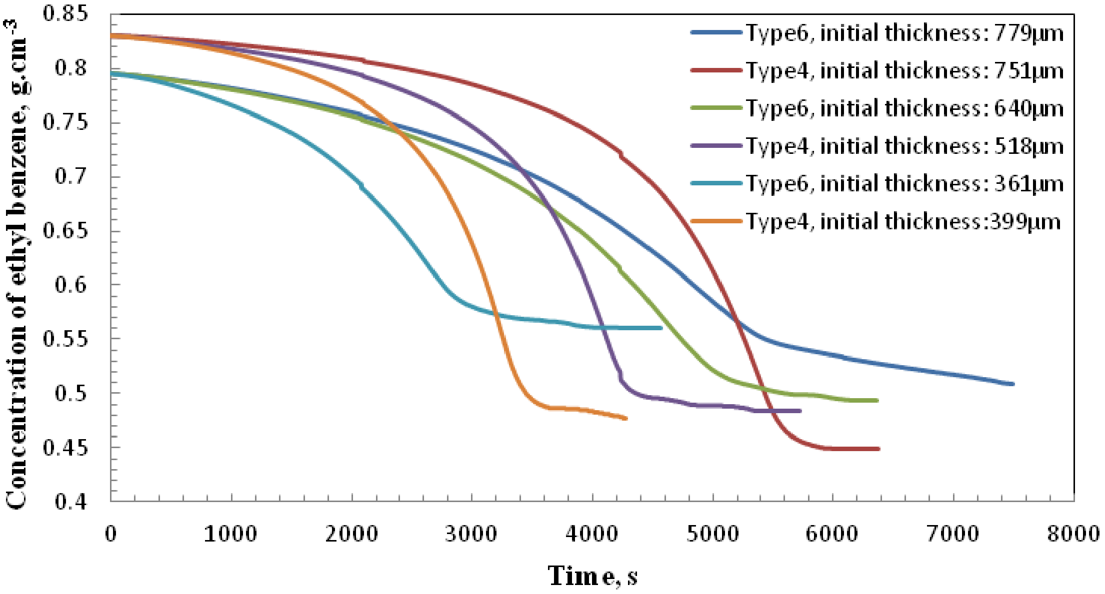


Figure 4.15: Concentration of ethylbenzene as a function of time in poly(styrene) – ethylbenzene system having crosslinked and uncrosslinked poly(styrene-co-divinyl-benzene) at 25°C.

4.4.4 Average Concentration of Polymer

Figure 4.16 depicts the average concentration of polymer (poly(styrene) and poly(styrene-co-divinylbenzene)) with time. It represents that the polymer concentration starts increasing with time due to evaporation of ethyl benzene from coating. In type 4, coatings the concentration of polymer increases exponentially up to 57 min 30 s, 70 min 45 s and 94 min 50 s in cases of coatings having initial thicknesses 399 µm, 518 µm, 751 µm respectively and then plateaus off. Type 6 coatings follows the same trend, the polymer concentration increases exponentially at slower rate up to 51 min, 86 min 15 s and 109 min 50 s in the cases of coatings having initial thicknesses 361 µm, 640 µm, and 779 µm respectively, and then plateaus off. With the increase in drying time there is increase in the concentration of the polymer due to more solvent removal from the coating.

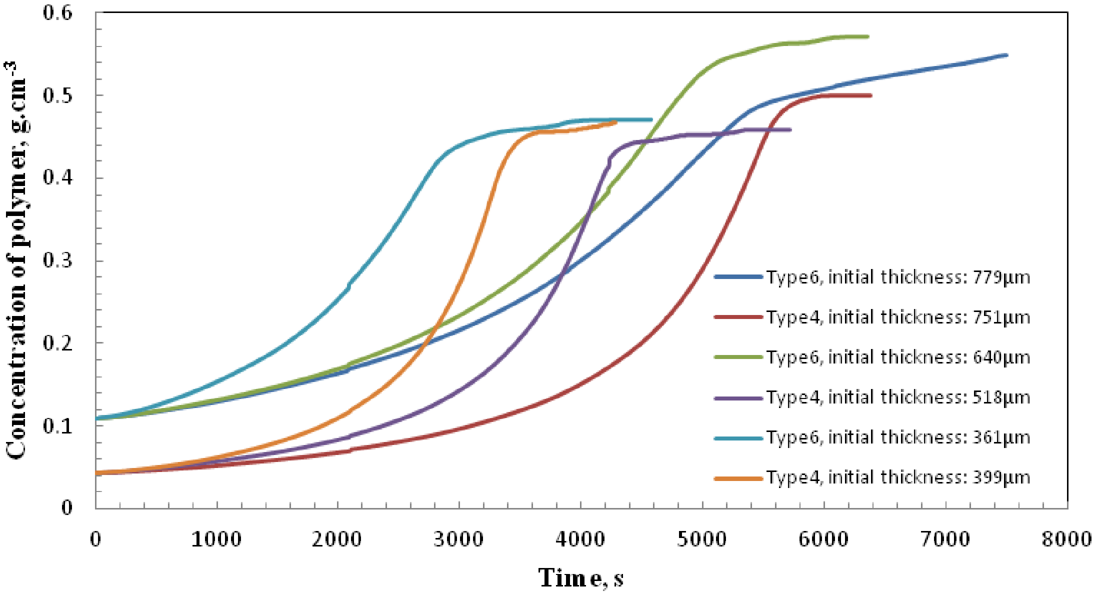


Figure 4.16: Concentration of polymer as a function of time in poly(styrene) – ethylbenzene system with and without crosslinked poly(styrene-co-divinylbenzene) at 25°C.

4.5 Surface Morphology

The surface morphology of different types of polymer coatings was assessed by scanning electron microscopy (SEM), (Hitachi S-3400N), the microscope was attached to a secondary electrons (SE) detector. The images were obtained using an accelerating voltage of 30 KV.

Figure 4.17 below shows the surface morphology of different types of polymeric coatings

(A) A polymer coating of 2.01% poly(styrene-co-divinylbenzene), 10.07% polystyrene and 87.92% *p*-xylene (initial thickness: 799 µm)

(B) A polymer coating of 2.08% poly(styrene-co-divinylbenzene), 9.98% polystyrene and 87.94% ethylbenzene (initial thickness: 779 µm)

(C) A polymer coating of 0.98% poly(styrene-co-divinylbenzene), 9.94% polystyrene and 89.08% *p*-xylene (initial thickness: 752 µm)

(D) A polymer coating of 2.08% poly(styrene-co-divinylbenzene), 9.98% polystyrene and 87.94% ethylbenzene (initial thickness: 1044 µm)

(E) A polymer coating of 0.99% poly(styrene-co-divinylbenzene), 10.01% polystyrene and 89% ethylbenzene (initial thickness: 1009 µm)

(F) A polymer coating of 2.01% poly(styrene-co-divinylbenzene), 10.07% polystyrene and 87.92% *p*-xylene (initial thickness: 683 µm)

(G) A polymer coating of 0.98% poly(styrene-co-divinylbenzene), 9.94% polystyrene and 89.08% *p*-xylene (initial thickness:872 µm)

(H) A polymer coating of 0.99% poly(styrene-co-divinylbenzene), 10.01% polystyrene and 89% ethylbenzene(initial thickness: 755 µm)

(I) poly(styrene-co-divinylbenzene).

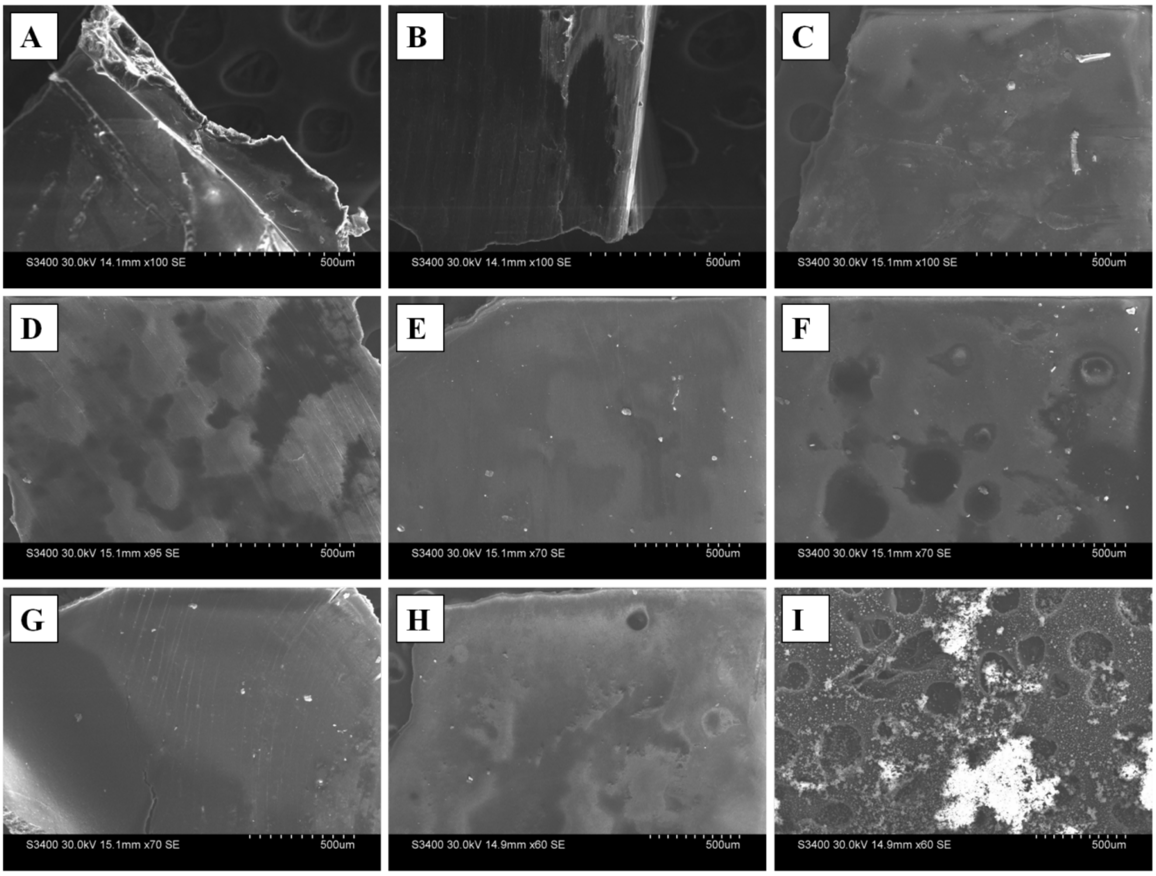


Figure 4.17: SEM images of different types of polymeric coatings.

Figure 4.17 shows the surface morphology of the polymer coatings and exhibits whether the crosslinked particle is uniformly distributed in the polymer coating or not. In (A), the crosslinked particles uniformly distributed in coatings and however the particle density near the edges of the coating is high as compared to the center of the coating and particles are arranging themselves in rod like shape, their typical sizes are 300 µm, 188 µm and 125 µm. In (B), the crosslinked particles are not uniformly distributed in the polymer coating. There are some blank patches and the particles are spherical in shape and their sizes are 62 µm and 25 µm. In (C), the crosslinked particles are uniformly distributed in the polymer coating and the particles are spherical and rods like in shape, their sizes are 19 µm, 119 µm and 125 µm. In (D) the crosslinked particles are not uniformly distributed in the polymer coating, and there are certain blank patches the particles are spherical in shape, and their size are 125 µm, 150 µm and 188 µm. In (E), the crosslinked particles are uniformly distributed in the polymer coatings and the particles are spherical, rectangle and rod like in shape, their sizes are 42 µm, 34 µm and 84 µm. In (F), the crosslinked particles are not uniformly distributed in the polymer coating. There are some hole formation in the coating and the particles are spherical and rod like in shape, their sizes is 42 µm and 34 µm. In (G), the crosslinked particles are uniformly distributed in the polymer coating, but there is a crack in the coating and the particles are spherical in shape of size 34 µm. In (H), the crosslinked particles are uniformly distributed in the polymer coating but there is a black hole in the film and the particles are spherical in shape of size 20 µm. In (I), poly(styrene-co-divinylbenzene) particles are tightly bound with each other but there are some hole, in which very small sized particles are distributed in these holes and the particles are spherical in shape, of size 40 µm.

The holes could be due to the presence of uncrosslinked polymer and these holes disappeared in case of low percentage of crosslink content in the coating because uncrosslinked content may get swelled due the presence of solvent which is observed in Figure 4.17 C, F, and G and these coating have 0.98% poly(styrene-co-divinylbenzene), 9.94% polystyrene and 89.08% *p*-xylene (initial thickness: 752 µm), 2.01% poly(styrene-co-divinylbenzene), 10.07% polystyrene and 87.92% *p*-xylene (initial thickness: 683 µm), and 0.98% poly(styrene-co-divinylbenzene), 9.94% polystyrene and 89.08% *p*-xylene (initial thickness:872 µm). Some dustering effect has been observed in Figure 4.17 D and these coating having 2.08% poly(styrene-co-divinylbenzene), 9.98% polystyrene and 87.94% ethylbenzene (initial thickness: 1044 µm). The crosslinked particles are getting settled to the edges of coating as can be seen in Figure 4.17 A and these coating having 2.01% poly(styrene-co-divinylbenzene), 10.07% polystyrene and 87.92% *p*-xylene (initial thickness: 799 µm).

Table 4.1 Residual solvent summarized in various coating studied.

Poly(styrene)	**Solvent**	**Crosslinked poly(styrene-co-divinylbenzene)**	**Initial coating thickness, µm**	**Final coating thickness, µm**	**% Residual solvent**
9.94%	89.08% *p*-xylene	0.98%	387	58	8.07
			566	92	9.55
			752	132	10.98
10.07%	87.92% *p*-xylene	2.01%	331	59	10.44
			603	118	12.38
			683	134	12.40
10.01	89% ethylbenzene	0.99%	423	85	13.50
			472	84	11.04
			755	144	12.45
9.98%	87.94% ethylbenzene	2.08%	361	84	16.34
			640	123	11.87
			779	154	12.74

Rate of residual solvent removal slows down with time, due to shifting of mass transfer process. In the beginning, the mass transfer process was the evaporation of the solvent which shifts to the diffusion controlled latter only. The solvent self-diffusion coefficient is strongly dependent on solvent mass fraction [54, 55]. Since the diffusion coefficient in polymer solvent system is also very strong function of free volume available for diffusion[54, 55]. It is observed that crosslinked coatings takes more time for drying, due to slow diffusion coefficient in polymer – solvent system and the presence of crosslinked polymer will significantly affect the diffusion coefficient value to a larger extent [46]. Residual solvent left in the coatings having ethylbenzene solvent is higher as compared to the coatings having *p*-xylene for both systems of crosslinked and uncrosslinked polymers. This could be due to change in polymer solution thermodynamic due to interaction of polymer and solvent.

Chapter 5

Conclusions and Future Scope

The results show that diffusion in crosslinked polymer is extremely slow and very negligible amount of solvent has been penetrated into the core of crosslinked polymer. This is proved by the SEM analysis which shows the particles of crosslinked polymer in a regular shape i.e. rod like or spherical. The distribution of crosslinked particles was also not uniformed in most of the cases except case having ethylbenzene as solvent i.e. H, E, and D. It may be because swelling of crosslinked particles due to high rate of penetration of ethylbenzene as compared to *p*-xylene. It may also be due to high dispersion of swelled crosslinked particles which may be forming a thin layer of themselves. Residual solvent data shows that coatings having crosslinked polymer are taking slightly more time as compared to coatings having linear polymer and retaining very high amount of solvent content. Residual solvent left in the coatings having ethylbenzene solvent is higher as compared to the coatings having *p*-xylene for both systems of crosslinked and uncrosslinked polymers. This could be due to change in polymer solution thermodynamic due to interaction of polymer and solvent.

In future, several other polymer- solvent system can be studied to validated the result obtained in this work. The NMR study can be performed to study the solvent diffusion in crosslinked polymer. The polymer solution can be crosslinked during the course of drying to study the effect of crossslinking on solvent diffusion in crosslinked polymer -solvent coatings. The depth profile study can be performed to study the concentration profile in the coating during the course of drying and at the end of drying.

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Chapter 1

Introduction

1.1 Polymeric Coatings

The surface of an object is basically covered with the different types of coatings. The main purpose of the coatings is to increase the life of the object, prevent the object from moisture, corrosion, cracking, blisters etc. The coating covers the substrate in a very homogenized manner. The substrate can be fully or partially coated depending on the requirement.

Polymeric coatings are prepared by several methods with or without solvent. The Polymers can be rubbery, crosslinked, or glassy in nature in the start of coating preparation. The crosslinked polymer films are used in various applications like protective coatings, paintings, barrier for separations of liquid and gases, storage media, semiconductors, micro fluidic devices, optical devices, fluorescent devices, surface acoustic wave devices drug release and encapsulation , and biomedical applications [1-11]. Multilayers and hybrid multilayers have attracted a lot of research due to their excellent properties like electrical, chemical, optical along with chemical and mechanical stability [12] .

Crosslinking hardens the coatings and reduces the penetration of external molecules into the coatings [13]. Crosslinking also improves the surface coverage and enhances electrophoretic separations [14]. Crosslinking improves mechanical strength, chemical resistance, thermal stability, separation characteristics, biomedical properties, and other functional properties [15]. Crosslinking can be done by various ways like UV irradiation, chemical crosslinking, and hyperthermal hydrogen induced crosslinking. Hyperthermal hydrogen induced crosslinking is an unique technique because it does not require any co-agents or solvents and it is able to crosslink the material upto several microns. The depth of crosslinked material is very important to find the material properties.

During crosslinking, linear polymer chains join together at a common junction point [16]. Crosslinking agents attach themselves to at least two chains. These agents are low molecular weight species. The properties of the polymer network are controlled by the degree of crosslinking. In case of a very high degree of crosslinking, the network will be very hard, brittle and solvent resistant [16]. Fluorescent devices require controlled deposition of crosslinked polymer based sensors [6]. The crosslinking degree can be manipulated to get the desired properties. This can be achieved by controlling curing temperature and crosslinking agent to monomer ratio.

All coatings degrade when they get exposed to UV radiations due to the complex photochemical process. The weather conditions like moisture, temperature, and pollutants, etc. enhance this degradation process. The coating will degrade when it absorbs UV radiations and that is sufficient enough to break the bonds of polymer. The pure polymers do not degrade because they do not absorb sufficient energy of radiations greater than $295\,nm$ wavelength, however the coatings will undergo degradation [2]. This shows that coatings have something other than the polymer. Improper drying and polymerization with other reacting species or ingredients are the main causes of degradation.

Durability of organic coatings can be enhanced by the addition of low molecular weight stabilizers [17]. These stabilizers absorb UV radiations which fall on the coating and hence, stop the photooxidation of the coating since it does not allow UV radiations to react with the binder used in the coating. These UV absorbers also protect the subsequent layers of the polymer film. A few light stabilizer compounds scavenge the free radical produced during the oxidation process and, hence, slow down the oxidation process. UV absorbers and free radical scavengers are chemically destroyed during the weathering process [17]. Due to the weathering process, the concentration of UV absorber at the surface decreases as compared to the deep inside the coating.

The transport of solvent in polymers or polymer films is affected by unsaturation, degree of crystallinity, crosslinks density, and glass transition temperature [5]. The glass transition temperature increases with the solvent evaporation. For instance, an addition of 20% toluene in poly(styrene) makes the glass transition equal to the ambient temperature

[3]. The diffusion coefficient decreases linearly with crosslink density and levels off at high values. The type of crosslinking governs the solvent uptake by the polymer.

1.2 Coating Preparation Methods

Initial, polymer melt or solution is being prepared. The melt can prepared by heating the pure or mixture of polymers. The melt may be spinned or sprayed over the substrate to get the film. This method is being using to coat the larger size objects. In dry casting, the hot object is being passed through the block of polymer to get the desired coating on the surface. The multifunctional and high quality thin films are generally being prepared by solution casting technique. In this technique, the polymer(s) are dissolved into the solvent(s) to get the homogeneous solution. The required amount of the solution is being spreaded on the substrate or may be poured into the geometry to be coated. Coating can be prepared in layer by layer , single layer, or simultaneous multilayer fashion to get the desired coating. The solution casting technique has following advantages:

- High temperature resistant films are prepared from non- thermoplastic soluble raw materials.
- Processed at low temperatures, which is valuable for incorporating temperature-sensitive active ingredients or thermally activated films.
- Simplified incorporation of fillers and additives.
- A huge range of material solutions can be casted into the film

Linear polymer(s) are generally being used to prepare the coating solution. However, the polymer(s) having low degree of crosslinking may also be used to prepare the coating solutions. These coating solutions may take very long time to get the homogeneity. The schematic representation of the crosslinked solution coating is shown in Figure 1.3.

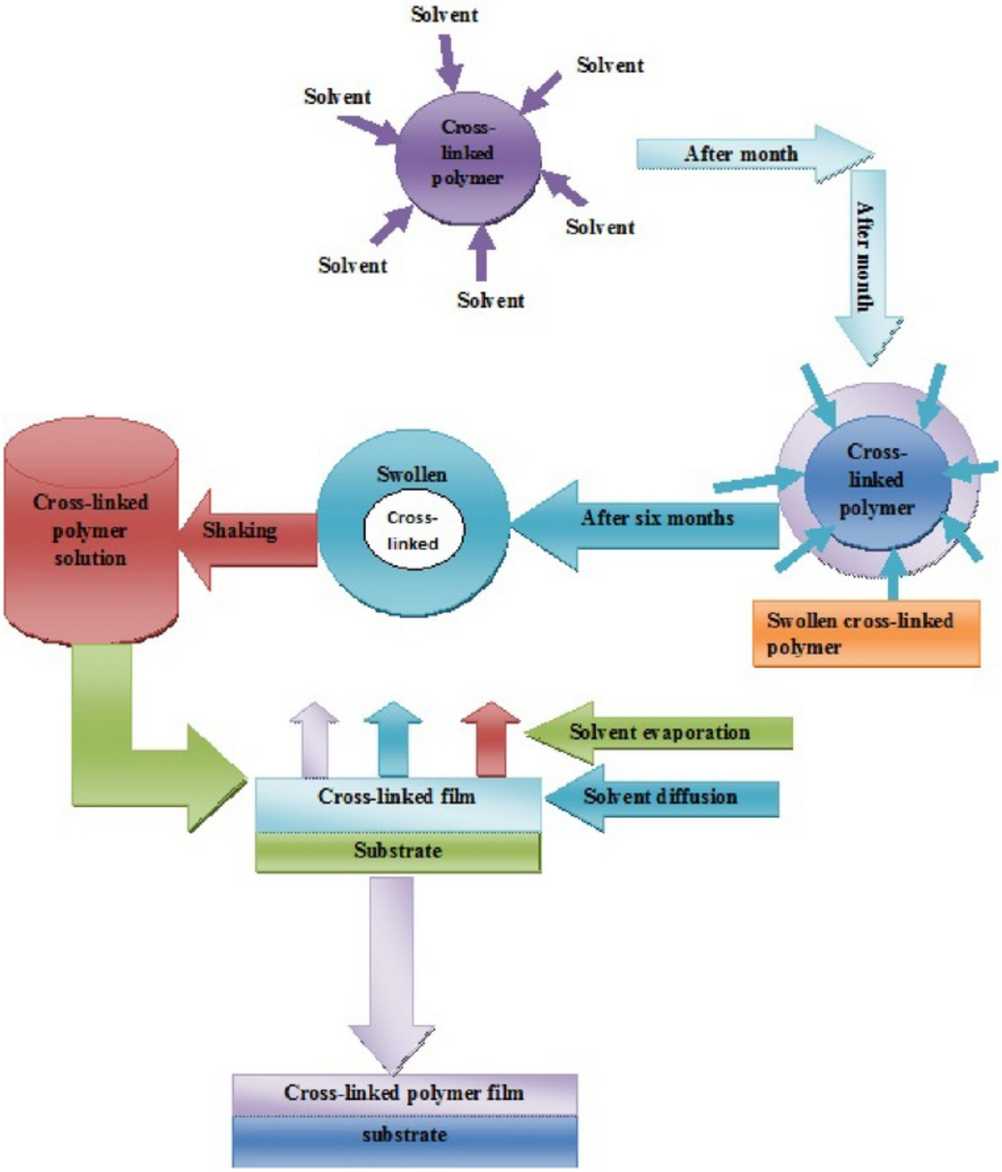

Figure 1.1: Schematic of crosslinked solution coating preparation.

1.3 Classification of Coatings

Broadly coatings are classified as crosslinked and uncrosslinked. These can be further classified as binary and multicomponent coating. In binary coating one polymer and one solvent is used however in multicomponent coatings more one polymer or solvents are used.In uncrosslinked polymers, there is lot of free volume available due to the flexibility of monomer chains. However, in the case of crosslinked polymers monomers chain are tightly packed and very less free volume is available. Polymer chains are joined at common junction point by the use of low molecular weight of crosslinking agents.

The coatings can be further classified into organic coatings and inorganic coatings. In organic coatings, organic solvents are used which are toxic and costly in nature. Therefore these coatings need to be dried completely in order to remove the entire solvent to avoid production losses and defects. In green coatings, inorganic solvents generally water. However, the water soluble polymers are very costly and these coatings require lot of energy in order to get the dried films.

1.4 Crosslinking

The lateral attachment of the polymer chains is called crosslinking or curing. The entire bulk of the polymer is converted into a three dimensional network structure. This makes the polymer harder and the mobility of the molecular chains decreases. The increase in degree of crosslinking enhances the molecular weight and glass transition temperature.Physical properties like density, viscosity, melting point, mechanical strength, elastomeric properties, etc. progressively improve with the increase in crosslink density. Oxygen permeability, water permeability, solubility, chemical resistance, etc. decrease with the increase in crosslink density. A highly crosslinked polymer behaves as a hard glassy material that is not recyclable. Thus, an initially thermoplastic polymer is converted to a thermosetting polymer as a result of curing. The thermosetting polymer does not show melting behaviour and instead burns or degrades upon heating [18].

Polymer crosslinking can be achieved by the application of heat, pressure, change in pH, and radiation. In the radiation method, the polymer is exposed to electron beam, gamma rays, ultra-violet, or visible light [19]. The typical wavelength range for the UV method is 200-400 *nm* and for the visible light the range is 380-450 *nm*. The radiation curing can take place via either free radical or cationic mechanism and follows initiation, propagation and termination steps. Commonly, 2-hydroxy-2-methyl-1-phenyl-propan-1-one and 1-hydroxycyclohexyl phenyl ketone are used as free radical photoinitiators and sulphonium salts are used as cationic photoinitiators. Adding a specific curing agent to a partially polymerized resin also facilitates crosslinking. If the curing agent is activated through UV radiations the process is called UV curing. The crosslinking of a polymer can be hastened by the addition of catalysts and accelerators to the curing agents. The accelerators increase the curing rate by catalyzing the reaction of the polymer chains with the curing agent [20]. Figure 1.2 shows various types of crosslinking.

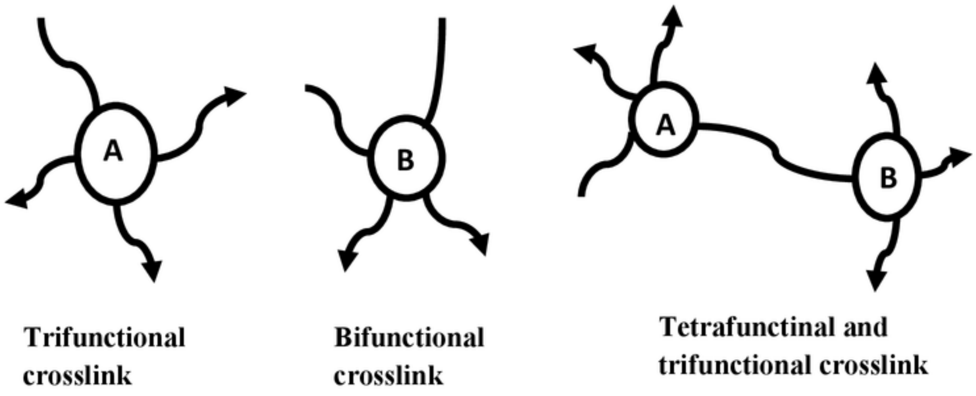

Figure 1.2: Various types of crosslinks.

1.5 Drying of Coatings

All solvents based coatings are subjected to drying. The solvent present in the coating is removed during the course of drying. The coatings may be heated or dried at room temperature depending on the requirement. The mass of the coating changes with time due to the loss of solvent from the coating into the surrounding medium. The thickness of the coatings shrinks in longitudinal direction towards the substrate. Initially drying is externally controlled due to presence of high amount of solvent on the top surface. During this period the rate of drying is nearly constant. As the time passes, the amount of solvent on the top decreases and drying rate starts falling due to slow diffusion of solvent from the coating to the coating air - interface. Figure1.1 shows the various drying process of polymeric coating.

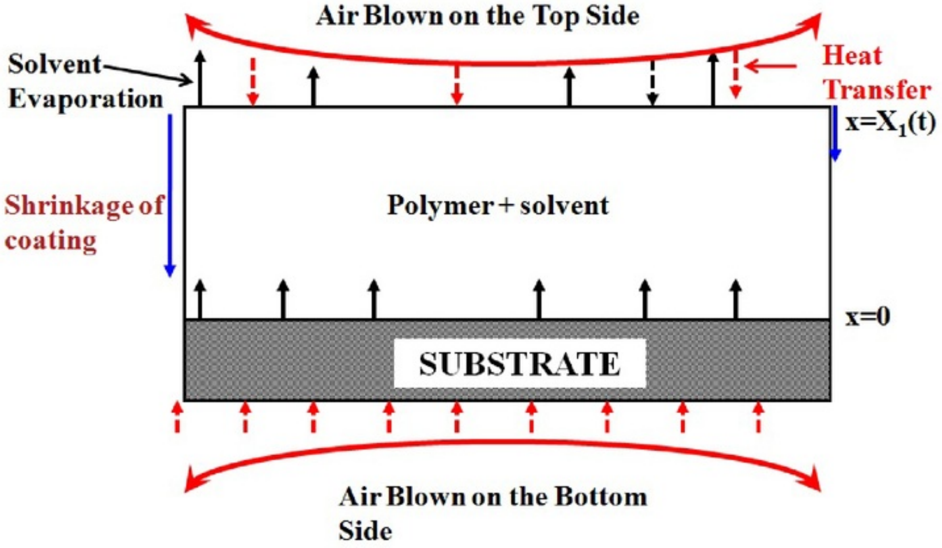

Figure 1.3: Schematic of drying of polymeric coating.

1.6 Objective

Based on the literature review and the gaps identified in chapter 2, the objective of the present work have been set as follows

To study the effect of crosslinked polymer on drying of binary polymeric coating

1.7 Dissertation Outlines

Chapter 1: A brief introduction about cross-linked coating, preparation of cross-linked coating, application of cross-linked coating, classification of coating, cross-linking and drying of coating.

Chapter 2: Literature review regarding preparation, characterization, application, and diffusion in cross-linked coating and their importance have been summarized.

Chapter 3: Materials and methods has been explained in details

Chapter 4: Results and discussions of various observations has been given.

Chapter 5: Conclusions of present study are documented.

Chapter 2

Literature Review

In this chapter the literature review of the cross-linked coating has been provided. The chapter is divided in several sections: preparations and characterization of cross-linked coatings, diffusion in cross-linked coating, and limitations and future scope of Study.

2.1 Preparations and Characterization of Crosslinked Coatings

Martin and Mandelkern [21] studied the glass transition behavior during the vulcanization of natural rubber. The glass transition and the temperature of application are important parameters to define the nature of polymer, i.e., whether it is rubber like or brittle. The free volume available in polymer is a measure of the ease of molecular rearrangement. They found that the specific volume of the vulcanized rubber keeps on decreasing with increase in the sulfur content. Hence, the glass transition temperature of the vulcanized rubber will increase with the sulfur content. They assumed a linear relationship of free volume with glass transition temperature as given by

$$\phi(T) = \phi_g + \Delta\alpha(T - T_g) \tag{1}$$

where, ϕ_g : free volume at glass transition temperature, T_g, $\Delta\alpha$: rate of change of free volume with temperature.

Various types of crosslinks are shown in Figure 1.2 [22]. The degree of crosslinking relates to the number of groups that interconnect monomer and crosslinking species. The degree of crosslinking is generally expressed in mole percent. The degree of cross linking can be determined using chemical and physical methods [23]. In the chemical method, the calibration curves are prepared to calculate the percentage of crosslinked bonds. In the physical method, the crosslinked material is put in the solvent for a sufficiently long time so that no change is observed in solution concentration. After that, unswollen material is filtered and dried and its mass is recorded. The physical degree of crosslinked can be calculated as follows

$$\text{Physical Degree of Crosslinking} = \frac{\begin{bmatrix}\text{Initial Mass of} \\ \text{Material}\end{bmatrix} - \begin{bmatrix}\text{Final Mass of} \\ \text{Unswollen Material}\end{bmatrix}}{\text{Initial Mass of Material}} \times 100 \qquad \textbf{(2)}$$

Mullins [24] determined the crosslinking degree in vulcanizates of natural rubber. The polymers of different molecular weights were taken to prepare seven samples having same crosslinking degree. Di-tert-butyl peroxide and sulfur vulcanization agents were used to prepare two types of vulcanizates. n-decane was used as a swelling agent. Volume of swelling and stress-strain properties were determined. He used the Flory-Huggin's equation to correlate network structure and equilibrium swelling degree. Several equations were developed to see the effect of initial molecular weights on the swelling volume. The average molecular weight of the rubber molecules between crosslinks (M_C) was given by

$$-\ln(1-v_r) - v_r - \mu v_r^2 = \rho v_0 M_c^{-1} v_r^{1/3} \qquad (3)$$

The force (f) required to extend the rubber was given by

$$f = 2A_0 v_r^{\frac{-1}{3}} (\lambda - \lambda^{-2})(C_1 + \lambda^{-1} C_2) \qquad (4)$$

$C_1(swollen) = \frac{1}{2}\rho RTM_c^{-1}$ From Flory theory was corrected for the chains ends because the chain ends are not contributing to the network, by replacing M_c^{-1} with $M_C^{-1}(1-2M_c M^{-1})$ which gave the following

$$C_1\left(swollen\right) = \frac{1}{2}\rho RTM_c^{-1} \quad \rho RTM^{-1} \qquad (5)$$

The swelling volume was given by

$$-\ln(1-v_r) - v_r - \mu v_r^2 = 2V_0 C_1(swollen) R^{-1} T^{-1} v_r^{1/3} \qquad (6)$$

where v_r:volume fraction of rubber in the swollen material, μ:interaction constant characteristic of the rubber and the swelling liquid, v_0: molar volume of the swelling liquid, $\boldsymbol{\lambda}$: extension ratio, R: gas constant, T: absolute temperature, M_c: average molecular weight of the rubber molecules between crosslinks, A_0: unstrained area of cross section, C_1, C_2: constants

Moore and Watson [23] also measured the crosslinking degree in vulcanizates of natural rubber by using chemical and physical methods. Di-tert-butyl peroxide was used as crosslinking agent. During the process, peroxide decomposed into tert-butanol, methane, and ethane. The crosslinked rubber prepared by this method was used in chemical method for determination of crosslinking degree. They found that the degree of crosslinking by chemical method was greater than the physical method.

Mullins [25] has further measured the crosslinking degree of vulcaniztes of rubber. During simple extension of vulcanizated rubber, he used statistical theory and gave the following expression:

$$f = A_0 \rho k T (\lambda - \lambda^{-2}) \tag{7}$$

where, A_0: unstrained cross-sectional area, T : absolute temperature, $\boldsymbol{\lambda}$: extension ratio, k : Boltzmann constant. f: force required to extend a sample of rubber.

He further studied deviations from the statistical theory for low and moderate extension, which was given by

$$f = 2A_O(\lambda - \lambda^{-2})(C_1 + \lambda^{-1}C_2), \quad C_1 = \frac{1}{2}\rho RTM_C^{-1} \tag{8}$$

where, ρ: density of the rubber, M_C: the number average molecular weight of the chain segents of rubber between adjacent crosslinks, R: gas constant.

He [25] developed two parameter relationship for stress-strain behavior using C_1 and C_2. Swelling reduced the number of network chains and the effect of this on finite extensibility was theoretically correlated. Finite extensibility swelling departure at low elongation was also considered in highly swollen rubber. He used the linear portion in stress-strain curves to determine parameters C_1 and C_2 . The linear portion becomes very limited because of very high degree of swelling departures. They found degree of crosslink using λ and network flaws in a simple extension stress-strain curve. They also used this technique for the degradation studies of vulcanized rubbers.

The dependence of C_1 and C_2 on the swelling degree was given by

$$\frac{1}{2} f A_O (\lambda - \lambda^{-2})^{-1} v_r^{\frac{1}{3}} = C_1(dry) v_r^{\frac{1}{3}} + \lambda^{-1} C_2(dry) v_r^{4/3} \qquad (9)$$

where, v_r:volume fraction of rubber in the swollen material, R: gas constant, T: absolute temperature, A_0: unstrained area of cross section, C_1, C_2: constants, $\boldsymbol{\lambda}$: extension ratio, f: force required to extend a sample of rubber.

Moore and Scanlan [26] determined the crosslinking degree of vulcanizates of natural rubber. Scissions of chains were observed during crosslinking using organic peroxide at 140^oC. They studied crosslinking kinetics and peroxide decomposition. They measured the stress relaxation in an extended sheet of rubber that was vulcanized. This was further crosslinked using di-cumyl peroxide in the presence of nitrogen. All the previous methods of crosslinking determination were not sensitive to chain scission. They found that the primary networks degraded during the secondary network formation which results in only 10% new crosslinks formation.

Mullins and Thomas [22] determined the crosslinking degree in natural rubber vulcanizates and its dependence on network flaws. The network flaws were observed due to free chain ends. They considered Flory's and Tobolsky's approaches in this work. According to Flory's approach, $(n-1)$ crosslinks were required to link n molecules for taking network flaws into account. The chain density was given by $= 2(v-n+1) - 2(v-n)$. They got correct gel point and its molecular weight dependence using this approach. However, the assumption used in Flory theory was unrealistic. Flory had assumed that each crosslink added two network chains.

Tobolsky's approach introduced cuts into the network which initially did not contain any free ends. Each cut produced two free chain ends that increased the value of n by 1 and reduced network chains by 1. In this approach, the chain density was given by

$c = 2v - n$. Mullins and Thomas [22] addressed the discrepancy between the above two approaches by making allowance for the differing functionality of crosslinks.

Mullins [27] modified the previous physical method for determination of degree of crosslinking [23] and used it to improve the stress-strain properties method for vulcanized rubber. He modified this method of determination by developing a relationship between elastic constant C_1, and swelling rubber free volume (v_r). He again compared the physical and chemical methods of measurements and made empirical corrections to incorporate network flaws and chain entanglements and found that the measured degrees of crosslinking from both the methods were nearly same.

Barie et al. [11] developed new material for surface acoustic wave devices using UV crosslinking of poly(siloxanes). The uncrosslinked sensor device showed significant sensitivity decrement in the first few days. The total decrease in sensitivity was 50% in six weeks time, however, in the case of the crosslinked ones the fall was only 8% in the first few days and 0.2% per day thereafter. Sensor stability and reproducibility of siloxanes were very high over a long period of time as these were greatly enhanced by crosslinking.

Esser et al. [28] studied waterbased crosslinkable surface coatings. These coating were prepared by simple crosslinking and are generally used in furniture applications. Coatings were prepared from the mixture of monomer and water by using emulsion polymerization. Monomers used were methacrylic acid, butyl acrylate, acetoacctoxyethyl methacrylate and methyl methylacrylate in the ratio of 12:37:30:21 by weight. The coatings were dried under ambient conditions. Their results showed that crosslinked coatings had excellent hardness and resistance to chemicals, heating, and wetting.

Hu et al. [7] used crosslinked coatings for electrophoretic separations in poly(dimethylsiloxane) microchannels. They used three different monomers of poly(ethylene glycol), acrylic acid ,and diacrylate poly(ethylene glycol) and then polymerized them with the help of ultraviolet light on the surface of poly(dimethylsiloxane) microdevice. They used three different surface coatings: the first one was single poly(ethylene glycol), the second one was a mixture of acrylic acid and poly(ethylene glycol) and the third one was a mixture of three poly(ethylene glycol), acrylic acid, and diacrylate poly(ethylene glycol). In this mixture, diacrylate poly(ethylene glycol) worked as a crosslinking agent. They measured monomer ratio, graft density, and contact angle. They used these coatings for separations and have found the best separations in case of crosslinked coatings. Low cost and disposable microfluidic devices can easily be fabricated using poly(methyl methacrylate) and poly(dimethylsiloxane). The electroosmotic fluid flow in microchannels can be controlled by using multilayers of poly(allylamine hydrochloride) and poly(styrene sulfonate).

Peters et al. [17] studied the mobility of UV light absorber in crosslinked coatings. They used tinuvin 900 UV absorber. Their results showed that the UV absorber was moving into the deeper side of the coating from the coating surface. These UV absorbers did not allow the UV radiations to reach the binder of coating by absorbing the UV radiations. These UV absorbers were chemically consumed during the weathering process. The glass transition temperature and cross linked density were very much affected by the UV exposure time. The glass transition temperature can increase or decrease with the crosslink density depending on the coating chemistry.

Ramaraj [29] studied the composite films of starch and crosslinked poly(vinyl alcohol). He studied the physicomechanical, thermal, and swelling properties of these films. He prepared and compared uncrosslinked and crosslinked films. In uncrosslinked films, the poly(vinyl alcohol) was blended with starch having different wt% of starch up to 50% in an increament of 10% starting with 10%. The crosslinked film was prepared by using glutaraldehyde as a crosslinking agent. Glutaraldehyde gave the crosslinked solution of poly(vinyl alcohol) that was spread on a glass substrate at room temperature for 48 hours to get a dried crosslinked film of poly(vinyl alcohol). He found that the crosslinked films had high tensile modulus, tensile strength, burst strength, tear resistance, and solubility resistance as compared to the uncrosslinked ones due to the crosslinked network formation. However, uncrosslinked films had a high moisture content, tensile elongation, swelling content, and moisture absorption as compared to the crosslinked films.

Al Akhrass et al. [3] studied the influence of progressive crosslinking on poly(styrene) dewetting. The behavior of partially crosslinked films and thickness get affected by the dewetting nature of the film. They found that 100% conversion of azide was not enough for the complete dewetting in 20 *nm* film. They also found that the nucleated holes diameter grew with time when dewetting of poly(styrene) thin film was done on poly(dimethylsiloxane) coated substrate. They found that crosslinking lead to macromolecular network which inhibited the dewetting and stopped residual stress relaxation. They also suggested that the films with long polymer chains can be successfully stabilized by crosslinking.

Akhrass et al. [12] designed several multilayer crosslinked hybrid thin films using poly(styrene) and platinum nanoparticles. They prepared these films using sequential spin coating followed by UV crosslinking. They studied the neutron reflectivity of these hybrid films and found that UV crosslinking at the room temperature is enough to stabilize the layers prior to the segregation of platinum nanoparticles.

Campos et al. [8] prepared chitoson cross-linked films that are used for drug delivery applications. They used acetic acid solution to dissolve the chitoson. Hexamethylene 1,6-bis was the cross-linking agent. They used the solvent evaporation technique to prepare three chitosan films: 30% crosslinked, 50% crosslinked, and un-crosslinked films. They characterized these films by Fourier transform infrared spectroscopy and found that the crosslinked films and their resolution were better than the uncrosslinked films. They found 0°contact angle for both the crosslinked films which shows that crosslinking enhances the hydrophobic characteristic of the crosslinked films. They also studied the swelling behavior and found that the films without crosslinking are more susceptible to swelling as compared to the crosslinked films. They suggested that the crosslinked films are more suitable as compared to the un-crosslinked films for drug delivery process.

Liang et al. [30] used selective crosslinking method to prepare single and double network films of chitosan and poly(vinyl alcohol). In the first method, they used borate as a crosslinking agent and the crosslinking depends on di-diol interaction between poly(vinyl alcohol) / chitosan and borate. Di-diol interaction is an interaction of two hydroxyl groups. In the second method, they have used tripolyphosphate as the crosslinking agent and the crosslinking depends on electrostatic interaction between poly(vinyl alcohol)/chitosan and tripolyphosphate. They prepared four films one was uncrosslinked while the remaining three were crosslinked using borate, tripolyphosphate, and a mixture of borate and tripolyphosphate. They found that crosslinking decreased the permeation value, improved the mechanical strength and elastic modulus. Their atomic force microscopy results showed different size particles and aggregates, however the original particles were nanoparticles of same size. This showed variation in the behavior of different types of crosslinking processes.

Bossi et al. [6] synthesized polymeric crosslinked coating using initiator, transfer agent, and terminator technique. The polymerization was initiated using UV irradiation. They were able to control the crosslinked thickness by changing the concentration of chain termination agent ($N,N-N',N'-$tetraethyl thiuram disulphide) between 5 and 130 *nm* crosslinked thickness and this effect plateaus off at higher concentration of the terminator. Their study showed greater variability with the irradiation time. The crosslinked films thickness increased with irradiation time but the increase was not very significant as the thicknesses were 5 *nm* and 6 *nm* for the irradiation times of 20 min and 40 min respectively. They also studied the effect of polymerization atmosphere on the crosslinked film thickness. They recorded 6 *nm* and 20 *nm* thicknesses when the atmosphere was purged with argon and atmosbag, respectively. Furthermore, they studied the effect of polymerization time on film thickness and recorded 70 *nm* and 100 *nm* for 40 min and 80 min polymerization respectively.

Das et al. [31] studied crosslinked starch/poly(vinyl alcohol) films. They prepared four crosslinked films and one simple film. The crosslinking agents used by them were borax, formaldehyde, epichlorohydrin, and ZnO. They used gelatinization by solution casting method to get the films. Their scanning electron microscopy results show that starch granules did not fully collapse during gelatinization process specially in the case of un-crosslinked film and ZnO film. They concluded that zinc oxide particles act as fillers and did not take part in chemical crosslinking reaction. They found that tensile stress and tensile modulus were higher in the case of borax crosslinker due to formation of tough network. The tough network was formed between three hydroxyl groups of the poly(vinyl alcohol), starch, and borax. They found that the storage modulus of all the crosslinked films were much greater than the uncrosslinked films due to the addition of crosslinker between poly(vinyl alcohol) and starch molecules. Their thermo gravimetric analysis showed low thermal degradation and high char yield in the case of crosslinked films with high degree of crosslinking. They found significant fall in moisture absorption in the crosslinked films as compared to the uncrosslinked one due to less number of hydroxyl groups.

Telford et al. [9] studied antifouling activities of thermally crosslinked poly(n-vinylpyrrolidone) films in biomedical applications. The crosslinked films were prepared by thermal annealing technique at temperature of 200°C for 3 hours. Thermal gravimetric analysis was done to determine the mass loss density during thermal annealing. It was noticed that there was no significant decomposition of the polymer. Their atomic force microscopy results showed that there was no change in the surface morphology during annealing. During annealing process, oxygen content increased by 30%, carbon content decreased by 5% and nitrogen remained unchanged as recorded by X-ray photoelectron spectroscopy. Their results showed that mass density and X-ray scattering length density increased during annealing process. They found that an insoluble network was formed due to $C-C$ interaction bonds of different radicals.

They [9] also checked the stability of coatings in different solvents like water, ethanol, and solution of peroxide in concentrated sulphuric acid and found no effect of these solvents on the films. They also studied the protein adsorption on poly(n-vinylpyrrolidone) coating. They used two type of proteins: fibrinogen (FGN) and IgG (Immunoglobulin G) having different structures. They used quartz crystal microbalance to find the adsorbed mass of IgG and FGN, which were 21 and 34 ng/cm^2 respectively. These findings show the improved biocompatibility of the crosslinked films in vivo devices.

Lu et al. [32] studied the crosslinkable poly(vinyl acetate) emulsions for furniture applications. They prepared the crosslinked films by the mixture of acetoacetoxyethyl methylacrylate and diamine solution using emulsion polymerization. They used vinyl acetate and veova 10(vinyl decanote) as copolymers. Enamine structures were formed by the reaction of acetoacetoxyethyl methylacrylate and diamines. The prepared films were characterized using Fourier transform infrared resonance and nuclear magnetic resonance. Glass transition temperature was measured using dynamic mechanical thermal analysis. They found that in the crosslinked films, the glass transition temperature and viscosity increased with increase in the amount of acetoacetoxyethyl methylacrylate. However, the trend was reversed in the case of uncrosslinked films.

Nguyen et al. [2] extensively studied the degradation modes of crosslinked coatings that were exposed to the photolytic environment. They found that the crosslinked coatings exposed to the UV environment underwent degradation. This degradation was very inhomogeneous. The degradation started with nanoscale pits that deepen and grew in size with exposure time. They gave a conceptual model to explain the degradation. They found that the degradation started at the hydrophilic sites that were randomly distributed in the densely crosslinked films. These hydrophilic sites were the unreacted and partially polymerized molecules and other additives. They found that the morphological changes were related to the gloss of the coatings. The coating gloss changed due non-uniform degradation of the films otherwise only films thickness would have changed without affecting the glossiness of the film. They found that degradation of an acrylic melamine film in the humid environment was much faster as compared to the dry UV degradation.

Carias et al. [4] have studied phototunable swelling in poly(N-isopropylacrylamide crosslinked coatings. They synthesized and characterized the crosslinked terpolymer coating. Terpolymer is a copolymer of three distinct monomers. The three monomers used were N-isopropylacrylamide (NIPAAm), methacryloxybenzophenone (MaBP), and phenacyl methacrylate (PHEm). NIPAAm (N-isopropylacrylamide) swelled and collapsed when the temperature was increased. MaBP is a photo-crosslinking agent that activates at 365*nm* wavelength. PHEm is a photolabile protected carboxyl group which can be deprotected at 254*nm* wavelength. They prepared the coating surfaces using different compositions of PHEm from 7.1% to 17%, but MaBP remained constant at 3%. They found that swelling increased with time. They also studied the effect of pH on swelling and found that swelling ratio increases with pH. They also studied the photocleavage properties by UV-VIS absorbance and found that the deprotection follows the first order kinetics. Photocleavage reaction starts at a lower wavelength that controls the transition temperature and swelling due to the production of free carboxylic groups, which depends on the exposure time. They found that phenacryl methacrylate loading is very important to control the swelling.

Kusuma et al. [10] studied cell growth media and membrane gas separation using crosslinked films. Thiol-functionalized polysiloxane films were crosslinked with poly(ethylene glycol) diacrylate (PEGDA) in the presence of poly(ethylene oxide) as a crosslinker. They checked biocompatibility of the films with the help of human adult mesenchymal stem cells. They also studied the viability and differentiation. Viability and differentiation were measured through experiments performed on polymer films in which the cell was put in polymer film. They found that 33% SH (ratio of 1 thiol to 4 acrylate) was highly viable as compared to 20% SH and 40% SH. In the membrane separation study, they found high gas permeability and $\frac{CO_2}{N_2}$ selectivity. Based on their results, they suggested that these films can be used in a variety of materials due to their potential in stem cell carrier materials in transplantation and performance in gas separation.

Guo et al. [15] characterized the crosslinked depth of polymeric films using atomic force microscopy. The films were crosslinked using hyperthermal hydrogen bombardment technique. They found that the presence of carbon nanotubes in the poly(isoprene) lowers the depth of crosslinking. Due to a shortage of double bonds in the therban and poly(acrylonitrile), the crosslinked depth came out to be 2.1 and 1.1 microns respectively. On the contrary, the carbon nanotubes have abundant double bonds but these were not helpful in deeper depth of crosslinking due to the formation of a large stable conjugate system that cannot help the carbon free radical propagation.

Birck et al. [33] studied the antimicrobial citric acid/poly(vinyl alcohol) crosslinked films. The poly(vinyl alcohol) films were prepared by solvent casting technique which were crosslinked by the mixture of citric acid and with or without hydroxypropyl-β-cyclodextrin. They found that the effect of citric acid and hydroxypropyl-β-cyclodextrin were not able to change the barrier properties of poly(vinyl alcohol). Their investigations showed that a high amount of sodium benzoate (NaBz) was released in the case of low citric acid content and low crosslinking time due to smaller network density. They also noticed an increase in the diffusion activity with crosslinking time with hydroxypropyl-β-cyclodextrin.

de Dicastillo et al. [34] studied the antioxidant activities, polymer flexibility, swelling characteristics and mechanical properties of crosslinked films. The films were prepared using methyl cellulose polymer and maqui berry as an antioxidant. The films were crosslinked using glutaraldehyde as crosslinking agent. They found that the polymer flexibility and degree of swelling reduced due to glutaradehyde. However, maqui berry decreased the crosslinking degree and increased the swelling degree of material as the ratio of glutaraldehyde was increased from 2.5 to 5%. They found that the crosslinked films improved the water vapor permeability properties and it was the highest when glutaraldehyde concentration was the highest. They found that the use of plasticizer increased the thermal stability between 360 to 380°C. However, the thermal stability decreased with the addition of glutaraldehyde. They found that the addition of maqui berry protected the film from thermal degradation. The film prepared using maqui berry was transparent and little pink in color. However, the addition of glutaraldehyde made the color yellowish. Tensile strength, elongation at break (%), and Young's modulus decreased as the percentage of glutaraldehyde increased from 2.5 to 7.5%. The release of active agents such as poly(phenols) on stimulant was higher when the concentration of glutaraldehyde was higher due to a higher antioxidant from the natural extract that acts as crosslinking agent. This film is environmentally friendly in nature.

2.2 Diffusion in Crosslinked Films

Hayes and Park [35] obtained diffusion coefficients of benzene in rubber by sorption-desorption technique. Samples of deproteinized crepe rubber that were crosslinked by peroxide process and sulphur crosslinking were used for experiments. It was observed that the diffusion coefficients obtained were unexpectedly high and were not significant in many systems while the concentrations were changed. It was noticed that the benzene diffusion coefficient at zero concentration decreased with the increase in crosslink density. The diffusion coefficient also became more dependent on the concentration of benzene with increasing crosslink density. The linearity of the diffusion coefficients with concentration of benzene was observed irrespective of the density of crosslinking. This indicated the absence of time-dependence complications of the process. The average diffusion coefficient of benzene was given by

$$D_{av} = D_0(1 + \alpha c) \tag{10}$$

Polymer swelling was incorporated into above expression to get the intrinsic diffusion coefficient as following

$$D = D_0(1 + 2\alpha c)/(1 - v)^3 \tag{11}$$

where D_{av}: Diffusion coefficient averaged out over the concentration of benzene from zero to the equilibrium concentration after the sorption stage, D_o: diffusion coefficient at zero concentration of benzene, c: mass of penetrant per unit mass of polymer, and V: volume fraction of the penetrant.

Aitken and Barrer [36] studied diffusion in crosslinked rubbers. In this work, they used pentanes and isomeric butanes as solvents. The rubber membranes were crosslinked using *tert*-butyl peroxide. They investigated the effect of crosslinking, concentration, temperature, and size and shape of molecules. The extent of crosslinking was estimated using average molecular weight between the crosslinks. The diffusion coefficient inversely varied almost linearly with the molecular weight between the crosslinks and, hence, decreased as the crosslinking increases. There was linear increament in diffusion coefficient with solvent at low solvent concentration. This observation was in agreement with the preceding study [35]. The diffusion coefficients at zero concentration was shown to decrease in the order of *n*-C_4H_{10} > *n*-C_5H_{12} > *iso*-C_4H_{10} > *iso*-C_5H_{12} > *neo*-C_5H_{12}.

Branching of CH_3 – groups decreased the magnitude of diffusion coefficient much higher as compared to the diffusion in the case of increased chain length by CH_3 – groups.

DiMarzio [37] exhibited how the glass transition for a crosslinked rubber has a thermodynamic basis. A relationship between the elevation in the glass transition temperature with the number of crosslinks was derived. Theoretical results were validated with the available experimental data for natural rubber, styrene-divinyl benzene copolymer, and methyl methacrylate-ethylene glycol dimethacrylate copolymer.

Chen and Ferry [38] studied the diffusion of *n*-hexadecane and *n*-dodecane solvents styrene-butadiene random , poly-isobutylene , several poly-butadienes, several styrene-butadiene block copolymers, poly-dimethylsiloxane, and natural rubber. The samples were crosslinked using tetramethylthiuram disulfide dicumyl peroxide, sulfur, and high-energy electrons. The diffusion coefficients for the two solvents were evaluated and found to be inversely proportional to their molecular length. The diffusion coefficient diminished slightly on increasing the crosslinking. Dicumyl peroxide decreased the free volume in the crosslinked natural rubber. The diffusion of *n*-hexadecane was governed by the following expression:

$$\log D = A_d \quad \frac{1}{2.303} f \qquad (12)$$

where, A_d: constant that depends on the nature of the solvent only and f: fractional free volume derived from the temperature dependence of viscoelastic relaxation.

Flisi and Crespi [39] studied the effect of crosslinking on polymer – solvent interaction parameters. They found that crosslinking efficiency in ethylene propylene copolymer is highly dependent on organic peroxides. Crosslinking efficiency of α,α'-di(tert-butylperoxy)diisopropylbenzene during of propylene - ethylene vulcanization was studied at variable composition of propylene from 27 wt% to 66.3 wt%. They found that degree of crosslinking and swelling was independent of the composition. Their result showed the 100% degree of crosslinking whereas the earlier researcher [40] found only 65% crosslinking for the same sample. Their calculation method over predicted the crosslink efficiency in high concentrated samples. They were also not able to find any relationship of interaction parameter with the composition. They calculated the degree of crosslinking using the following relation

$$\sigma = \nu_e RT\left(\lambda \quad \frac{1}{\lambda^2}\right)\nu_r^{-1/2}, \; \nu = \nu_e \quad \frac{2\rho}{\bar{M}_n} \tag{13}$$

where, σ :elastic force per unit cross section of unstretched and unswollen test piece, R : gas constant, T : absolute temperature, λ : extension ratio, ν_r :volume fraction of polymer, ν_e :degree of crosslinking, ρ :specific gravity of material, $\bar{M}_n$: average molecular weight of polymer before crosslinking, ν :crosslinking efficiency.

Arkhangelsky et al. [41] developed a method to calculate the molecular weight of the crosslinked chain using sorption data when the polymer – solvent interaction parameter was concentration dependent. They did the sorption study of hexane in crosslinked poly(methylphenylhydrosiloxane). The following equations were given by them

$$\frac{\left[\ln\left(\frac{a_1}{\phi_{1a}}\right) - \phi_{2a}\right]}{\phi_{2a}^2} = \chi \quad \left(\frac{\rho\bar{V}_1}{M_c^{cr}}\right)\phi_{2a}^{-5/3} \tag{14}$$

$$\frac{\left[\ln\left(\frac{a_1}{\phi_{1a}}\right) - \phi_{2a}\right]}{\phi_{2a}^2} = \chi \quad \left(\frac{\rho\bar{V}_1}{M_c}\right)\left[\phi_{2a}^{\frac{1}{3}} \quad \frac{2}{f}\phi_{2a}\right]\phi_{2a}^2 \tag{15}$$

ϕ_{1a} : volume fraction of solvent absorbed, ϕ_{2a} : volume fraction of the polymer, M_c :molecular mass of chain section between the cross links, χ : polymer – solvent interaction parameter, $a_1 = \frac{p}{p_0}$: relative vapor pressure, ρ : density of polymer, $\bar{V}_1$: molar volume of polymer, M_c^{cr} : average molecular mass of chain element between crystallites, f : functionality of crosslink, M_c : molecular mass of chain section between the crosslinks.

Kulkarni and Mashelkar [42] developed a mathematical model to correlate diffusivity and structure in crosslinked polymers. The model was based on a Maxwell model and considered diffusion in a two-phase system consisting of a crosslinked discrete phase dispersed in a continuous uncrosslinked matrix. This model was used to explain the effect of the crosslinking degree (f_c) on diffusion of Chlorazol Sky Blue FF dye and chrysophenine G dye in cellophane crosslinked with bishydroxyethyl sulphone and dimethylol ethylene urea. The equilibrium dye absorption as well as the rate of dyeing decreased considerably with increased crosslinking in the limiting conditions. This was attributed to the decrease in diffusivity. The molecular size and affinity of dye governed the diffusion of the dye under consideration. Increment in the crosslink density decreased interaction sites and free volume for dye diffusion. The diffusion of chlorazol Sky Blue FF was much sensitive to crosslink density as compared to Chrysophenine G. Other practical inferences from the developed model had also been drawn in this work. The following equation was given for the diffusivity:

$$D = D^{*}\left(\frac{1}{1+\frac{f_c}{2}}\right) + D_0 \tag{16}$$

where f_c: fraction of the dispersed crosslinked phase, and D^* and D_o are constants characteristic of the polymer-solvent system.

Peppas and Reinhart [43] developed a theoretical model for predicting diffusion coefficients of solute in swollen membranes and polymeric network. The theoretical model was satisfactorily verified with experimental results of cellulose-based semi-crystalline membranes. The model is described as under:

$$\frac{D_{2,13}}{D_{2,1}} = f\left(\frac{\overline{M}_C - \overline{M}_C^{*}}{\overline{M}_n - \overline{M}_C^{*}}\right)\exp\left(\frac{\pi r_s^{2} l}{V_1(Q_m - 1)}\right) \tag{17}$$

Peppas and Moynihan [44] extended the above model for moderately swollen networks and given following model equations:

$$\frac{D_{2,13}}{D_{2,1}} = f\left(v_{3,s}^{-\frac{3}{4}}\right)\exp\left[k_3\left(\bar{M}_c - \bar{M}_n\right) - \pi r_s^2 l_s \phi(V)\right] \tag{18}$$

$$\phi(V) = \frac{V_1 - V_3}{(Q-1)V_1^2 + V_1 V_3} \qquad k_3 = \frac{-2\Delta E}{\overline{M}_n R T_F} \tag{19}$$

where $D_{2,13}$: diffusion coefficient for solute through water swollen polymeric membrane, $D_{2,1}$: diffusion coefficient for solute through water, M_c: number average molecular weight between crosslinks, M_n: upper limit of M_c, number average molecular weight of the uncrosslinked polymer, M_c^*: lower limit of M_c below which no diffusion of a specific solute occurs, r_s: stokes hydrodynamic radius of the solute, l: characteristic length, equal to or less than the translational jump length, V_1: free volume of the pure diluent (water), and Q_m: ratio of the voumes of the swollen gel to the dry polymer, Q:quilibrium degree of swelling, Q, **r :** the hydrodynamic radius of the solute, M**:** number average molecular weight between crosslinks, $f(\xi)$: a function of the mesh size ξ, $v_{3,s}$: polymer volume fraction at isothermal swelling equilibrium, $\Phi(V)$: free volume contribution , V_1 and V_3: free volumes of the pure diluent (water) and polymer, and constant k_3 , ΔE: internal energy, R: universal gas constant, and T_f: forming temperature of the polymer.

Smith and Peppas [45] studied the effect of crosslinking degree on penetrant transport in crosslinked poly(styrene). In this study, they used the cyclohexane as penetrant. Anomalous behavior of penetrant in crosslinked poly(styrene) was observed. The volume fraction of cyclo-hexane deceased as the degree of crosslinking increased. This behavior was observed due to the coupling of diffusion and relaxation mechanisms. The thickness of solvent penetration into the polymer was very low in highly crosslinked systems as compared to the loosely crosslinked ones. Average molecular weight of the crosslinked polymer was calculated using following expression:

$$\frac{1}{M_C}=\frac{1}{M_n}-\frac{v\left[\ln(1-v_2)+v_2+\chi v_2^2\right]\left[1-\frac{v_2^{2/3}}{N}\right]^3}{V_1\left[v_2^{1/3}-0.5v_2\right]\left[1+\frac{v_2^{1/3}}{N}\right]^2},\ \frac{M_c}{M_R}=N \tag{20}$$

$$\chi=0.4433v_2^2+0.2308v_2+0.507,\ v_2=Q^{-1}=\frac{W_a^{'}-W_W^{'}}{\rho_w} \tag{21}$$

M_c: average molecular weight of crosslinked polymer, M_n : average molecular weight of uncrosslinked polymer, $W_a^{'}$: weight of sample in air, $W_W^{'}$: weight of sample in water , V_1 : volume fraction of polymer

Vrentas and Vrentas [46] developed the model to predict the self diffusion in crosslinked polymer by modifying earlier free volume theory [47, 48]. They made several assumptions while modifying the free volume theory of amorphous polymers. The assumptions were D_0, E, solvent properties: $\hat{V}_1^*, M_{j1}, \hat{V}_{FH1}$, polymer properties: γ, M_{j2}, thermal expansion coefficient, specific volume of polymer, and interstitial free volume were assumed to be independent of the crosslinking degree. These assumptions forced that self–diffusion coefficient can be affected by $\hat{V}_{FH2}$ and temperature only. The $\hat{V}_{FH2}$ was related to the pure polymer free volume and was calculated using density data. The calculations were simpler because they did not require the nature of crosslinking, rather the volumetric properties of crosslinked polymer. They found the decrement in diffusion coefficient with increment in crosslink density. They tested their model for natural rubber and found very good agreement with the volumetric expansion data. They gave the following self–diffusion equation:

$$D_1=D_0\exp\left(-\frac{E}{RT}\right)\exp\left[-\frac{w_1\hat{V}_1^*+w_2\xi\hat{V}_2^*}{w_1\frac{\hat{V}_{FH1}}{\gamma}+w_2\frac{\hat{V}_{FH2}}{\gamma}\delta}\right],\ \xi=\frac{\hat{V}_1^*M_{j1}}{\hat{V}_2^*M_{j2}} \tag{22}$$

$$\delta = \frac{\hat{V}_{FH2(T,X)}}{\hat{V}_{FH2(T,0)}} \; \frac{\hat{V}_{2(0,X)}}{\hat{V}^{0}_{2(0,0)}} \; \frac{\hat{V}^{0}_{2(T,X)}}{\hat{V}^{0}_{2(T,0)}} \; \frac{\hat{V}^{0}_{2(T_1,X)}}{\hat{V}^{0}_{FH2(T_1,0)}} \tag{23}$$

where, w_i : mass fraction of species i, $\hat{V}_i^*$:specific hole free volume of component i, ξ : ratio of critical molar volume of solvent jumping unit to the polymer jumping unit, M_{ji} : molecular weight of jumping unit of species i, E : activation energy for diffusion, D_0 : preexponential factor, γ : overlapping factor

Best and Moylan [49] studied the diffusion of water into a photopolymer film. They prepared the crosslinked film of dimethacrylate UV-cured polymer. They performed a sorption experiment to determine the diffusion coefficient and solubility in water vapor at 21°C and 19 torr. Sorption of water vapor was measured by quartz crystal microbalance. They also measured the diffusion coefficient for liquid water sorption by gravimetrical and spectroscopic techniques. After that, they compared the diffusion coefficients and water uptake from all the three techniques. They found that the quartz crystal microbalance data were much more accurate than the remaining techniques. From their results, they concluded that this photopolymer could not prevent the water sorption to films for a long period of time under ambient conditions for polymer thickness less than 1 cm.

Liyina and Sillescu [50] measured the self–diffusion coefficient of toluene in linear and crosslinked poly(styrene). In the linear poly(styrene), they found that self diffusion data follows the Arrhenius law in the beginning up to 230 K. They suggested that activation energy for diffusion is a function of temperature and concentration due to which deviations were observed beyond 230K. They considered two step diffusion of toluene in poly(styrene) to explain this deviation. They found higher value of self diffusion of toluene in crosslinked poly(styrene) as compared to linear poly(styrene). Their results showed that self–diffusion coefficient was not much affected by the crosslinks at high polymer concentrations. It was just same as that for uncrosslinked poly(styrene) at same concentration.

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Mateo et al. [51] prepared crosslinked block copolymer of styrene-butadiene-styrene by exposing to UV radiations using photo-initiators. Weight gain experiments were conducted to study the sorption and diffusion of chloroform and toluene. The results conformed to the Fickian model up to nearly 60% of reaching the equilibrium swelling value. A higher crosslinking density and higher molecular size of the solvent expectedly yielded smaller equilibrium swelling value. The observed deviation from the Fickian model was due to di-phasic morphology of the SBS copolymer diffusion in more swollen part. Micro-phase separation was decreased by increasing crosslinking temperature which changed the diffusion behavior to nearly Fickian. The diffusivity was determined from the following relation:

$$D = \pi\left(\frac{h.\theta}{4.Q_{eq}}\right)^2 \tag{24}$$

where Q_{eq}: moles of liquid sorbed per 100 g of the polymer at equilibrium, y: slope of the linear part of the sorption curves before attainment of 50% equilibrium, and h: the initial sample thickness.

The interaction parameters for the crosslinked styrene-butadiene-styrene block copolymer-solvent χ and the crosslinking density v were correlated from Flory-Rehner equation [51].

$$\left[\ln\left(1-v_r\right)+v_r+\chi v_r^2\right]=vV_sA_\phi\left(v_r^{\frac{1}{3}} \quad 2\frac{v_r}{f}\right) \tag{25}$$

where v_r: volume fraction of polymer in the swollen sample, v: number of effective network chains/cm^3 of crosslinked polymer (chain density or network density), V_s: the molar volume of the solvent, f: crosslink functionality, number of chains emanating from each crosslink (generally 4), and A_f: structure factor which depends on how much the deformation deviates from the affine limit, in which the displacements of the crosslinks are a simple linear function of the macroscopic strain.

The molar mass between crosslinks was given by

$$M_C = -\frac{d_p V_S A_\phi (v_r^{1/3} - v_r / 2)}{\ln(1 - v_r) + v_r + \chi v_r^2} \tag{26}$$

where, d: the polymer density (0.94), and $A_{\Phi} =$ (1 - 2/*f*) for these highly swelling systems.

There was strong interaction between polymer and solvent as supported by calculated values of χ interaction parameters 0.41 and 0.40 for toluene and chloroform respectively. The densities of crosslinking were relatively low as indicated by the M_c values which ranged from 23000 to 5000 for 30 min to 120 min irradiation time respectively for the irradiated styrene-butadiene-styrene block copolymer [51].

Zhao et al. [52] measured the infinite dilution diffusion coefficients of *n*-decane, *n*-hexane, and *n*-heptane in crosslinked silicone rubber using inverse gas chromatography. They used several crosslinking agents in varying amount to crosslink the silicone rubber. Solvent, crosslinking agent and prepolymer polydimethylsiloxane (PDMS) were dissolved to get the crosslinked silicone rubber. The effects of small molecule solvent and crosslinking agent concentrations on the diffusion coefficient were studied. The enhancement in CH_2 group in solvent alkane series decreased the diffusion coefficient in infinite dilution. Higher amount of crosslinking agent concentration decreased the infinite dilution diffusion coefficient. The log of diffusion coefficient increased linearly with an increase in the free volume. The diffusion coefficients were determined according to the following Van Deemter equation:

$$D^{\infty} = \frac{8 d_p^{\,2}}{\pi^2 C} \cdot \frac{k}{(1+k)^2} \tag{27}$$

where d_p: thickness of the polymer coated on the column material, k: partition ratio, and C is related to the column characteristics and depends on probe diffusion in the liquid phase. d_p was determined from the equation:

$$d_p = \frac{w_p \rho_d d_d}{6 \rho_p w_d} \tag{28}$$

where w_p: the mass of the silicone rubber inside the carrier, w_d: the mass of carrier, ρ_p: silicone rubber density, ρ_d: carrier density, and d_d: carrier average diameter.

Krongauz [1] studied the diffusion in polymer and its dependence on the crosslink density. They studied the evaporation of N-methyl pyrrolidone from the photo crosslinked poly(acrylate). The degradation of polymer was controlled by controlling the diffusion of volatile and oxygen into the film. He found that the swelling of the polymer depends on the chain length and crosslinked density. He calculated molar concentration of crosslinks, glass transition temperature, and average number of atoms in crosslinks to explain the crosslinking. He found that the rate of diffusion increased with the temperature. The increment in crosslinked density decreased the activation energy. However, the increased chain length enhanced the activation energy for water diffusion in monolayer.

2.3 Limitations and Future Scope of Study

The literature on crosslinked polymeric coatings can be summarized in the following noteworthy points which can be helpful for further studies:

- The literature reported so far is limited mainly to the methods of crosslinking and the characterization of the crosslinked thickness [2-4, 6-12, 15-17, 21, 22, 24-34, 53].
- Sufficient literature is available to show the importance of the crosslinked polymers and coatings and their applications in the emerging areas like biosensors, biomedical, optics, physical and chemical separations, and control drug delivery [1-12].
- Very limited studies and data are available regarding the diffusion of solvent with the crosslinked polymer – solvent coatings. The literature available is limited to the sorption and that is fully developed i.e. mathematical model to explain the penetration fronts etc [1, 35-39, 41-47, 49-52]
- Neither experimental nor computational study is reported regarding the residual solvent analysis in the crosslinked polymeric coatings which plays very important

role related to stability of coatings, production defects like phase separation, blister formation, cracking, etc.

- Only one diffusion model is available to predict the self-diffusion coefficient in crosslinked polymeric coatings [46]. There were several assumptions in this model. Hence, there is an urgent need to validate this model with experimental diffusion coefficient data. The model can be further expanded to calculate the mutual diffusion coefficient which will require the activity coefficient model for crosslinked polymer – solvent systems and this too is not available in the literature.
- Vrentas and Vrentas [46] is based on free volume theory. The free volume, swelling and solvent absorption can be greatly reduced by crosslinking the coating. The crosslinking also reduces the rate of solvent evaporation from the film [1] due to decrease in free volume. Hence, crosslinked coatings will retain large amount of solvent in it, which will give rise to the production defects like phase separation, blister formation, cracking, etc. Therefore, a parameter study of free volume theory parameters is required to study the effect of variation of these parameters on the diffusion coefficient and hence the residual solvent remaining.
- The diffusion model should also be validated with depth profiling data using confocal Raman spectroscopy.
- Morphological study should be performed during the course of drying. The top layer will be highly dense as compared to the bottom layer due more amount of solvent retained. This could be an easy way to produce high mechanical strength asymmetric membranes.

Chapter 3

Materials and Methods

3.1 Chemicals Used

Poly(styrene) was provided by Sigma Aldrich, Germany (density: 1.04 $g.cm^{-3}$, molecular weight: 192000), *p*-xylene was provided by Spectrochem, India (density: 0.861 $g.cm^{-3}$, molecular weight: 106.16), Ethyl benzene was provided by Spectrochem, India (density: 0.866 $g.cm^{-3}$, molecular weight: 106.17), Poly(styrene-co-divinylbenzene) was provided by Sigma Aldrich, Germany (density: 0.29 $g.cm^{-3}$) and its chemical structure are shown in Figure 3.1. All chemicals were utilized as provided with no further purification.

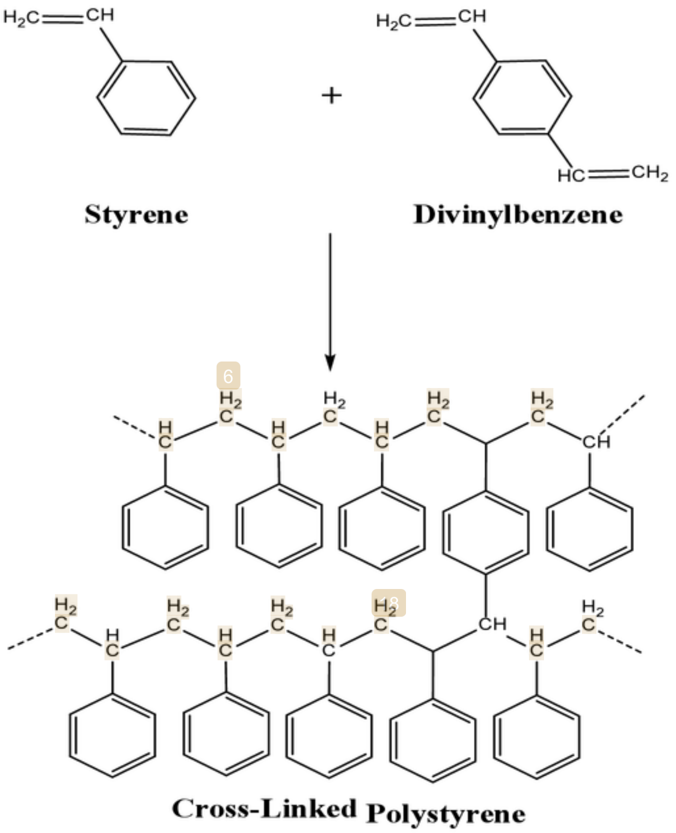

Figure 3.1: Poly(styrene) crosslinked with divinylbenzene.

3.2 Methodology

As described in Chapter 1, the solution casting technique was followed for the preparation of coatings in the present work. A predecided amount of polymer solution was poured into the sample holder to get the desired initial coating thickness. In this work, the coatings of poly(styrene) and crosslinked poly(styrene-co-divinylbenzene) were prepared in *p*-xylene and ethylbenzene. Crosslinked poly(styrene-co-divinylbenzene) mass fraction was varied in poly(styrene) solution to see the effect of the proportion of crosslinked poly(styrene-co-divinylbenzene) on the residual solvent.

Two solutions of poly(styrene) were prepared in *p*-xylene and ethylbenzene having 10.12% and 9.93% poly(styrene) by weight respectively. Another two solution of poly(styrene), Poly(styrene-co-divinylbenzene) and *p*-xylene were prepared having their weight percentage (9.94% , 0.98% , and 89.08%) and (2.01%, 10.07% , and 87.92%) respectively. Another two solution of poly(styrene), Poly(styrene-co-divinylbenzene) and ethylbenzene were prepared having their weight percentage (10.01% , 0.99%, and 89%) and (2.08%, 9.98% and 87.94%) respectively. These solutions were prepared by taking the required quantity of solvent and polymer(s) in reagent bottles. These solutions were shaken mechanically for 24 hours and left for swelling of crosslinked polymer around 3 months to swell the uncrosslinked polymer. Manual shaking was done every day for around 30 minutes to get the homogeneous solutions.

Several coatings of different initial thicknesses were prepared by pouring varied quantity of polymer solutions by using micropipette in the circular sample holder having 12.24mm diameter and1000 µm depth of sample holder is shown in Figure 3.2. Solvent evaporates from the coating immediately after pouring, resulting the loss in weight of the coating solution. The sample weight was recorded as a function of time by using Sartorius Analytical weighing balance (ES225SM-DR) having accuracy of ± 0.0001 g. The weight data with time were recorded until no further change in two consecutive weight data to make sure that drying process has been stopped for practical purpose. Coatings were dried under natural convection. All the experiments were conducted at 25±1°C or as stated.

3.3 Calculations of Various Coating Parameters

Let the mass of solution in any time is “m” of polymer solution having 10.16% polymer and 89.84% solvent respectively.

Mass of polymer, $M_p = m \times \frac{10.16}{100}$

Initial mass of solvent, $M_S = m \times \frac{89.84}{100}$

Volume of coating, $V_{\text{Coating}} = \frac{M_p}{\text{density of polymer}} + \frac{M_S}{\text{density of solvent}}$

% Residual Solvent = $\frac{\text{Instantaneous coating mass} - m}{M_s} \times 100$

Thickness of coating, L = $\frac{V_{\text{Coating}}}{\text{Cross - sectional area of sample holder}}$

Concentration of polymer = $\frac{m \times 10.16}{V_{\text{coating}}}$

Concentration of solvent = $\frac{\text{Instantaneous coating mass} - M_P}{V_{\text{Coating}}}$

Figure 3.2: Circular sample holder.

Chapter 4

Results and Discussions

The effect of cross-linked polymer content on the drying behavior of polymeric coatings was studied. Poly(styrene)–ethylbenzene and poly(styrene)–*p*-xylene systems have chosen for the present study. Poly(styrene-co-divinylbenzene) has been chosen as the crosslink polymer having 1% crosslinking. The effect of crosslink content in the poly(styrene) – ethylbenzene and poly(styrene) – *p*-xylene systems has been studied and reported in this chapter.

4.1 Drying of Poly(styrene) – *p*-xylene Coating having 0.98% Poly(styrene-co-divinylbenzene)

Two solutions of poly(styrene), one having linear poly(styrene) and the other having linear poly(styrene) and poly(styrene-co-divinylbenzene) were prepared in *p*-xylene. The *p*-xylene weight percentages in linear and crosslinked solutions were 89.88% and 89.08% respectively. These solutions are named as type 1 and type 2. Several coatings of each type have been prepared to study the effect of crosslink content on residual solvent, coating thickness, concentrations of poly(styrene) and solvent, and the drying time.

Type 1: 10.12% poly(styrene) and 89.88% p-xylene

Type 2: 9.94% poly(styrene), 89.08% p-xylene and 0.98% poly(styrene-co-divinyl-benzene)

4.1.1 Percentage of Residual Solvent

The change of residual *p*-xylene content with time is shown in Figure 4.1. It shows that the percentage of residual *p*-xylene is decreasing with time. In type 1, the residual *p*-xylene linearly decreases up to 110 min 43 s, 141 min 10 s, and 185 min 52 s respectively in the cases of coatings having initial thicknesses 408 µm, 654 µm, 816 µm respectively, Up to 98.28%, 97.13%, and 96.8% *p*-xylene has been removed in, and the remaining 1.72%, 2.87% and 3.2% *p*-xylene is permanently trapped in the coatings respectively. The coatings of Type 2 solution have followed the same trend and the residual *p*-xylene is also decreasing linearly up to 110 min 34 s, 121 min 50 s, and 163 min 14 s in the cases of coatings having initial thickness 387 µm, 566 µm, and 752 µm respectively. Up to 91.93%, 90.45% and 89.02% *p*-xylene has been removed, in and the remaining 8.07%, 9.55% and 10.98% *p*-xylene is permanently trapped in the coatings respectively. With the increase in time, the percentage of residual *p*-xylene is decreasing at extremely slow rate due to poor diffusion of *p*-xylene at later stages of drying. In the beginning, the percentage of residual *p*-xylene decreases at a very fast rate, due to fast evaporation of *p*-xylene from the top surface and huge amount of *p*-xylene was present in the coating in the beginning and drying process is externally controlled. It was observed that type 2 takes more time for drying because of the presence of nearly 1% crosslinked polymer, due to which there is very less availability of free volume and the solvent cannot diffuse easily as compared to the uncrosslinked polymer, i.e., type1.

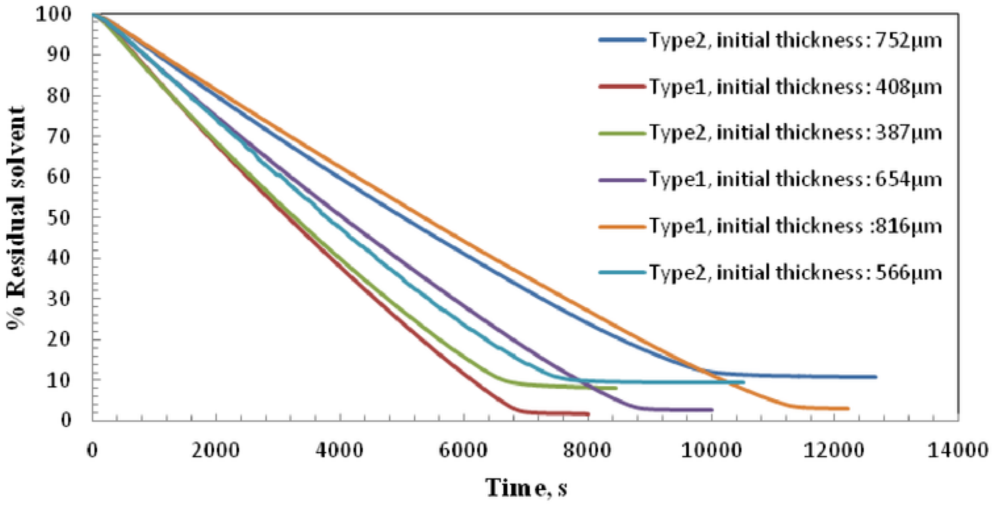

Figure 4.1: Residual solvent as a function of time in poly(styrene) – *p*-xylene system with and without crosslinked poly(styrene-co-divinylbenzene) at 18°C.

4.1.2 Coating Thickness

Figure 4.2 shows the variation of coating thickness with time. It shows that the thickness starts decreasing with time due to evaporation of *p*-xylene from the coating into surrounding. In the beginning, the thicknesses of type 1 coatings were 408 µm, 654 µm, and 816 µm respectively, and decreases linearly up to 114 min 18 s, 144 min 14 s and 185 min 18 s respectively and then it plateaus off. The Thickness of type 2 coatings in the beginning were 387 µm, 566 µm and 752 µm respectively, and also decreases linearly up to 110 min 53 s, 123 min 17 s and 159 min 38 s respectively and then it plateaus off. The coatings having very small amount of crosslinked poly(styrene-co-divinylbenzene) (0.98%) are left thicker at the end of drying process. It is due to the more amount of *p*-xylene has been trapped in these coatings since, the poly(styrene) content in type 1 and type 2 coatings are 10.12% and 9.94% respectively. For an instance, initial coatings thickness: 408 µm and 387 µm of type 1 and type 2 solution respectively are giving the dried coating thickness of 25 µm and 58 µm respectively at the end of 133 min 31 s and 140 min 56 s.

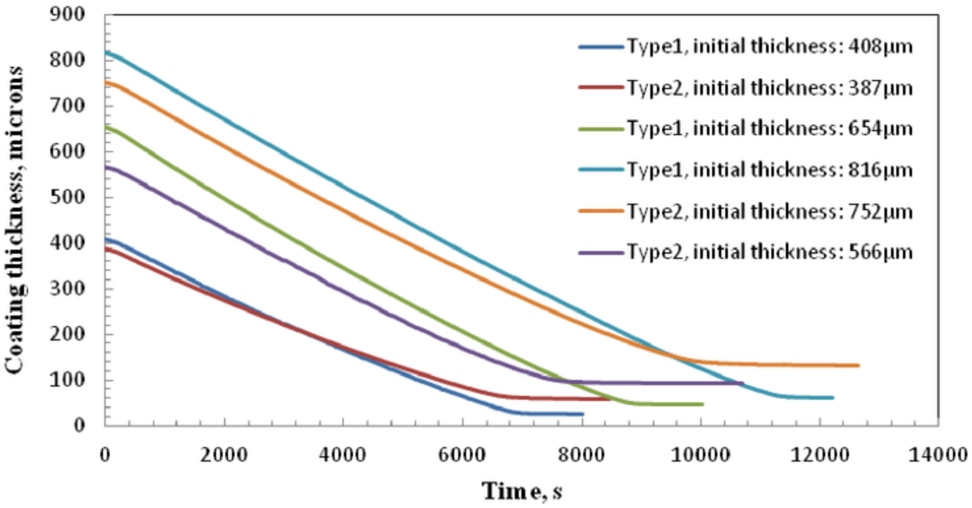

Figure 4.2: Thickness as a function of time in poly(styrene) – *p*-xylene system having crosslinked and uncrosslinked poly(styrene-co-divinylbenzene) at 18°C.

4.1.3 Average Concentration of p-xylene

The average concentration of *p*-xylene with time is shown in Figure 4.3. It describes that the *p*-xylene is evaporating from the coating and its concentration start decreasing with time. In type 1, the concentration of *p*-xylene decreases exponentially up to 118 min 21 s, 147 min 52 s and 189 min 17 s in the cases of the coatings having initial thicknesses of 408 µm, 654 µm, and 816 µm respectively, and then it leveled off. Type 2 coatings follows the same trend, the *p*-xylene concentration decreases exponentially at slow rate up to 109 min 22 s, 123 min 20 s and 162 min 52 s in the cases of coatings having initial thicknesses 387 µm, 566 µm, and 752 µm respectively, and then it leveled off. The final concentration of *p*-xylene in type 1 coating were 0.237 $g.cm^{-3}$, 0.334 $g.cm^{-3}$ and 0.356 $g.cm^{-3}$ for coatings having initial concentration 0.823 $g.cm^{-3}$, 0.823 $g.cm^{-3}$ and 0.823 $g.cm^{-3}$, and thicknesses 408 µm, 654 µm, and 816 µm respectively. The final concentration of *p*-xylene in type 2 coating were 0.434 $g.cm^{-3}$, 0.470 $g.cm^{-3}$ and 0.499 $g.cm^{-3}$, for coatings having initial concentration 0.797 $g.cm^{-3}$, 0.797 $g.cm^{-3}$ and 0.797 $g.cm^{-3}$, thicknesses 387 µm, 566 µm, and 752 µm respectively.

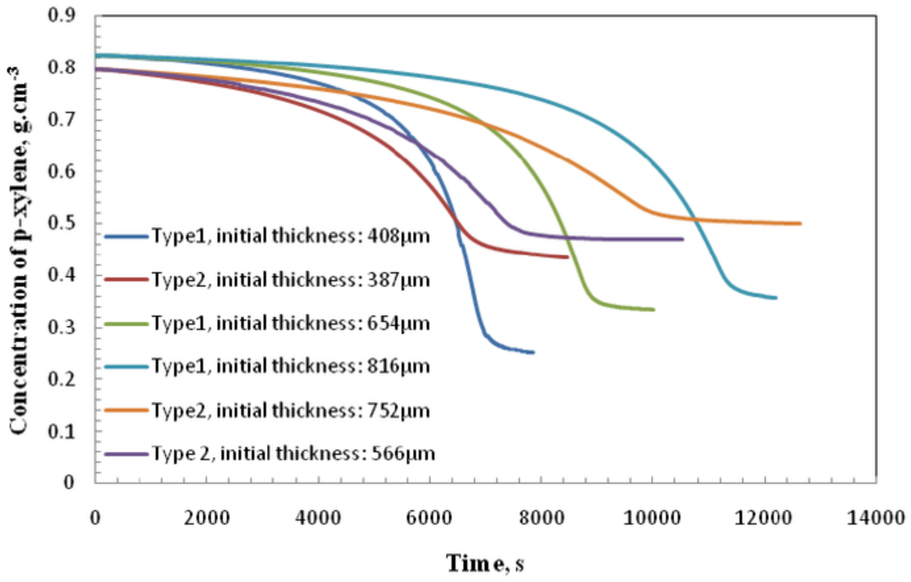

Figure 4.3: Concentration of *p*-xylene as a function of time in poly(styrene) – *p*-xylene system having crosslinked and uncrosslinked poly(styrene-co-divinylbenzene) at 18°C.

4.1.4 Average Concentration of Polymer

Figure 4.4 depicts the average concentration of polymer (poly(styrene) and poly(styrene-co-divinylbenzene)) with time. It represents that the polymer concentration start increasing with time due to evaporation of *p*-xylene from coating. In type1, coatings the concentration of the polymer increases exponentially up to 116 min 54 s, 148 min 17 s and 188 min 50 s respectively in cases of coatings having initial thickness of 408 µm, 654 µm, and 816 µm respectively and then plateaus off. Type 2 coatings also follow the same trend, the polymer concentration increases exponentially at slow rate up to 113 min 50 s, 123 min 44 s and 163 min 44 s in the cases of coatings having initial thicknesses of 387 µm, 566 µm, and 752 µm respectively and then plateaus off. With the increase in drying time, there is increase in the concentration of the polymer due to more solvent removal from the coating.

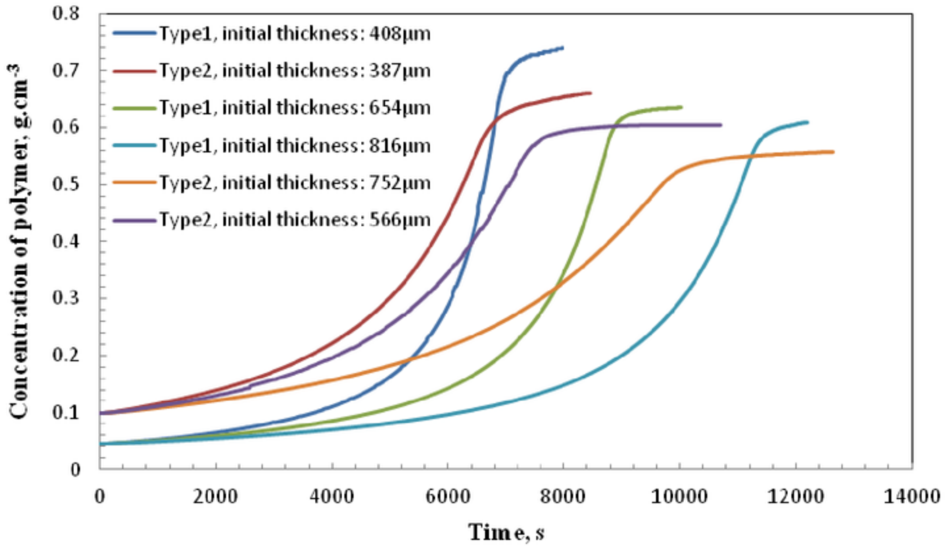

Figure 4.4: Concentration of polymer as a function of time in poly(styrene) – *p*-xylene system with and without crosslinked poly(styrene-co-divinylbenzene) at 18°C.

4.2 Drying of Poly(styrene) – *p*-xylene Coating having 2.01% Poly(styrene-co-divinylbenzene)

Two solutions of poly(styrene) one having linear poly(styrene) and the other having linear poly(styrene) and poly(styrene-co-divinylbenzene) were prepared in *p*-xylene. The *p*-xylene weight percentages were 89.88% and 87.92% respectively. These solutions are named as type 1 and type 3. Several coatings of each type have been prepared to study the effect of crosslink content on residual solvent, coating thickness, concentrations of poly(styrene) and solvent, and the drying time.

Type 1: 10.12% poly(styrene) and 89.88% *p*-xylene

Type 3: 10.07% poly(styrene), 87.92% *p*-xylene, and 2.01% poly(styrene-co-divinyl-benzene)

4.2.1 Percentage of Residual Solvent

The change of residual *p*-xylene content with time is shown in Figure 4.5. It shows that the percentage of residual *p*-xylene decreasing with time. In type 1, the residual solvent linearly decreases up to 62 min 35 s, 97 min 20 s, and 110 min 35 s respectively in the cases of coatings having initial thicknesses of 446 μm, 632 μm, and 872 μm respectively. Up to 94.17%, 96.41%, and 93.61% *p*-xylene has been removed, and the remaining 5.83%, 3.59% and 6.39% solvent permanently trapped in the coatings respectively. The coatings of Type 3 solution have followed the same trend and the residual *p*-xylene is also decreasing linearly up to 56 min 55 s, 96 min 10 s, and 101 min 10 s in the cases of coatings having initial thicknesses of 331 μm, 603 μm, and 683 μm respectively. Up to 89.56%, 87.62% and 87.6% *p*-xylene has been removed, and the remaining 10.44%, 12.38% and 12.40% *p*-xylene is permanently trapped in the coatings respectively. With the increase in time, the percentage of residual *p*-xylene is decreasing at extremely slow rate due to poor diffusion of *p*-xylene at later stages of drying. In the beginning, the percentage of residual *p*-xylene decreases at a very fast rate, due to fast evaporation of *p*-xylene from the top surface and huge amount of *p*-xylene was present in the coating in the beginning and drying process is externally controlled. It was observed that type 3 takes more time for drying because of the presence of nearly 2% crosslinked polymer, due to which there is very less availability of free volume and the solvent cannot diffuse easily as compared to the uncrosslinked polymer, i.e., type1.

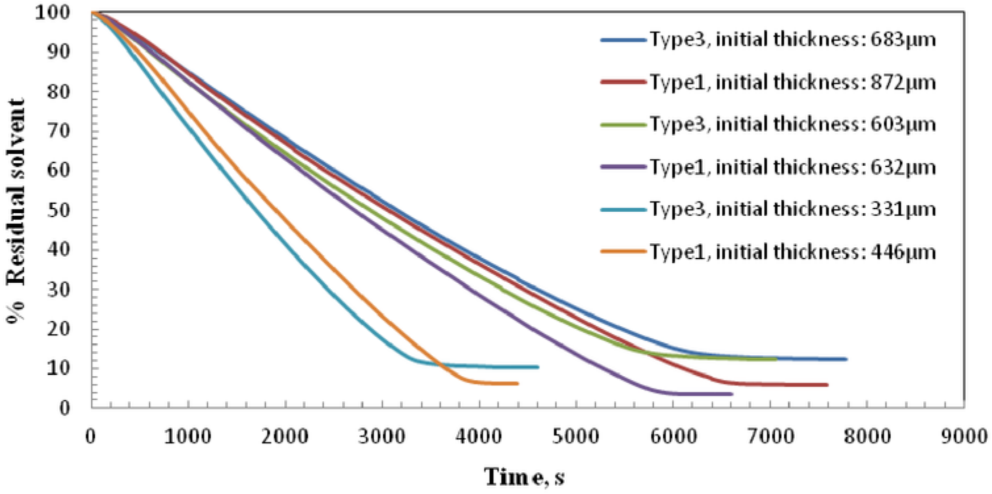

Figure 4.5: Residual solvent as a function of time in poly(styrene) – *p*-xylene system with and without crosslinked poly(styrene-co-divinylbenzene) at 25°C.

4.2.2 Coating Thickness

Figure 4.6 shows the variation of coating thickness with time. It shows that the thickness starts decreasing with time due to evaporation of *p*-xylene from the coating into surrounding. In the beginning, the thicknesses of type 1 coatings were 446 μm, 632 μm, and 872 μm respectively and decreases linearly up to 61min 45 s, 97 min 25 s and 107 min 20 s respectively and then it plateaus off. The thickness of type 3 coatings in the beginning were 331 μm, 603 μm and 683 μm respectively and also decreases linearly up to 54 min 10 s, 95 min 25 s and 102 min 10 s respectively and then it plateaus off. The coatings having very small amount of crosslinked poly(styrene-co-divinylbenzene) (2.01%) are left thicker at the end of drying process. It is due to the more amount of *p*-xylene has been trapped in these coatings since, the poly(styrene) content in type 1 and type 3 coatings are 10.12% and 10.07% respectively. For an instance, initial coatings thickness: 632 μm and 603 μm of type 1 and type 3 solution respectively are giving the dried coating thickness of 50 μm and 118 μm respectively at the end of 110 min 5 s and 117 min 35 s.

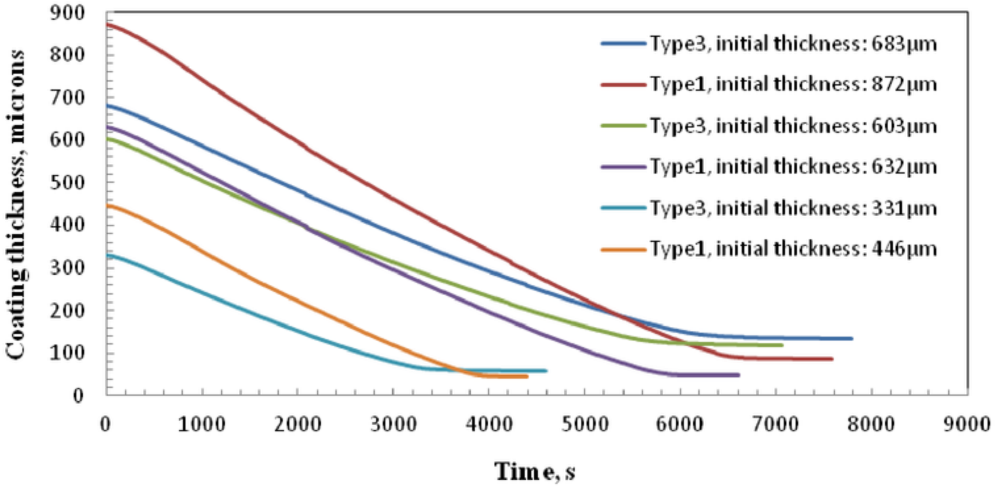

Figure 4.6: Thickness as a function of time in poly(styrene) – *p*-xylene system having crosslinked and uncrosslinked poly(styrene-co-divinylbenzene) at 25°C.

4.2.3 Average Concentration of *p*-xylene

The average concentration of *p*-xylene with time is shown in Figure 4.7. It describes that the solvent is evaporating from the coating and its concentration start decreasing with time. In type 1, coatings the concentration of *p*-xylene decreases exponentially up to 66 min 20 s, 91 min 10 s and 111 min 40 s in the cases of the coatings having initial thicknesses of 446 μm, 632 μm, and 872 μm respectively and then it leveled off. Type 3 coatings follows the same trend, the *p*-xylene concentration decreases exponentially up to 55 min 10 s, 97 min 35 s and 98 min 50 s in the cases of coatings having initial thicknesses 331 μm, 603 μm, and 683 μm respectively and then it leveled off. The final concentration of *p*-xylene in type 1 coatings were 0.504 g.cm^{-3}, 0.381 g.cm^{-3}, and 0.485 g.cm^{-3}, for coatings having initial concentration 0.823 g.cm^{-3}, 0.823 g.cm^{-3} and 0.823 g.cm^{-3}, and thicknesses 446 μm, 632 μm, and 872 μm respectively. The final concentration of *p*-xylene in type 3 coatings were 0.464 g.cm^{-3}, 0.501 g.cm^{-3}, and 0.501

$g.cm^{-3}$, for coatings having initial concentration 0.790 $g.cm^{-3}$, 0. 7906 $g.cm^{-3}$ and 0.790 $g.cm^{-3}$, and thicknesses 331 µm, 603 µm, and 683 µm respectively.

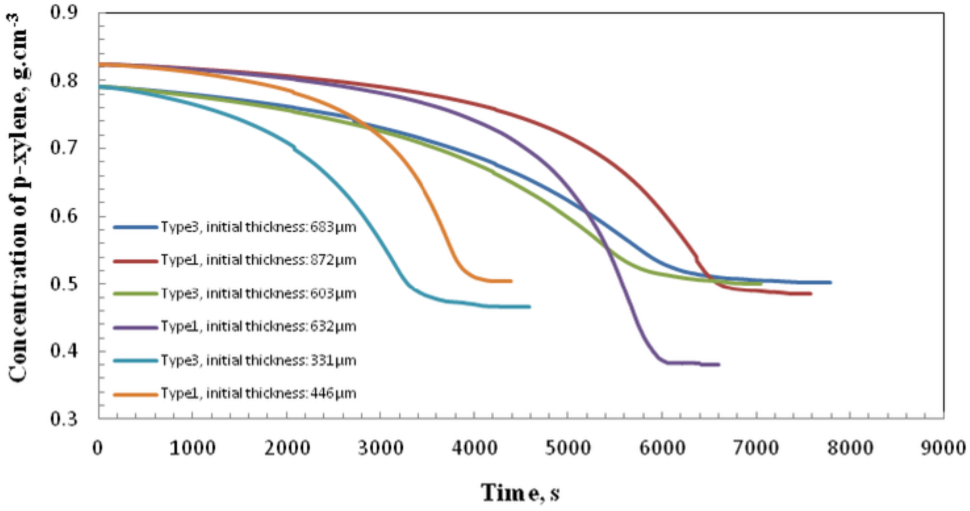

Figure 4.7: Concentration of p-xylene as a function of time in poly(styrene) – *p*-xylene system having crosslinked and uncrosslinked poly(styrene-co-divinylbenzene) at 25°C.

4.2.4 Average Concentration of Polymer

Figure 4.8 depicts the average concentration of polymer (poly(styrene) and poly(styrene-co-divinylbenzene)) with time. It represents that the polymer concentration start increasing with time due to evaporation of *p*-xylene from coating. In type 1, coatings the concentration of polymer increases exponentially up to 64 min, 99 min 55 s and 109 min 10 s respectively in cases of coatings having initial thicknesses of 446 µm, 632 µm, and 872 µm respectively and then plateaus off. Type 3 coatings also follow the same trend, the polymer concentration increases exponentially at slow rate up to 55 min 10 s, 95 min 55 s and 105 min 20 s in the cases of coatings having initial thicknesses 331 µm, 603 µm, and 683 µm respectively and then plateaus off. With the increase in time, there is increase in the concentration of the polymer due to more solvent removal from the coating.

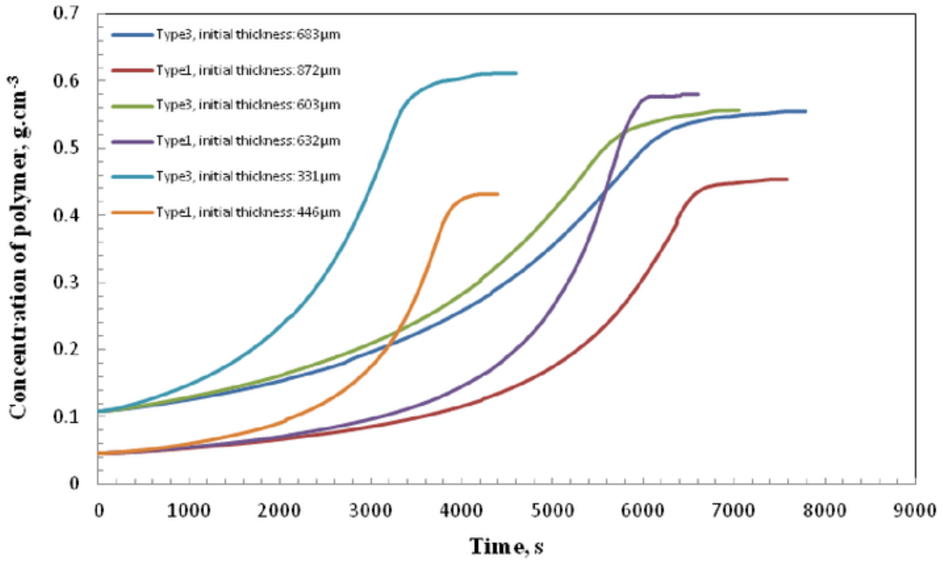

Figure 4.8: Concentration of polymer as a function of time in poly(styrene) – *p*-xylene system with and without crosslinked poly(styrene-co-divinylbenzene) at 25°C.

4.3 Drying of Poly(styrene) – ethylbenzene Coating having 0.99% Poly(styrene-co-divinylbenzene)

Two solutions of poly(styrene) one having linear poly(styrene) and the other having linear poly(styrene) and poly(styrene-co-divinylbenzene) were prepared in ethylbenzene. The ethylbenzene weight percentages were 90.07% and 89% respectively. These solutions are named as type 4 and type 5. Several coatings of each type have been prepared to study the effect of crosslink content on residual solvent, coating thickness, concentrations of poly(styrene) and solvent, and the drying time.

Type 4: 9.93% poly(styrene) and 90.07% ethylbenzene

Type 5: 10.01% poly(styrene), 89% ethylbenzene, and 0.99% poly(styrene-co-divinylbenzene)

4.3.1 Percentage of Residual Solvent

The change of residual ethylbenzene content with time is shown in Figure 4.9. It shows that the percentage of residual ethylbenzene decreasing with time. In type 4, the residual ethylbenzene linearly decreases up to 54 min 10 s, 69 min 20 s, and 95 min 45 s respectively in the cases of coatings having initial thicknesses 399 μm, 518 μm, and 751 μm respectively. Up to 95.25%, 94.43%, and 94.61% ethylbenzene has been removed, and the remaining 4.75%, 5.57% and 5.39% ethylbenzene permanently trapped in the coatings respectively. The coatings of type 5 solutions have followed the same trend and the residual ethylbenzene is also decreasing linearly up to 60 min 25 s, 64 min 35 s, and 106 min in the cases of coatings having initial thicknesses 423 μm, 472 μm, and 755 μm respectively. Up to 86.5%, 88.96% and 87.55% ethylbenzene has been removed, and the remaining 13.50%, 11.04% and 12.45% ethylbenzene is permanently trapped in the coatings respectively. With the increase in time, the percentage of residual ethylbenzene is decreasing at extremely slow rate due to poor diffusion of ethylbenzene at later stages of drying. In the beginning, the percentage of residual ethylbenzene decreases at a very fast rate, due to fast evaporation of ethylbenzene from the top surface and huge amount of ethylbenzene was present in the coating in the beginning and drying process is externally controlled. It was observed that type 5 takes more time for drying because of the presence of nearly 1% crosslinked polymer, due to which there is very less availability of free volume and the solvent cannot diffuse easily as compared to the uncrosslinked polymer, i.e., type 4.

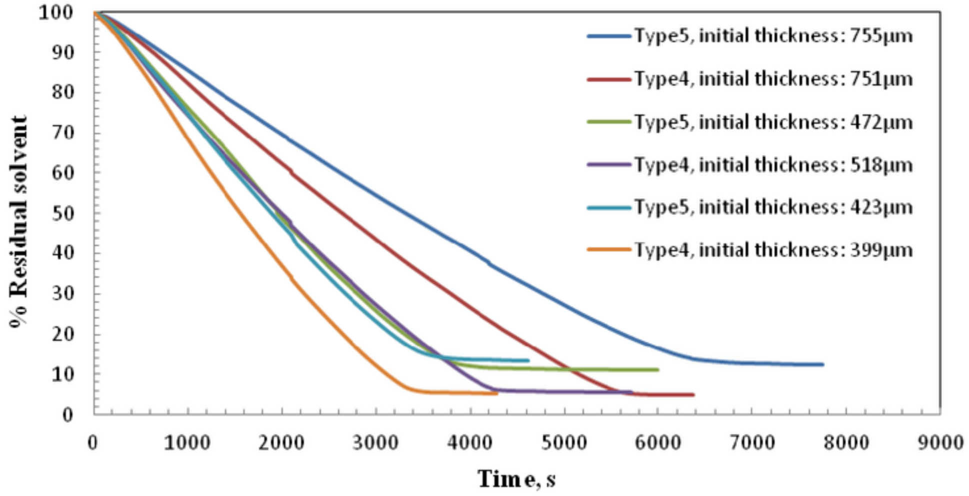

Figure 4.9: Residual solvent as a function of time in poly(styrene) – ethylbenzene system with and without crosslinked poly(styrene-co-divinylbenzene) at 25°C.

4.3.2 Coating Thickness

Figure 4.10 shows the variation of coating thickness with time. It shows that the thickness starts decreasing with time due to evaporation of ethylbenzene from the coating into surrounding. In the beginning, the thicknesses of type 4 coatings were 399 μm, 518 μm, and 751 μm respectively and decreases linearly up to 54 min 55 s, 70 min 20 s and 91 min 55 s respectively and then it plateaus off. The thickness of type 5 coatings in the beginning were 423 μm, 472 μm and 755 μm respectively and also decreases linearly up to 57 min 30 s, 60 min 40 s and 105 min 35 s respectively and then it plateaus off. The coatings having very small amount of crosslinked poly(styrene-co-divinylbenzene) (0.99%) are left thicker at the end of drying process. It is due to the more amount of ethylbenzene has been trapped in these coatings since, the poly(styrene) content in type 4 and type 5 coatings are 9.93% and 10.01% respectively. For an instance, initial coatings thickness: 399 μm and 423 μm of type 4 and type 5 solution respectively are giving the dried coating thickness of 38 μm and 85 μm respectively at the end of 71 min 15 s and 76 min 55 s.

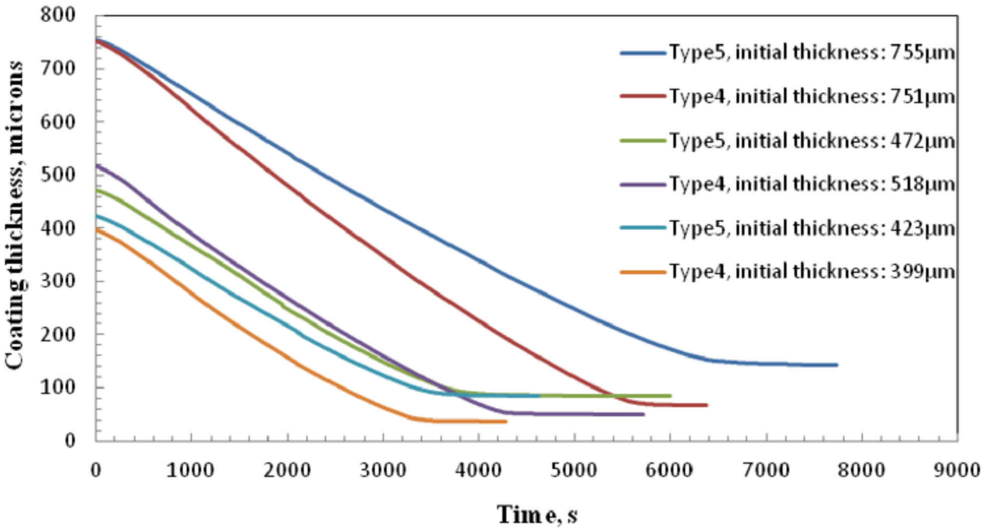

Figure 4.10: Thickness as a function of time in poly(styrene) – ethylbenzene system having crosslinked and uncrosslinked poly(styrene-co-divinylbenzene) at 25°C.

4.3.3 Average Concentration of Ethylbenzene

The average concentration of ethylbenzene with time is shown in Figure 4.11. It describes that the ethylbenzene is evaporating from the coating and its concentration start decreasing with time. In type 4, the concentration of ethylbenzene decreases exponentially up to 56 min 45 s, 72 min 25 s and 93 min 10 s in the cases of the coatings having initial thicknesses 399 µm, 518 µm, and 751 µm respectively, and then it leveled off. Type 5 coatings follows the same trend, the ethylbenzene concentration decreases exponentially at slow rate up to 49 min, 66 min 45 s and 107 min 30 s in the cases of coatings having initial thicknesses 423 µm, 472 µm, and 755 µm respectively, and then it leveled off. The final concentration of ethylbenzene in type 4 coatings were 0.476 $g.cm^{-3}$, 0.484 $g.cm^{-3}$, and 0.449 $g.cm^{-3}$, for coatings having initial concentration 0.829 $g.cm^{-3}$, 0.829 $g.cm^{-3}$and 0.829 $g.cm^{-3}$, and thicknesses 399 µm, 518 µm, and 751 µm respectively. The final concentration of ethylbenzene in type 5 coatings were 0.542 $g.cm^{-3}$, 0.500 $g.cm^{-3}$, and 0.525 $g.cm^{-3}$, for coatings having initial concentration 0.801 $g.cm^{-3}$, 0.801 $g.cm^{-3}$ and 0.801 $g.cm^{-3}$, and thicknesses 423 µm, 472 µm, and 755 µm respectively.

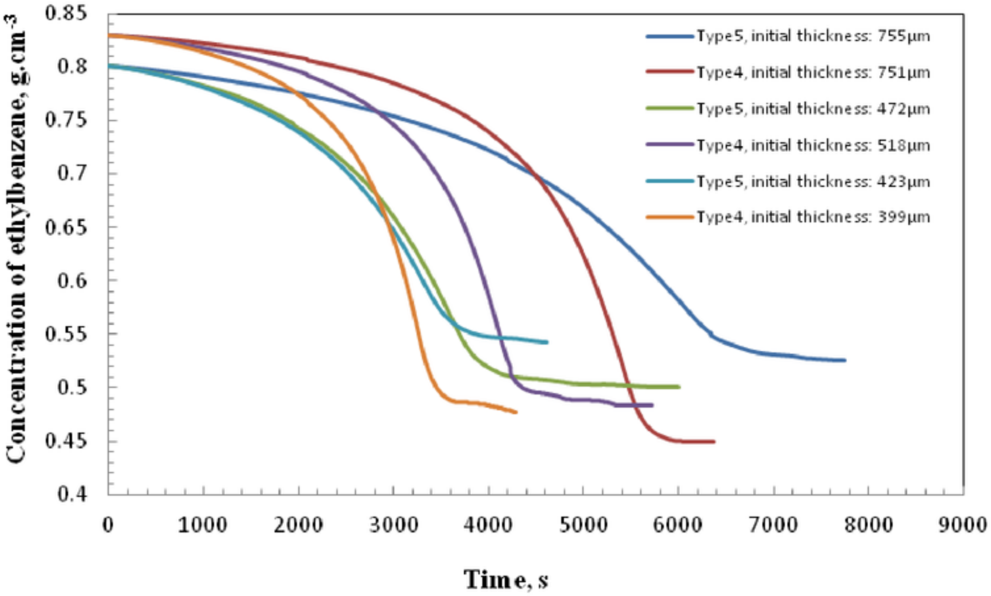

Figure 4.11: Concentration of ethyl benzene as a function of time in poly(styrene) – ethylbenzene system having crosslinked and uncrosslinked poly(styrene-co-divinyl-benzene) at 25°C.

4.3.4 Average Concentration of Polymer

Figure 4.12 depicts the average concentration of polymer (poly(styrene) and poly(styrene-co-divinylbenzene)) with time. It represents that the polymer concentration start increasing with time due evaporation of ethylbenzene from coating. In type 4, coatings the concentration of the polymer increases exponentially up to 57 min 30 s, 70 min 45 s and 94 min 50 s in the cases of coatings having initial thicknesses 399 µm, 518 µm, and 751 µm respectively, and then plateaus off. Type 5 coatings also follow the same trend, the polymer concentration increases exponentially at slow rate up to 60 min 20 s, 65 min 40 s and 109 min 30 s in the cases of coatings having initial thicknesses 423 µm, 472 µm, and 755 µm respectively, and then plateaus off. With the increase in drying time, there is increase in the concentration of the polymer due to more solvent removal from the coating.

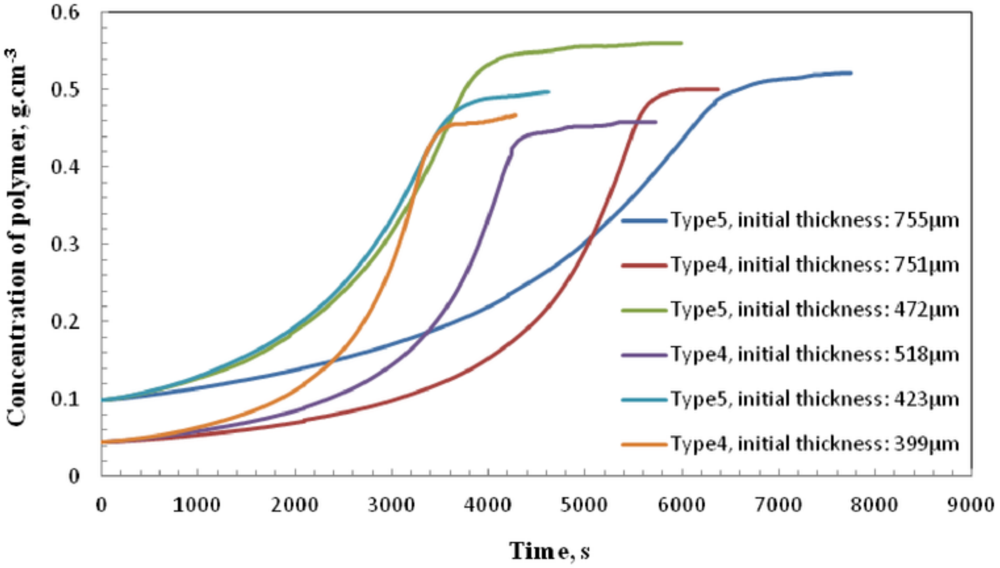

Figure 4.12: Concentration of polymer as a function of time in poly(styrene) – ethylbenzene system with and without crosslinked poly(styrene-co-divinylbenzene) at 25°C.

4.4 Drying of Poly(styrene) – ethylbenzene Coating having 2.08% Poly(styrene-co-divinylbenzene)

Two solutions of poly(styrene) one having linear poly(styrene) and the other having linear poly(styrene) and poly(styrene-co-divinylbenzene) were prepared in ethyl benzene. The ethylbenzene weight percentages were 90.07% and 87.94% respectively. These solutions are named as type 4 and type 6. Several coatings of each type have been prepared to study the effect of crosslink content on residual solvent, coating thickness, concentrations of poly(styrene) and solvent, and the drying time.

Type 4: 9.93% poly(styrene) and 90.07% ethylbenzene

Type 6: 9.98% poly(styrene), 87.94% ethylbenzene, and 2.08% poly(styrene-co-divinylbenzene)

4.4.1 Percentage of Residual Solvent

The change of residual ethylbenzene content with time is shown in Figure 4.13. It shows that the percentage of residual ethylbenzene decreasing with time. In type 4, the residual ethylbenzene linearly decreases up to 54 min 10 s, 69 min 20 s, and 95 min 45 s respectively, in the cases of coatings having initial thicknesses 399 µm, 518 µm, and 751 µm respectively. Up to 95.25%, 94.43%, and 94.61% ethylbenzene has been removed, and the remaining 4.75%, 5.57% and 5.39% ethylbenzene permanently trapped in the coatings respectively. The coatings of type 6 solutions have followed the same trend and the residual ethylbenzene is also decreasing linearly up to 48 min 39 s, 83 min 40 s, and 91 min 40 s in the cases of coatings having initial thicknesses of 361 µm, 640 µm, and 779 µm respectively. Up to 83.66%, 88.13% and 87.26% ethylbenzene has been removed, and the remaining 16.34%, 11.87% and 12.74% ethyl benzene permanently trapped in the coatings respectively. With the increase in time, the percentage of residual ethylbenzene is decreasing at extremely slow rate due to poor diffusion of ethylbenzene at later stages of drying. In the beginning, the percentage of residual ethylbenzene decreases at a very fast rate, due to fast evaporation of ethylbenzene from the top surface and huge amount of ethylbenzene was present in the coating in the beginning and drying process is externally controlled. It was observed that type 6 takes more time for drying because of the presence of nearly 2% crosslinked polymer, due to which there is very less availability of free volume and the solvent cannot diffuse easily as compared to the uncrosslinked polymer, i.e., type 4.

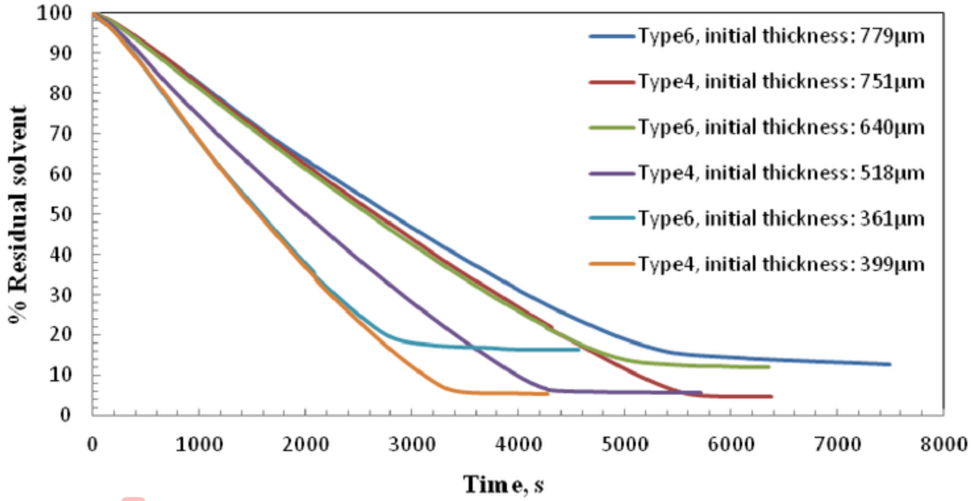

Figure 4.13: Residual solvent as a function of time in poly(styrene) – ethylbenzene system with and without crosslinked poly(styrene-co-divinylbenzene) at 25°C.

4.4.2 Coating Thickness

Figure 4.14 shows the variation of coating thickness with time. It shows that the thickness starts decreasing with time due to evaporation of ethylbenzene from the coating into surrounding. In the beginning, the thicknesses of type 4 coatings were 399 µm, 518 µm, and 751 µm respectively and decreases linearly up to 54 min 55 s, 70 min 20 s and 91 min 55 s respectively and then it plateaus off. The thickness of type 6 coatings in the beginning were 361 µm, 640 µm and 779 µm respectively and also decreases linearly up to 47 min 30 s, 80 min 10 s and 90 min 25 s respectively and then it plateaus off. The coatings having very small amount of crosslinked poly(styrene-co-divinylbenzene) (2.08%) are left thicker at the end of drying process. It is due to the more amount of ethylbenzene has been trapped in these coatings since, the poly(styrene) content in type 4 and type 6 coatings are 9.93% and 9.98% respectively. For an instance, initial coatings thickness: 399 µm and 361 µm of type 4 and type 6 solution respectively are giving the dried coating thickness of 38 µm and 84 µm respectively at the end of 71 min 15 s and 76 min 10 s.

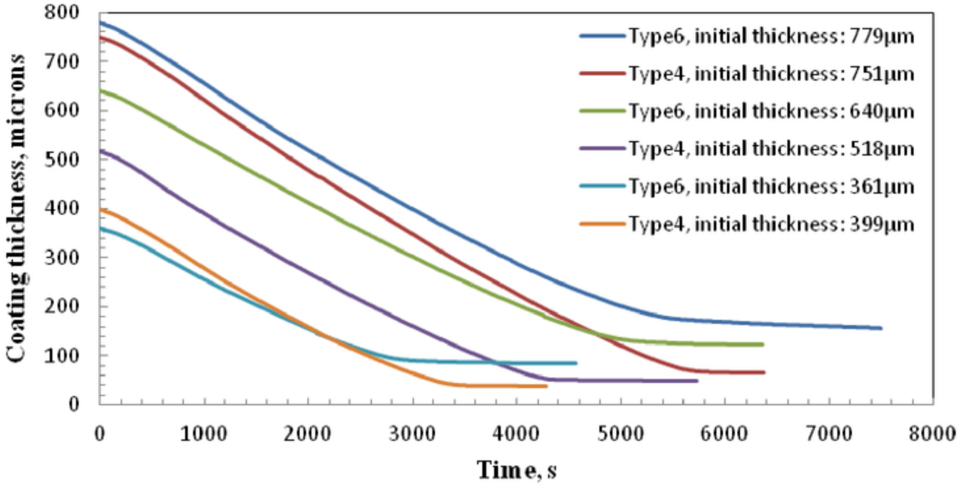

Figure 4.14: Thickness as a function of time in poly(styrene) – ethylbenzene system having crosslinked and uncrosslinked poly(styrene-co-divinylbenzene) at 25°C.

4.4.3 Average Concentration of Ethylbenzene

The average concentration of ethyl benzene with time is shown in Figure 4.15. It describes that the solvent is evaporating from the coating and its concentration start decreasing with time. In type 4, the concentration of solvent decreases exponentially up to 56 min 45 s, 72 min 25 s and 93 min 10 s in the cases of coatings having initial thicknesses 399 µm, 518 µm, and 751 µm respectively, and then it leveled off. Type 6 coatings follows the same trend, the ethylbenzene concentration decreases exponentially at slow rate up to 49 min 10 s, 85 min 25 s and 87 min 5 s in the cases of coatings having initial thicknesses 361 µm, 640 µm, and 779 µm respectively, and then it leveled off. The final concentration of ethylbenzene in type 4 coatings were 0.476 g.cm^{-3}, 0.484 g.cm^{-3}, and 0.449 g.cm^{-3}, for coatings having initial concentration 0.829 g.cm^{-3}, 0.829 g.cm^{-3}and 0.829 g.cm^{-3}, and thicknesses 399 µm, 518 µm, and 751 µm respectively. The final concentration of ethylbenzene in type 6 coatings were 0.559 g.cm^{-3}, 0.494 g.cm^{-3}, and 0.508 g.cm^{-3}, for coatings having initial concentration 0.794 g.cm^{-3}, 0.794 g.cm^{-3} and 0.794 g.cm^{-3}, and thicknesses 361 µm, 640 µm, and 779 µm respectively.

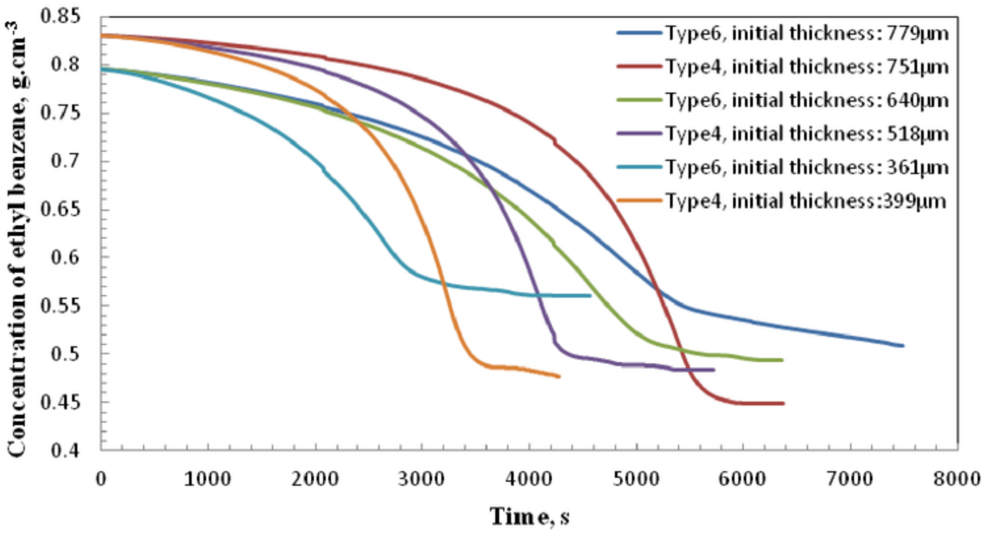

Figure 4.15: Concentration of ethylbenzene as a function of time in poly(styrene) – ethylbenzene system having crosslinked and uncrosslinked poly(styrene-co-divinyl-benzene) at 25°C.

4.4.4 Average Concentration of Polymer

Figure 4.16 depicts the average concentration of polymer (poly(styrene) and poly(styrene-co-divinylbenzene)) with time. It represents that the polymer concentration starts increasing with time due to evaporation of ethyl benzene from coating. In type 4, coatings the concentration of polymer increases exponentially up to 57 min 30 s, 70 min 45 s and 94 min 50 s in cases of coatings having initial thicknesses 399 µm, 518 µm, 751 µm respectively and then plateaus off. Type 6 coatings follows the same trend, the polymer concentration increases exponentially at slower rate up to 51 min, 86 min 15 s and 109 min 50 s in the cases of coatings having initial thicknesses 361 µm, 640 µm, and 779 µm respectively, and then plateaus off. With the increase in drying time there is increase in the concentration of the polymer due to more solvent removal from the coating.

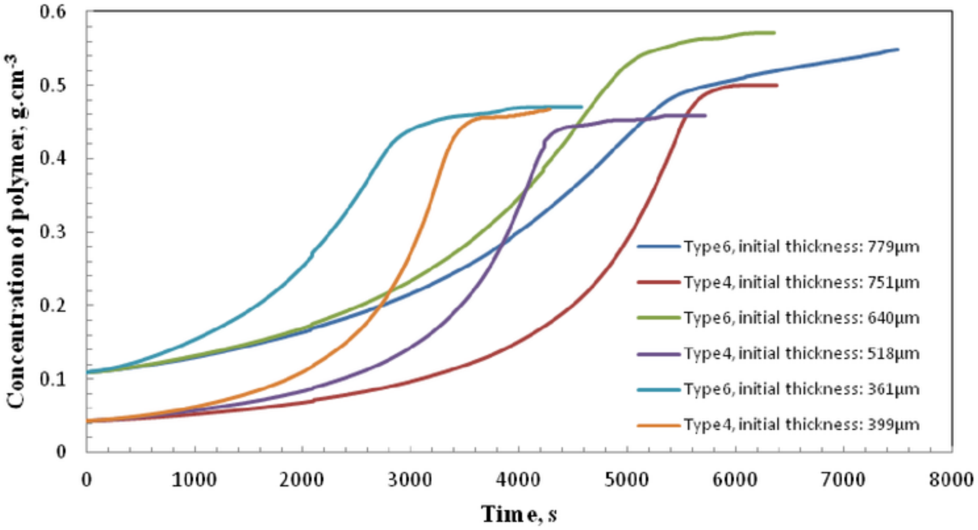

Figure 4.16: Concentration of polymer as a function of time in poly(styrene) – ethylbenzene system with and without crosslinked poly(styrene-co-divinylbenzene) at 25°C.

4.5 Surface Morphology

The surface morphology of different types of polymer coatings was assessed by scanning electron microscopy (SEM), (Hitachi S-3400N), the microscope was attached to a secondary electrons (SE) detector. The images were obtained using an accelerating voltage of 30 KV.

Figure 4.17 below shows the surface morphology of different types of polymeric coatings

(A) A polymer coating of 2.01% poly(styrene-co-divinylbenzene), 10.07% polystyrene and 87.92% *p*-xylene (initial thickness: 799 µm)

(B) A polymer coating of 2.08% poly(styrene-co-divinylbenzene), 9.98% polystyrene and 87.94% ethylbenzene (initial thickness: 779 µm)

(C) A polymer coating of 0.98% poly(styrene-co-divinylbenzene), 9.94% polystyrene and 89.08% *p*-xylene (initial thickness: 752 µm)

(D) A polymer coating of 2.08% poly(styrene-co-divinylbenzene), 9.98% polystyrene and 87.94% ethylbenzene (initial thickness: 1044 µm)

(E) A polymer coating of 0.99% poly(styrene-co-divinylbenzene), 10.01% polystyrene and 89% ethylbenzene (initial thickness: 1009 µm)

(F) A polymer coating of 2.01% poly(styrene-co-divinylbenzene), 10.07% polystyrene and 87.92% *p*-xylene (initial thickness: 683 µm)

(G) A polymer coating of 0.98% poly(styrene-co-divinylbenzene), 9.94% polystyrene and 89.08% *p*-xylene (initial thickness:872 µm)

(H) A polymer coating of 0.99% poly(styrene-co-divinylbenzene), 10.01% polystyrene and 89% ethylbenzene(initial thickness: 755 µm)

(I) poly(styrene-co-divinylbenzene).

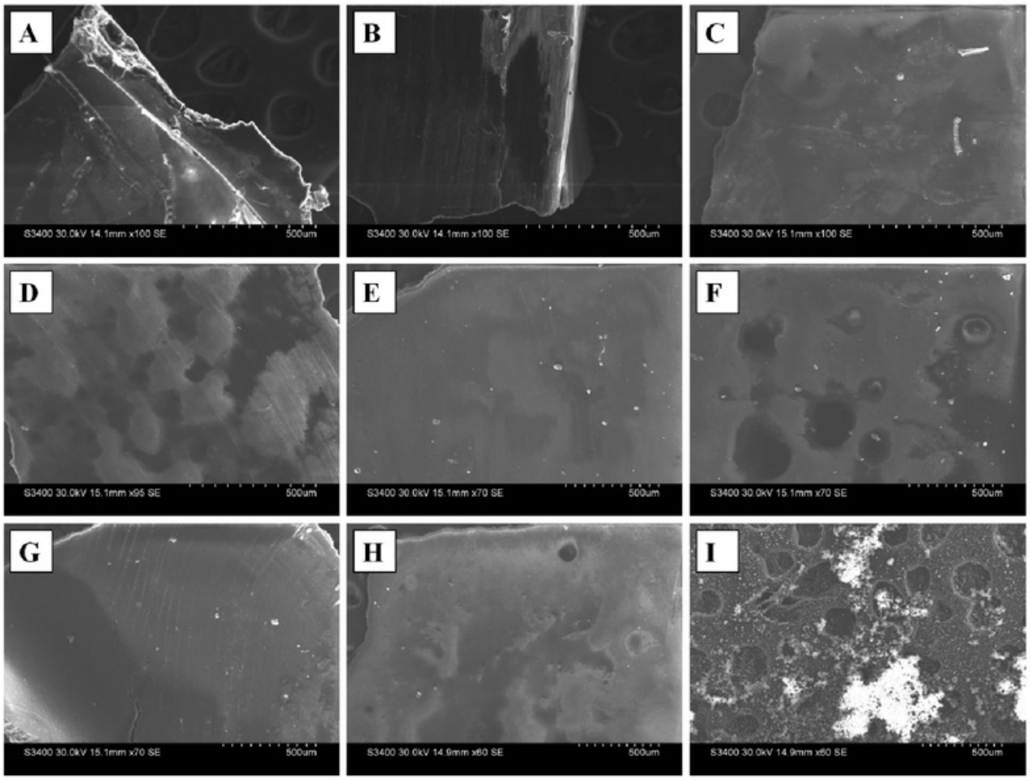

Figure 4.17: SEM images of different types of polymeric coatings.

Figure 4.17 shows the surface morphology of the polymer coatings and exhibits whether the crosslinked particle is uniformly distributed in the polymer coating or not. In (A), the crosslinked particles uniformly distributed in coatings and however the particle density near the edges of the coating is high as compared to the center of the coating and particles are arranging themselves in rod like shape, their typical sizes are 300 μm, 188 μm and 125 μm. In (B), the crosslinked particles are not uniformly distributed in the polymer coating. There are some blank patches and the particles are spherical in shape and their sizes are 62 μm and 25 μm. In (C), the crosslinked particles are uniformly distributed in the polymer coating and the particles are spherical and rods like in shape, their sizes are 19 μm, 119 μm and 125 μm. In (D) the crosslinked particles are not uniformly distributed in the polymer coating, and there are certain blank patches the particles are spherical in shape, and their size are 125 μm, 150 μm and 188 μm. In (E), the crosslinked particles are uniformly distributed in the polymer coatings and the particles are spherical, rectangle and rod like in shape, their sizes are 42 μm, 34 μm and 84 μm. In (F), the crosslinked particles are not uniformly distributed in the polymer coating. There are some hole formation in the coating and the particles are spherical and rod like in shape, their sizes is 42 μm and 34 μm. In (G), the crosslinked particles are uniformly distributed in the polymer coating, but there is a crack in the coating and the particles are spherical in shape of size 34 μm. In (H), the crosslinked particles are uniformly distributed in the polymer coating but there is a black hole in the film and the particles are spherical in shape of size 20 μm. In (I), poly(styrene-co-divinylbenzene) particles are tightly bound with each other but there are some hole, in which very small sized particles are distributed in these holes and the particles are spherical in shape, of size 40 μm.

The holes could be due to the presence of uncrosslinked polymer and these holes disappeared in case of low percentage of crosslink content in the coating because uncrosslinked content may get swelled due the presence of solvent which is observed in Figure 4.17 C, F, and G and these coating have 0.98% poly(styrene-co-divinylbenzene), 9.94% polystyrene and 89.08% *p*-xylene (initial thickness: 752 μm), 2.01% poly(styrene-co-divinylbenzene), 10.07% polystyrene and 87.92% *p*-xylene (initial thickness: 683 μm), and 0.98% poly(styrene-co-divinylbenzene), 9.94% polystyrene and 89.08% *p*-

xylene (initial thickness:872 µm). Some dustering effect has been observed in Figure 4.17 D and these coating having 2.08% poly(styrene-co-divinylbenzene), 9.98% polystyrene and 87.94% ethylbenzene (initial thickness: 1044 µm). The crosslinked particles are getting settled to the edges of coating as can be seen in Figure 4.17 A and these coating having 2.01% poly(styrene-co-divinylbenzene), 10.07% polystyrene and 87.92% *p*-xylene (initial thickness: 799 µm).

Table 4.1 Residual solvent summarized in various coating studied.

Poly(styrene)	**Solvent**	**Crosslinked poly(styrene-co-divinylbenzene)**	**Initial coating thickness, µm**	**Final coating thickness, µm**	**% Residual solvent**
9.94%	89.08% *p*-xylene	0.98%	387	58	8.07
			566	92	9.55
			752	132	10.98
10.07%	87.92% *p*-xylene	2.01%	331	59	10.44
			603	118	12.38
			683	134	12.40
10.01	89% ethylbenzene	0.99%	423	85	13.50
			472	84	11.04
			755	144	12.45
9.98%	87.94% ethylbenzene	2.08%	361	84	16.34
			640	123	11.87
			779	154	12.74

Rate of residual solvent removal slows down with time, due to shifting of mass transfer process. In the beginning, the mass transfer process was the evaporation of the solvent which shifts to the diffusion controlled latter only. The solvent self-diffusion coefficient is strongly dependent on solvent mass fraction [54, 55]. Since the diffusion coefficient in polymer solvent system is also very strong function of free volume available for diffusion[54, 55]. It is observed that crosslinked coatings takes more time for drying, due to slow diffusion coefficient in polymer – solvent system and the presence of crosslinked polymer will significantly affect the diffusion coefficient value to a larger extent [46]. Residual solvent left in the coatings having ethylbenzene solvent is higher as compared to the coatings having *p*-xylene for both systems of crosslinked and uncrosslinked polymers. This could be due to change in polymer solution thermodynamic due to interaction of polymer and solvent.

Chapter 5

Conclusions and Future Scope

The results show that diffusion in crosslinked polymer is extremely slow and very negligible amount of solvent has been penetrated into the core of crosslinked polymer. This is proved by the SEM analysis which shows the particles of crosslinked polymer in a regular shape i.e. rod like or spherical. The distribution of crosslinked particles was also not uniformed in most of the cases except case having ethylbenzene as solvent i.e. H, E, and D. It may be because swelling of crosslinked particles due to high rate of penetration of ethylbenzene as compared to *p*-xylene. It may also be due to high dispersion of swelled crosslinked particles which may be forming a thin layer of themselves. Residual solvent data shows that coatings having crosslinked polymer are taking slightly more time as compared to coatings having linear polymer and retaining very high amount of solvent content. Residual solvent left in the coatings having ethylbenzene solvent is higher as compared to the coatings having *p*-xylene for both systems of crosslinked and uncrosslinked polymers. This could be due to change in polymer solution thermodynamic due to interaction of polymer and solvent.

In future, several other polymer- solvent system can be studied to validated the result obtained in this work. The NMR study can be performed to study the solvent diffusion in crosslinked polymer. The polymer solution can be crosslinked during the course of drying to study the effect of crossslinking on solvent diffusion in crosslinked polymer -solvent coatings. The depth profile study can be performed to study the concentration profile in the coating during the course of drying and at the end of drying.

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