SURFACTANT ENHANCED DRYING OF WATERBASED POLYMERIC COATINGS

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by

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Certificate

This is to certify that the dissertation work entitled "**SURFACTANT ENHANCED DRYING OF WATER BASED POLYMERIC COATINGS**" submitted by **Daisy Sharma (Roll. No. 301502010)** in partial fulfillment for the award of degree of Master of Science in Chemistry 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.

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Declaration

I hereby declare that the work being presented in the dissertation report entitled **"SURFACTANT ENHANCED DRYING OF WATER BASED POLYMERIC COATINGS"** by me in the partial fulfillment of the requirements for the award of degree of Master of Science 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.

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Abstract

Coatings of poly(vinyl alcohol)-water based system have been studied. Different types of ionic, non ionic and fluoro based surfactants were used. The effect of surfactant on drying behavior of coatings was studied. Ionic surfactant could not change the drying mechanism of the coatings. Whereas in non ionic surfactant changed to the drying behavior to a small extent. The significant change was observed in fluoro based surfactant. The drying rate in fluoro based surfactant was moderate for a longer time which then caused the more solvent recovery. Different solution of polymer concentration needs different amount of surfactant for significant change in drying behavior.

Keywords: waterbased coatings, surfactant enhanced drying, thin films, polymeric coatings.

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Chapter 1

Introduction

Polymeric coatings have become a major part of various industries. The different types of polymeric coatings are used in textile industry, electronic industry, automobile industry, food industry and many more [1-3]. The main purpose of polymer coatings is to increase the life span of the material or surface, protecting it from moisture, cracks and basically act as a shield.

1.1 Classification and Preparation of Polymeric Coatings

Polymer systems are generalised in two parts binary or multi-component polymeric systems. Polymeric coatings are prepared by using solvent or without solvents. They are being used as protective colloid, in corrosion protection, ink-jet printing technologies, LCD-panels, edible polymeric coatings and medical test strips [4].

Polymer coatings are prepared by using various techniques. Spin casting, solution casting, thermal spraying, dip casting and drop casting. The easiest and simplest method for the preparation of coatings is solvent casting technique especially in academic area. Solvent casting technique is unique technique for a blister free and uniform polymeric coating. It involves the formation of a homogeneous solution of polymer and solvent. The benefits of this technique are described below

- It can be processed at low temperature, beneficial for polymer coatings which are thermally active or which contain active ingredients sensitive to temperature.
- Easy addition of fillers and additives.
- Ability for production of high-temperature resistant films from non-thermoplastic but raw materials.
- Wider range of choice of materials, any solvent based coatings can be used either solvent or aqueous.

1.2 Drying of Polymeric Coatings

Several methods are used for drying of coatings such as thermal drying, condensation drying and controlled drying. The drying mechanism is explained on various levels of different component system. Controlling the drying conditions are maintaining to get good quality of polymeric coatings. Many researchers are working on reducing the residual solvent percentage to least amount because it gives defect free polymeric coatings. Residual solvent is the amount of solvent that is left in the dried polymeric coating which then diffuses into the coating at the later stage. Solvent transport in coatings is explained using free volume theory given by Vrentas and Duda [5, 6] in combination with Flory-Huggins theory of polymer solution thermodynamics. This theory speculates the drying behaviour of coatings which has been prepared by use of high volatile solvents. The observed drying rates are in accordance with predictions of model [7, 8] in case of high volatile solvents. However, for low volatile solvents the experimental results are not in such agreement with the model [8]. Price Jr and Cairncross [9] mathematically optimized the drying conditions in single zone dryers. A detailed drying model with automatic optimization is used to find optimal drying conditions to avoid the defects and minimize the residual solvent.

1.3 Green coatings

In industrial area, a huge of amount of organic solvents is used in the preparation of polymeric coatings which is not at all environmental friendly. Organic solvent damage nature and can end up being toxic. In present work, double distilled water is used as a solvent in the synthesis of polymeric coatings using PVA. These coatings can also be termed as green coatings due to their environment free nature. Many industries have been paying attention to the importance of green coatings because they do not cause pollution and they are cost effective. In water based coatings, the drying time is usually higher as compared to organic solvent based coatings because organic solvents are more volatile than water. Slow drying rate requires high energy for very long drying time of coatings which eventually needs higher amount of energy.

1.4 Surfactant in Polymeric Coatings

The introduction of a third component into a binary solution has shown promising results and enhancement in drying of the polymer solution by changing the solution structure at molecular level [10]. Now a days, Polymer-surfactant systems are high interest of the research because of their interactions, drying rate, film formation, wetting performances and other applications [11]. The surfactant plays a crucial role in drying and levelling of polymeric coatings [12]. Even a small amount of surfactant brings about an appreciable change in the polymeric films. The polymer/surfactant system in which the pairs are of opposite charges have been of special interest [13]. There are mainly three forces which are present in the polymer/surfactant system: hydrophobic, dipole-ion interactions, and strong columbic forces. The same charge polymer/surfactant has feeble association where as if they are of opposite charges they have strong electrical interaction. Hydrophobicity of the polymer can be a ruling factor in case opposite charges polymer/surfactant system [14]. The reactivity of the system is controlled by many factors. The surface tension of these systems has been studied a lot in order to reduce the surface tension of the solution and levelling effect. The surfactant head group determines surfactant properties and classification. The critical aggregation number (cac)/critical micelle aggregation (cmc) tells a lot about the binding of polymer to the surfactant. Below this critical micellation number, association is promoted and above this value there is found to a decrease in total aggregation number [12].

In spite of that it has essential properties to prevent coagulation, particle aggregation and foremost reducing the surface tension leading to reduction of residual solvent [15].

As described above surfactant based coatings are said to better than other type of coatings because of their drying characteristics.

1.5 Dissertation outlines

This thesis has been arranged as following:

Chapter 1: A brief introduction about the classification and preparation of coatings, use of surfactant, drying of polymeric coatings and green coatings is given in this chapter

Chapter 2: A detailed literature review regarding interactions of surfactant and polymer, drying of polymeric coatings, diffusion in polymeric coatings and research gap is given here.

Chapter 3: Methodology and materials used are given.

Chapter 4: Comparison between drying study of different coatings is given in this chapter.

Chapter 5: Conclusion and further scope of study is

Chapter 2

Literature Review

In this chapter, recent literature related to the residual solvent study in coatings has been reviewed. The literature review has been divided into following parts: interaction between surfactant and polymer, drying of polymeric coatings and other properties.

2.1 Interaction of surfactant and polymer

Anthony et al. [12] studied the interaction between two polymers and a surfactant which are, PS1: poly(maleic acid -*co*- methyl vinyl ether), PS4: poly(maleic acid -*co*- ethyl vinyl ether) and DTAC (dodecyltrimethylammonium chloride) respectively. The interactions are affected by the hydrophobicity of polymer. The aggregate number of polymer bounds was found to be independent of the bound surfactant concentration. The binding of surfactant with polyelectrolyte was found to be cooperative and further adding cooperative binding of PS1 with surfactant was in range $0<\alpha<1$ and for PS4 was $0.5<\alpha<1$. The difference in interaction is because of the hydrophobicity of PS4 with surfactant molecules whereas in PS1, surfactant operates through short range electrostatic interaction and the polymer is less hydrophobic. The polymer bound aggregates have larger fluorescence lifetime of pyrene and higher viscosity as compared to the polymer which are free of surfactant micelles. It is probably because of the binding of polymer and surfactant ion and also the tight binding of polymer-surfactant charged ion groups and polymer main chain. The surfactant counter ions were excluded from the surface of aggregate because of the binding.

Balaza et al. [16] studied the interaction of surfactant in dilute solutions as function of surfactant concentration. A critical surfactant concentration is required for surfactant – polymer interaction. Lower than this value, the addition of surfactant enhances the solution viscosity due to aggregation. Higher than this value, adding up surfactant causes stearic hindrance in the association leading to low aggregation number and viscosity from its optimal value. They used an algorithm similar to diffusion-limited aggregation (DLA) for simulation study. This shows that increasing

the surfactant by small fractions increases the average functionality because it exposes the end of polymer which is otherwise used in loops. As amount of surfactant (mono-functional units) is increased the average functionality decreases which in turn decreases the aggregation number. They used Carothers equations as given below

$$X_n = (1 - f_{avg})^{-1} \quad (1)$$

Where f_{avg} : average monomer functionality and X_n : degree of polymerization.

Meconi et al. [15] studied the adsorption and desorption of ionic and non-ionic surfactants on polymer surfaces. The surfactants used were sodium dodecyl sulphate (SDS) and polyethylene glycol-polyethylene block copolymer (PEG-PE) respectively. At low surfactant concentrations, non-ionic surfactants had higher adsorbing power, higher attractive forces, and lesser stability at the surface as compared to ionic surfactants and further adding they do not alter the final product significantly. Physio-chemical properties of head parts are responsible for this difference. Ionic surfactant formed a self-assembled structure while non-ionic formed a disordered layer as they had hydrophilic head groups which weaken the interaction with water molecules in aqueous medium. The reduction in surface tension relative to chemical potential change of surfactant was measured by Gibbs adsorption theorem as given by

$$\frac{d\gamma}{d\mu_{\text{surfactant}}} = -\Gamma \quad (2)$$

Where, $d\gamma$ = change in surface tension, $d\mu_{\text{surfactant}}$ = change in chemical potential and

Γ = surfactants molecules per unit area.

Ruckenstein et al. [17] studied about the aggregation of surfactants in presence of polymers. The surfactants used were SDS, dodecyltrimethylammonium chloride (DTAC) and triton X-100 in presence of polyethylene oxide. The changes of interfacial free energy between polymer and surfactant molecules, bound aggregates and microenvironment were calculated by developed model. Very small amount of surfactant headgroup was able to decrease overall surface energy and hence better aggregation. However, no micelle formation was observed in case of large headgroup surfactant due to enhancement in interfacial energy between microenvironment and micelles. In this case, the micelle bound to macromolecule form at a concentration below cmc of free micelles. On the other hand, if the headgroup is large the overall

interfacial energy increases between microenvironment and micelles leading to no micelle formation. This explained the fact that surfactant with smaller head trigger the formation of bound micelles and large headgroups do not stimulate the formation.

2.2 Drying of Polymeric Coatings

Kajiya et al. [10] studied the drying of the polymer solution droplets using small amounts of surfactant. They found that on adding small amount of surfactants, the polymer film become levelled instead of taking a concave shape. The polymer solution of monodispersed polystyrene was used in this work. The surfactants used were fluorosurfactant F470 and F489 which are oligomers with perfluoroalkyl hydrophobic and lipophobic groups. The main use of surfactant was to lower the surface tension of the polymer liquid which also affected the contact angle. They observed that without the surfactant, most of the polymer was found at the edge; there was ringlike profile formation. On the other side, while they added surfactants, the polymer instead of edge was at the centre and polymer film was flatter. The Marangoni force required was very small to restrain the outward flow. This behaviour was seen in some other cases too where the polymer concentration was very high. They found that a very small quantity of surfactant can cause levelling effect and enhanced the drying process.

Okazaki et al. [18] studied the drying mechanism of coated films of poly(vinyl alcohol) films. They focused on the diffusion process of water and the shrinkage of volume of the film. They measured the diffusion coefficients over a period of time using different methods like drying the film using hot air. Numerical solutions were obtained using transport equations for water and were compared with experimental results. The dependency of diffusion coefficient on concentration, dependency of equilibrium vapour pressure of water on concentration and effect of shrinking in the volume followed due to evaporation of water were considered to simulate the drying process of coated PVA film. The mutual diffusion was measured for low, intermediate and high concentration of PVA. The experimental and calculated results show that diffusion coefficient is a reliable factor between both results. They used Boltzmann's equation for calculating diffusion constant D as a function of concentration.

$$D = -\frac{1}{2t}\left(\frac{d_z}{d\Omega}\right)\int_0^{\Omega} z\,d\Omega \tag{3}$$

Cairncross et al. [19] studied the residual solvent in polymeric coatings. At constant temperature, they found that the rate of drying continuously falls and drops to zero and residual solvent plateaus. Their drying model predicted the dependency of residual solvent on temperature, diffusion properties and concentration of solution. There are different drying periods which shows the trend in residual solvent behaviour, drying rate, and temperature. In these periods the drying rapidly increases whereas the rate of drying is constrained by diffusion mass transport by keeping the uniform solvent concentration throughout the coating. Moving to other rate period, drying is diffusion controlled and drying rate approaches zero. Eventually, the rate of drying approached to zero which was termed as diffusional plateau and considerable amount of solvent left in the coating. The final residual solvent is controlled by the internal diffusion resistance to mass transfer in dried polymer coating.

Yamamura et al. [20] studied the effect of fluorosurfactant on drying of solvent of liquid film coatings . The use of fluorosurfactant has shown 10% increase in solvent evaporation within a certain range. They used CAB (Cellulose acetate butyrate) and MEK (methyl ethyl ketone) solution and a fluorine based surfactant. Continuous weighing showed that drying rates were initially increased and then afterwards decreased with increase in surfactant mass fraction. The enhanced solvent drying is ascribed to diffusion coefficient increasing rather than variation in vapour pressure.

Gu et al. [21] studied the drying of aqueous surfactant solutions. The block copolymers Pluronic F127 and Pluronic L64 were used. They studied equilibrium adsorption isotherm, surface evaporation, internal diffusion, degree of hydration and self assembled structure. It was observed that initially percentage of water loss was linearly increasing with drying time and then nonlinearly coming to a plateau. The drying rate was affected by relative humidity (RH), surface evaporation and nanostructure of polymer. Drying rate was relatively constant for all polymers and it changes differently for different polymer. Hydration levels of pluronic hydrogels played an important role in drying of solution rather than the self-assembled nanostructure.

2.3 Diffusion in Polymeric Coatings

Muller et al. [22] studied diffusion in thin films. They used non-volatile moieties as penetrant in thin films. The experiment showed that drying conditions were affecting the formation of non-volatile compound. It was distributed inhomogenously in the final step and influencing the required product. They observed the mobility of additive and concentration dependent diffusion coefficient using Infrared-Micro-Raman-Spectroscopy (IMRA). They analysed a multi-component system containing a polymer (cellulosetriacetate (TAC) for LCD-panel foils), a non-volatile component (triphenylphosphate (TPP) used as plasticizer) and methylenchlorid (MeCl) used as solvent. They noticed the formation of a distinctive layer because of inhomogeneous distribution of polymer and additive. They used the 'Two layer experiment': one consisted of a mixture of solvent, polymer, and non-volatile additive and second one with polymer, solvent only. The layers were put on the two thin glass plates and joined together. Diffusion of additive equalized the additive concentration gradient after the layers were in contact. The process of equalization was a function of time and with decrease in solvent loading there was significant increase of equilibrium-time. There was a thin film formation in case of slow loading of solvent. Slow loading is the only limitation of this procedure. To overcome this, other setup was used in which solvent partial on coating-air interface was used to check loading of solvent in the two layers.

Muller et al. [4] studied the effect of non-volatile plasticizer on solvent diffusion in polymers coatings. The drying curves were affected when the solvent loading was too slow and then plasticizer loading played the important role. The solvent having high plasticizer loading had higher drying rate. The solvent diffusion coefficient increased with the high amount of plasticizer loading which in turn decreased the drying time of polymers coatings. They used triphenylphsosphat (TPP), methylenchlorid (MeCl) and poly(vinyl acetate) (PVAc) as non-volatile plasticizer, solvent and polymers respectively. The small quantity of plasticizer had significant effect on the mutual diffusion coefficient. The accelerating effect of plasticizer was then observed for the description of drying curves of such solvent system. They used changed the plasticizer loading from 0 to 0.15 g_{TPP} / g_{PVAc} with an increment of 0.05. The initial solvent loading in each experiment was $X_{MeCl} = 0.9 g_{TPP} / g_{PVAc}$, with a

polymer coating of thickness 115µm keeping and other drying conditions were kept same. The drying curves were almost identical till the solvent loading of $X_{MeCl} = 0.2 g_{MeCl} / g_{PVAc}$ because the drying rate was controlled by gas phase transport resistance and not by solvent loading. With the solvent loading less than $X_{MeCl} = 0.2 g_{MeCl} / g_{PVAc}$ the drying rate was limited due to solvent diffusion. The solvent with high TPP had the highest drying rate and with no TPP had lowest. The diffusion coefficient became the function of plasticizer and solvent loadings and is given by

$$D = \exp\left(\frac{a + b.X_1}{1 + c.X_1}\right)\left[m^2.s^{-1}\right] \quad (4)$$

Where D= mutual diffusion coefficient, X_1= solvent loading in $g_{solvent} / g_{TPP}$ and a, b, and c are parameters that had to be fitted to experimental data

Ravichandran et al. [23] used ultrasonic method to study the thermo acoustical properties of sodium dodecyl sulphate (SDS) in poly(vinyl alcohol) (PVA) solution. They measured density, viscosity and ultrasonic velocity over a range of composition. The factors increased linearly with the concentration of 0.25N surfactant at 2% PVA solution up to a certain value. A sudden decrease of velocity was seen at a particular concentration in both solutions, disconnection was velocity indicated critical micelle concentration. At low concentration, the solutions remained clear but as the concentration of surfactant increased, they were no longer clear. The increment in sodium dodecyl sulphate decreased ultrasonic velocity in 0.5N solution due to high hydrophobic nature of SDS and hydrophilic parts at higher concentration which form micelle rods.

Table 1 to 2 show residual solvent in various types of coatings: Single layer, multilayer, multi-component and binary coatings. Some amount of solvent has been left in all coatings and its percentage varies from system to system and the type of coating mechanism used. The residual solvent left in single layer was much lesser as compared of multilayer to get nearly same dried thickness. The residual solvent in layer by layer multilayer was much higher than simultaneous multilayer. Residual solvent was also dependent on the system order being coated. The coatings having on the system order being coated. The coatings having polymer of high glass transition

temperature retained much solvent when it was coated on the top as an be solvent when it was coated on the top as can be seen in PMMA-THF (top) and PS-THF (bottom) system in Table 1. PVAc-toluene coating retained 5-13% toluene even if they were dried at 70ºC as can be seen in Table 2.

Table 1. Residual solvent in multilayer polymeric coatings[24].

S. No.	Top Layer	Bottom Layer	Coating Technique	% Residual Solvent
1	Poly(methyl methacrylate)(10.14%)–Tetrahydrofuran(89.86%)	Poly(styrene)(10.07%)- Tetrahydrofuran (89.93%)	Layer by Layer	12.79
2	Poly(styrene)(5%) – Tetrahydrofuran (95%)	Poly(methyl methacrylate)((10.14%)-Tetrahydrofuran (89.86%)	Layer by Layer	14.60
3	Poly(styrene)(10.07%)– Tetrahydrofuran (89.93%)	Poly(methyl methacrylate)(10.14%)–Tetrahydrofuran (89.86%)	Layer by Layer	11.07
4	Poly(styrene)(15.13%)– Tetrahydrofuran (84.87%)	Poly(methyl methacrylate)((10.14%)–Tetrahydrofuran (89.86%)	Layer by Layer	17.18
5	Poly(methyl methacrylate)(10.14%)–Tetrahydrofuran (89.86%)	Poly(styrene)(5%) – Tetrahydrofuran (95%)	Layer by Layer	16.79
6	Poly(methyl methacrylate)(10.14%)–Tetrahydrofuran (89.86%)	Poly(styrene)(15.13%)– Tetrahydrofuran (84.87%)	Layer by Layer	18.28
7	Poly(styrene)(15.13%)– Tetrahydrofuran (84.87%)	Poly(methyl methacrylate)(10.14%)–Tetrahydrofuran (89.86%)	Simultaneous	18.52
8	Poly(methyl methacrylate)(10.14%)–Tetrahydrofuran (89.86%)	Poly(styrene)(5%) – Tetrahydrofuran (95%)	Simultaneous	6.50
9	Poly(methyl methacrylate)(10.14%)–Tetrahydrofuran (89.86%)	Poly(styrene)(15.13%)– Tetrahydrofuran (84.87%)	Simultaneous	14.8
10	Poly(styrene)(5%)– Tetrahydrofuran (95%)	Poly(methyl methacrylate)(10.14%)–Tetrahydrofuran (89.86%)	Simultaneous	5.80
11	Poly(methyl methacrylate)(10.14%)–Tetrahydrofuran (89.86%)	Poly(styrene)(10.07%)– Tetrahydrofuran (89.93%)	Simultaneous	8.84

Table 2. Residual Solvent left in polymeric coatings.

S. No.	Coatings Method	Coating Composition	Initial Thickness, μm	Ultimate Thickness, μm	% Residual Solvent	Drying Time, s	Reference(s)
1.	Single Layer	PVAc: 30%–toluene:70% at 118°C	----	----	5.44	30	[9, 25]
2.	Layer by layer	PS:9.75% - *p*-xylene: 90.25% at 32°C	563	218	15.44	6480	[26]
3.	Layer by layer	PS:5.01% - THF: 94.99% at 32°C	533 each	120	9.98	2260	[26]
4.	Single Layer	PS:5.01% - THF: 94.99% at 32°C	1010	61	1.88	3240	[26]
5.	Single Layer	PVAc: 10%–toluene:90% at 40°C	-----	-----	10.60	5000	[19]
6.	Single Layer	Cellulose Acetate: 17.2%–Acetone:82.8% at 70°C	----	-----	3.17	100	[27]
7.	Layer by layer	PS:10.06% - THF: 89.94% at 32°C	525 each	229	19.71	3240	[26]
8.	Single Layer	PS:10.06% -THF: 89.94% at 32°C	1327	174	4.92	3472	[26]
9.	Single Layer	PVAc : 10%–toluene:90% at 100°C	-----	-----	2.38	5000	[19]
10.	Single Layer	PS:15.14% -THF: 84.86% at 32°C	1891	409	9.78	7144	[26]
11.	Single Layer	PVAc: 30%–toluene:70% at 120°C	135.29		1.716		[28]
12.	Single Layer	PVAc: 30%–toluene:70% at 118°C	----	----	5.44	30	[9, 25]
13.	Single Layer	Cellulose Acetate: 17.2%–Acetone:82.8% at 70°C	----	-----	3.17	100	[27]

2.4 Research gap

- In the earlier literature [4, 10, 12, 15-18, 20, 21, 23] mainly interactions of different polymers and surfactant have been studied and analyzed. Drying mechanism of polymer coating using a surfactant has caught less attention.
- Few researches [4, 22] have used plasticizer such as TPP and fluorine based surfactant to study the effect on the mutual diffusion coefficients, drying rate, levelling effect of polymer/surfactant solution. The results showed an enhancement in drying rate by almost 10-15%.
- Fluorine based surfactants has been studied by few researches [10, 20] in organic solvents and study has been referred in water based coatings.
- Table 1 and 2 listed above show that there is always a certain amount of residual solvent left in the polymeric coatings.
- In this work, application of various surfactants on residual solvent content in water based polymeric coatings has been studied. In this work water soluble anionic, non ionic and fluorosurfactant has been used to study the effect caused by them on the polymer coating. PVA-water system has been selected to study surfactant effect on drying behaviour

2.5 Objectives

i. To reduce the amount of residual solvent present in water base polymeric coatings: PVA-water system.
ii. To find the suitable surfactant for water based polymers.
iii. To find the optimum amount of surfactant to be used for maximum solvent recovery.

Chapter 3

Materials and methods

3.1 Chemicals used

Poly(vinyl alcohol) (PVA) was provided by Lobachemie, India (density: 1.19g cm^{-3}, molecular weight: 115,000), poly(ethylene glycol) 6000 (PEG 6000) was provided by Spectrochem, India (density: 1.08g cm^{-3}, molecular weight: 5000-7000), Sodium dodecyl sulphate (SDS) was provided by SD Fine Chemicals, India (density: 1.01g cm^{-3}, molecular weight: 238.33). The solvent used was double distilled water (DD water), fluorosurfactant CAPSTONE FS-63 (35% solids, 20% isopropyl alcohol and 45% water) was provided by Rishichem distributors Pvt. Ltd, India (density: 1.1g cm^{-3}).

3.2 Methodology

The polymeric coatings are prepared using solution casting technique. The solutions were prepared by using above chemicals in different weight percentage. The weighed chemicals were poured in reagent bottles. Afterwards, the bottles were kept in digital water bath (LWB 311D, Daihan Labtech India Pvt. Ltd., India) at a temperature of 95ºC to dissolve PVA. After complete dissolution of PVA the bottles were kept for shaking in a mechanical shaker for 4 hours. The solutions were left overnight. Known amount of solution was poured into the sample holder to get the desired initial coating thickness. The schematic representation of the process is given below in Figure 3.1. In this work, the coatings of poly(vinyl alcohol) and poly(ethylene glycol)6000, poly(vinyl alcohol) and sodium dodecyl sulphate and poly(vinyl alcohol) and CAPSTONE FS-63 were dissolved in double distilled water.

Several solutions were prepared having different polymer mass fractions. The polymer mass fractions were kept 5% and 10% respectively. In all solution, the surfactant mass fractions were also kept same but their type has been changed. Only one surfactant was used at a time.

Solution 1: PVA (polymer): 5.00%, DD water (solvent): 95.00%

Solution 2: PVA (polymer): 5.02% PEG 6000 (surfactant): 1.03% DD water (solvent): 93.95%

Solution 3: PVA (polymer): 5.05%, SDS (surfactant): 1.02%, DD water (solvent): 93.93%

Solution 4: PVA (polymer): 4.99%, CAPSTONE FS-63 (surfactant): 0.96%, DD water (solvent): 94.05%

Solution 5: PVA (polymer): 10.00%, DD water (solvent): 90.00%

Solution 6: PVA (polymer): 9.99%, PEG 6000 (surfactant): 1.00%, DD water (solvent): 89.01%

Solution 7: PVA (polymer): 10.00%, SDS (surfactant): 1.00%, DD water (solvent): 89.00%

Solution 8: PVA (polymer): 10.1%, CAPSTONE FS-63 (surfactant): 1.11% DD water (solvent): 88.79%

Various coatings were prepared of different initial thicknesses by pouring a known amount of polymer solution in the circular sample holder by the use of micropipette. The dimensions of circular sample holder are diameter: 12.24 mm, depth: 1000 µm as shown in the Figure 3.2. As the solution is poured into the circular sample holder, it spreads out into the entire area, the solvent starts to evaporate from the coating, resulting in weight loss of coating solution. The weight of sample was recorded as a function of time using Precisa analytical weighing balance (ES225SM-DR) having an accuracy of ± 0.0001 g. The method was continuous weighing until the weight of sample comes to a point where two or more consecutive weight becomes constant to confirm that drying process is stopped. For practical purposes drying of coatings was under natural convection. All the experiments were carried out at room temperature 27±1°C or as stated.

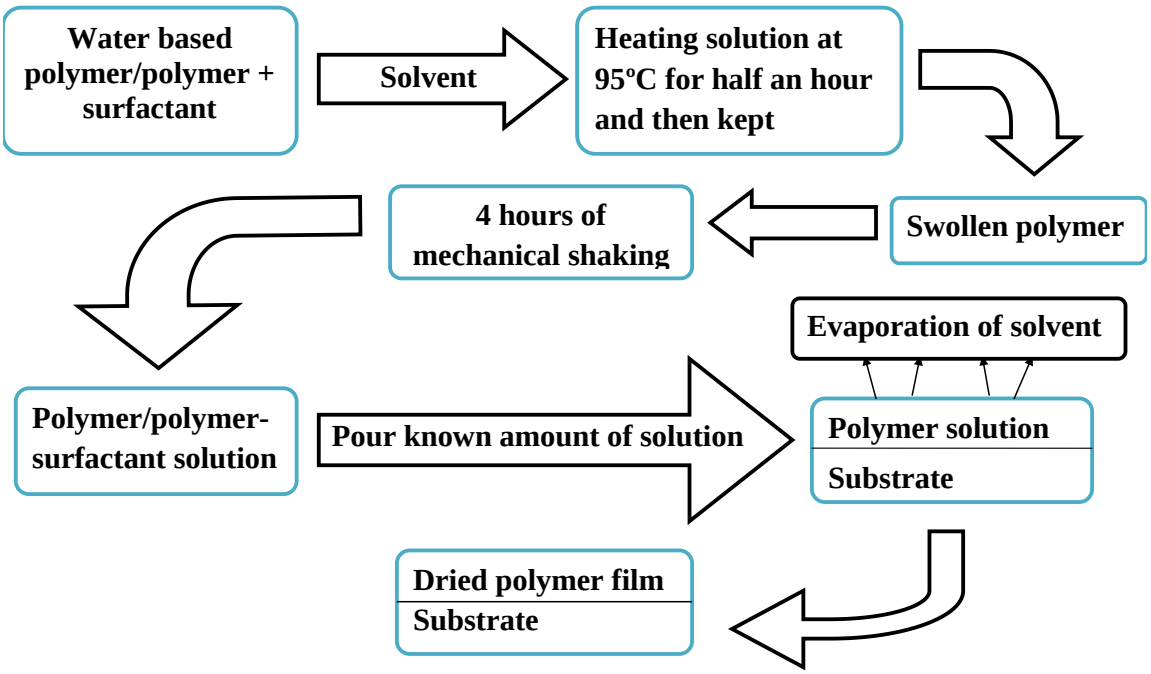

Figure 3.1: Schematic representation of polymer/polymer-surfactant solution for coating preparation

Figure 3.2: Circular sample holder

3.3 Calculations of various coating parameters:

Let the total mass of solution at 0 second is 3635.38 mg of polymer solution having 5.02% polymer and 94.97% solvent respectively.

Total mass of solution = 3635.38 mg

Weight of sample holder = 3558.24 mg

Exact mass of solution = 3635.38 – 3558.24 = 0.07714 g

Mass of polymer = $0.07714 \times \frac{5.02}{100} = 0.003872$ g

Mass of solvent = 0.07714 - 0.003872 = 0.07326 g

Density of polymer = 1.04 g cm^{-3}

Volume of polymer = $\frac{0.003872}{1.04} = 0.003723$ cm^3

Density of solvent = 0.866 g cm^{-3}

Volume of solvent = $\frac{0.07326}{0.866} = 0.084596$ cm^3

Total volume =0.003723 + 0.084596 = 0.088319 cm^3

Concentration of polymer = $\frac{0.003872}{0.088319} = 0.043846$ g cm^{-3}

Concentration of solvent = $\frac{0.07326}{0.088319} = 0.082949$ g cm^{-3}

Cross-sectional area of circular sample holder = 1.177 cm^2

Thickness = $\frac{0.088319 cm^3}{1.177\ cm^2} \times 10000 = 752 \mu m$

% Residual solvent = $100 \times \frac{0.07326g}{0.07326g} = 100\%$

Chapter 4

Results and Discussion

The effect of different types of surfactant on drying behaviour of poly(vinyl alcohol)-water coatings haven been studies and discussed here.

4.1 Drying study of Coating having 5% poly(vinyl alcohol)

Four solutions of poly(vinyl alcohol) were prepared in double distilled water.

Solution 1: poly(vinyl alcohol) and double distilled water

Solution 2: poly(vinyl alcohol), poly(ethylene glycol) and double distilled water

Solution 3: poly(vinyl alcohol), sodium dodecyl sulphate and double distilled water

Solution 4: poly(vinyl alcohol), Capstone FS-63 and double distilled water

The weight percentage of all the components in above solutions is given in Chapter 3.

Set 1: Drying study of 5% PVA coatings of nearly 600µm thickness

4.1.1 Percentage of Residual Solvent

The change is residual double distilled water in show in Figure 4.1. It shows that the percentage of double distilled water is decreasing with time. In solution 1, the residual DD water linearly decreases up to 2 hr 34 minutes having initial thickness 583µm. Up to 96.56% of solvent has evaporated and remaining 3.44% will be permanently trapped in the coating. The coating of solution 2, 3 and 4 have followed the same trend, the residual solvent is decreasing linearly upto 2 hr 14 minutes, 2 hr 29 minutes and 4 hr 51 minutes having initial thicknesses of 448µm, 592µm and 557µm respectively. Upto 98.67%, 93.12% and 99.44% solvent have evaporated, leaving 1.33%, 6.88% and 0.56% permanently trapped in the coatings. More amount of solvent has been removed in the large drying time. At first, it is decreasing linearly but at a fast rate due to presence of high amount of solvent at top surface. After a certain time, the rate decreases due to poor diffusion of solvent and also the process becomes diffusion controlled [19]. Least amount of residual solvent was left in

coatings having fluorosurfactant as can been seen in the solution 1 which is in agreement with the earlier findings about the effect of surfactant [20]. However, in solution 2 and solution 3, the percentage of residual solvent is lower and higher than solution 1 respectively. Solution 3 is having an anionic surfactant which forms a self assembled structure and holds tightly to solvent water molecules whereas in non ionic surfactant is solution 2 the hydrophobic part tries to stay away from water causing the water to evaporate easily.

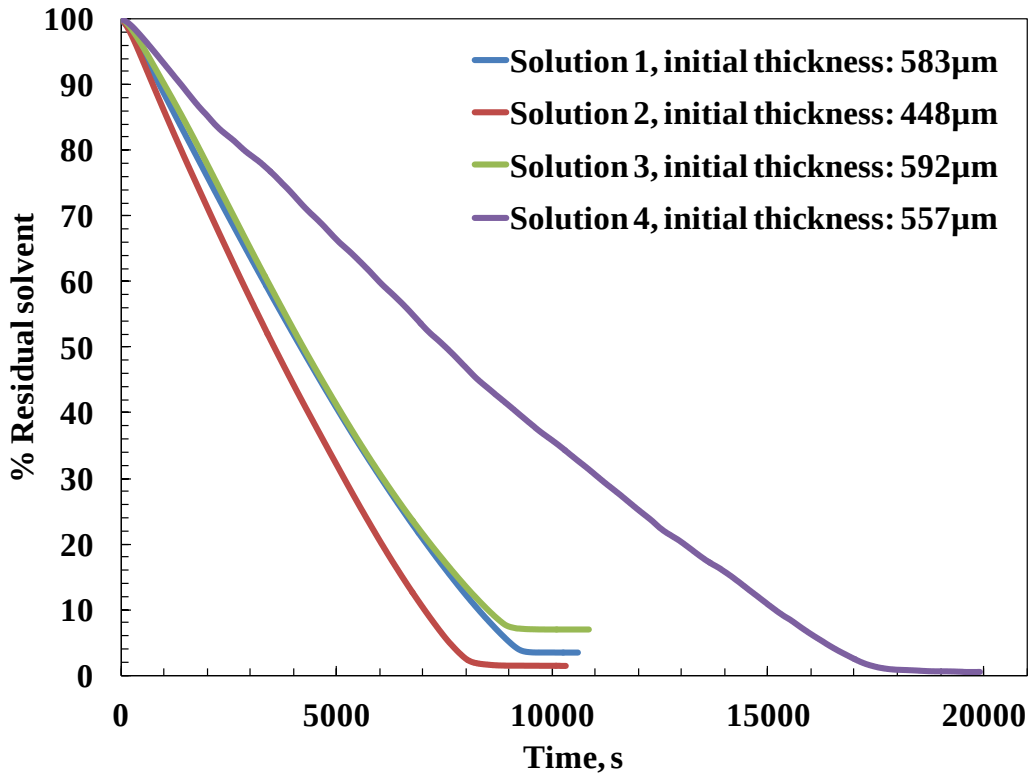

Figure 4.1: Residual solvent as a function of time.

4.1.2 Coating Thickness

The variation of coating thickness with respect to time is shown in Figure 4.2. It shows that the thickness of polymeric coating is decreasing with time. This is due to evaporation of solvent from the coatings. In solution 1, the thickness begins to decrease linearly till 2 hr 35 minutes having an initial thickness of 583µm. It decreases linearly as the solvent evaporates with time. Similarly in solution 2, 3 and 4 follows the same trend, the thickness decreases linearly up to 2 hr 14 minutes, 2 hr 28 minutes and 4 hr 50 minutes having initial thicknesses 448µm, 592µm and 557µm.

The coating left with more thickness has high amount of solvent trapped in them. The final thickness of solution 1, 2, 3 and 4 is 44µm, 30µm, 70µm and 28µm respectively. As it is clear from the values that coating of solution 3 is thickest of them all which imply that there is high amount of solvent left in the coating. However solution 2 has the minimum thickness but the initial thickness in that case was also lower as compared to the other solutions. Solution 4 has the lowest amount of residual present in the coating leaving it thin and completely dried. Coatings of solution 4 have least amount of solvent left due to presence of fluorosurfactant.

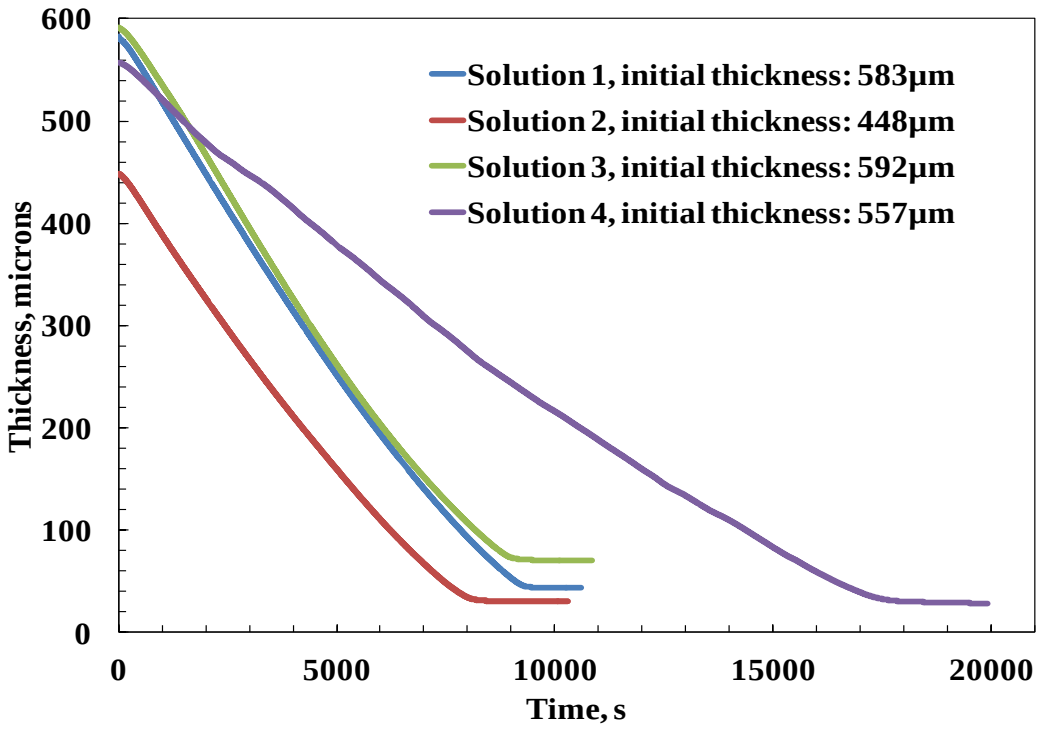

Figure 4.2: Coating thickness as a function of time.

4.1.3 Average Concentration of Double Distilled Water

The average concentration of double distilled water with respect to time is shown in Figure 4.3. It shows that concentration of double distilled water is decreases with time as it starts to evaporate. It decreases exponentially with time and levels off after a certain point. In solution 1 the solvent exponentially decreases up to 2 hr 40 minutes having an initial thickness of 583µm. Solution 2, 3 and 4 following the same trend decreases up to 2 hr 26 minutes, 2 hr 33 minutes and 4 hr 58 minutes having initial thicknesses of 448µm, 592µm and 557µm respectively. Solution 4 is having the

least concentration of double distilled water with a final concentration of 0.108g cm^{-3} where initial concentration was 0.955g cm^{-3}.It is observed that solution 4 coatings take more time for drying because of slow diffusion. The final concentration of solution 1, 2 and 3 are 0.440g cm^{-3}, 0.195g cm^{-3} and 0.551g cm^{-3} with initial concentrations of 0.958 g cm^{-3}, 0.948g cm^{-3} and 0.947g cm^{-3} respectively.

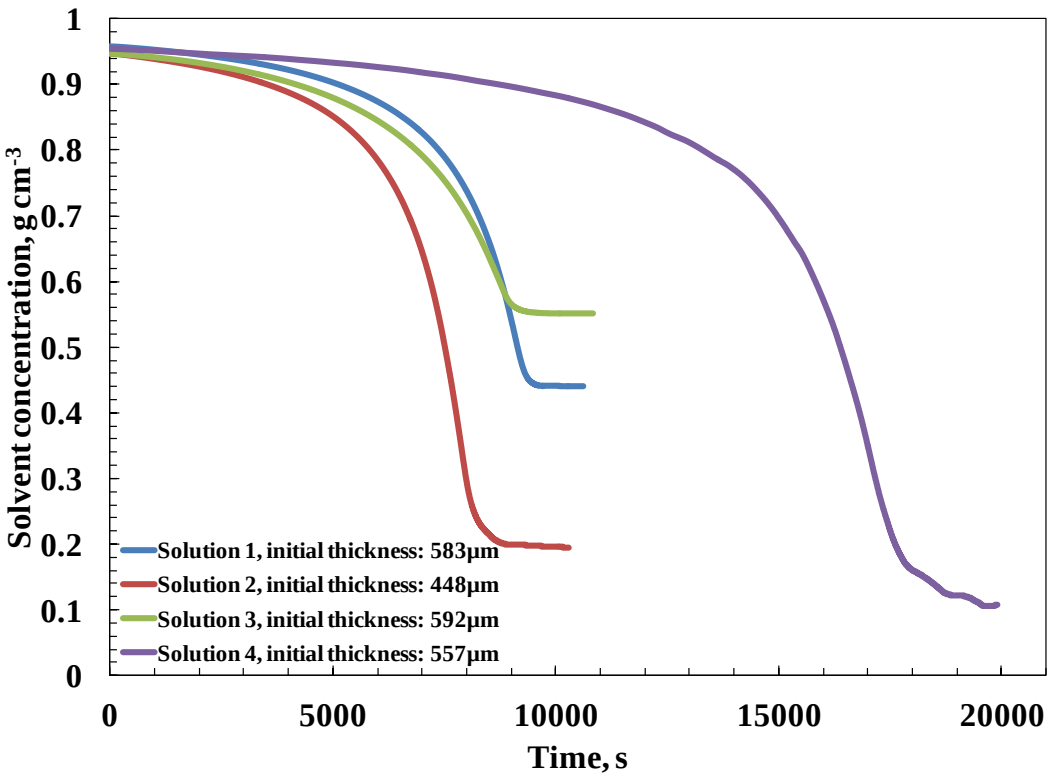

Figure 4.3: Solvent concentration as a function of time.

4.1.4 Average Concentration of Solid

Figure 4.4 shows the average concentration of solid [poly(vinyl alcohol) and surfactant] with time. Solid concentration increases exponentially with time and then levels off after a certain value. In solution 1, the solid concentration of coating exponentially increases up to 2 hr 39 minutes having initial thickness of 583µm. Other solution follows the same trend as described before, solution 2, 3 and 4 increases exponentially up to 2 hr 28 minutes, 2 hr 33 minutes, 4 hr 58 minutes having initial thicknesses 448µm, 592µm and 557µm respectively. The initial concentration of solution 1, 2, 3 and 4 were 0.050g cm^{-3}, 0.061g cm^{-3}, 0.061g cm^{-3} and 0.054g cm^{-3} and after evaporation of solvent the final concentration was 0.667g cm^{-3}, 0.942g cm^{-3},

0.518g cm^{-3} and 1.072g cm^{-3} respectively. The coatings with high solid concentration will have lowest percentage of residual solvent present in it. The solution with highest drying time and highest solid concentration is solution 4. It has low diffusion coefficient so solvent takes much time to evaporate but the final results are better than other solutions. The diffusion process in solution 4 is completely different than solution 1, 2, and 3 respectively. In solution 4, the evaporation of solvent is slow as compared to other solutions. The evaporation process is almost equal to the rate of diffusion of solvent within the polymer. Therefore, solution 4 is taking more time. The final concentration of solid is highest in this due to high amount of solvent removal. It may due to low glass transition of these coating and remains rubbery for longer period.

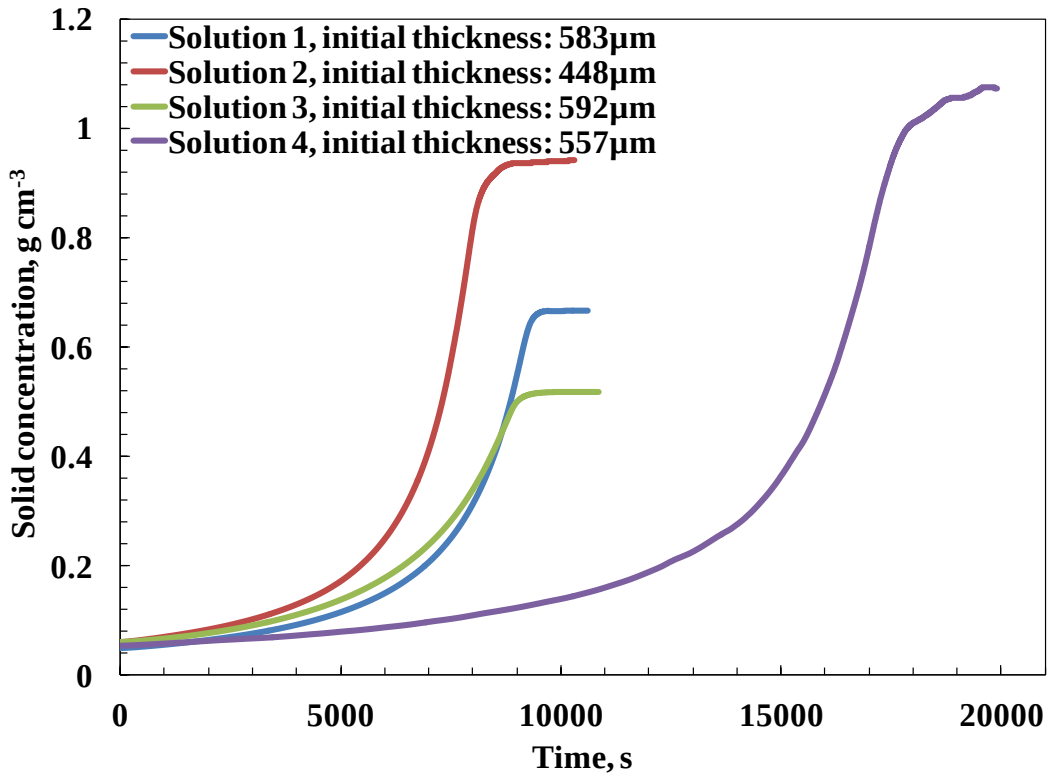

Figure 4.4: Solid concentration as a function of time.

Set 2: Drying study of 5% PVA coatings of nearly 700µm thickness

4.1.5 Percent of Residual Solvent.

Figure 4.5 depicts the change of residual double distilled water with time. It shows the percentage of residual solvent for all coatings is decreasing with time. In solution 1, the residual solvent linearly decreases up to 5 hr 24 minutes having an initial thickness of 703µm. Up to 91.96% of solvent has been evaporated and remaining 8.04% is remained trapped forever. Solution 2, 3 and 4 follow the same trend and linearly falls up to 4 hr 50 minutes, 5 hr 58 minutes and 5 hr 25 minutes having initial thicknesses of 675µm, 740µm and 672µm. In previous solutions 2, 3 and 4, the percentage of residual solvent evaporated is 95.72%, 97.28% and 99.97% leaving 4.28%, 2.72% and 0.30% permanently trapped in the coating. Solution 4 is having the least amount of percentage residual solvent left in the coating as compared to all the other coatings. Fluorosurfactant reduces the surface tension of the solution to a greater extent causing the solvent to move freely within the coating to the top surface and leaving less percentage behind.

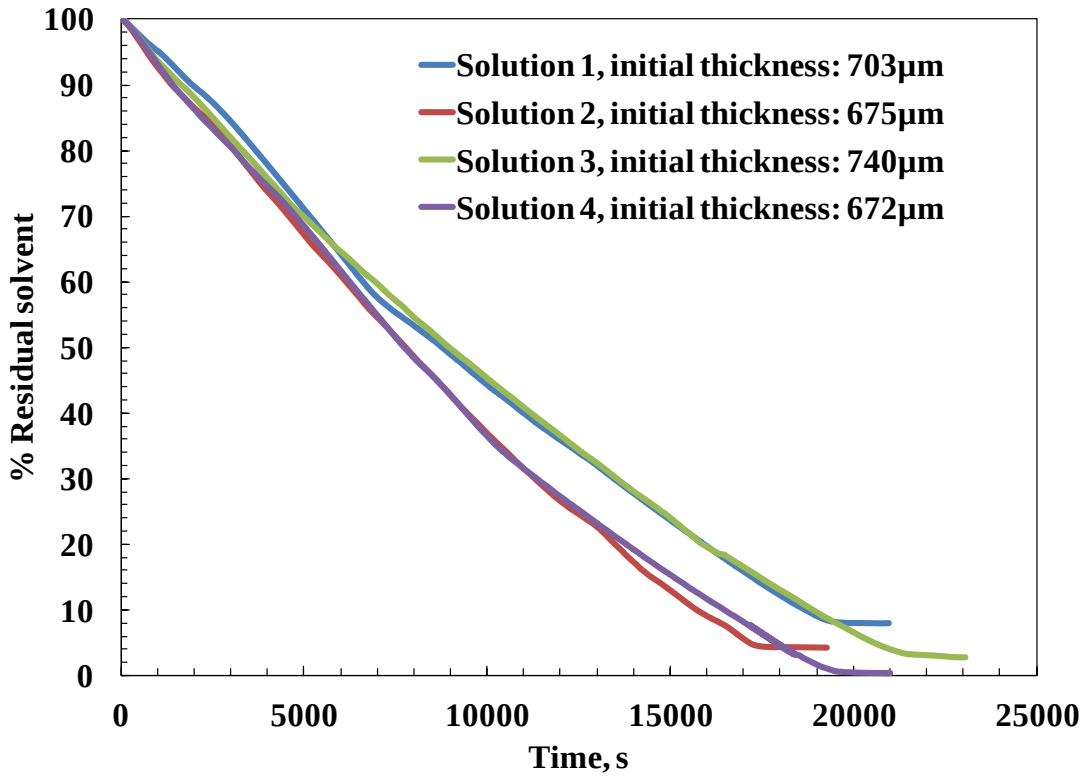

Figure 4.5: Residual solvent as a function of time.

4.1.6 Coating Thickness

Instantaneous coating thickness is shown in Figure 4.6. Coating thickness decreases linearly with time up to a certain point and then plateaus off. In solution 1 the thickness decreases linearly up to 5 hr 21 minutes and then reaches to a final value of 52µm, the initial thickness of the coating was 703µm. Solutions 2, 3 and 4 follows the same trend of linearly decreasing with time and levelling off; it decreases up to 4 hr 48 minutes, 5 hr 57 minutes and 5 hr 24 minutes reaching to a final thickness of 63µm, 100µm and 31µm respectively. The initial thicknesses of the solution were 675µm, 740µm and 672µm. The coating with more thickness will have a significant amount of percentage residual solvent left in it causing it to be thicker. However, the least thickness will have a very small amount of residual solvent present in it. The solution 4 has least thickness and is completely dried up with very less residual solvent content.

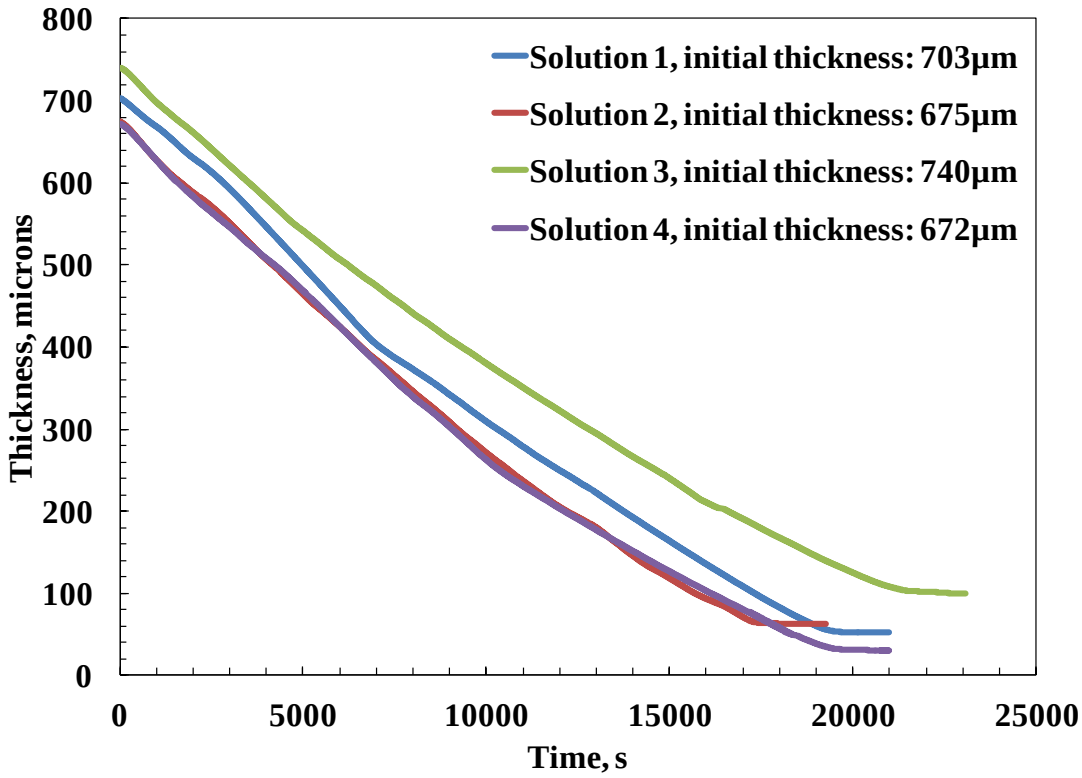

Figure 4.6: Coating thickness as a function of time.

4.1.7 Average Concentration of Double Distilled Water

Figure 4.7 describes the change in average concentration of double distilled water with time. The trend followed here is exponential decrease to a specific value and then levelling off. In solution 1, the solvent concentration decreases up to 5 hr 27 minutes having an initial thickness of 703µm. Solution 2, 3 and 4 followed the same trend and exponentially decreased up to a value of 4 hr 53 minutes, 5 hr 59 minutes and 5 hr 29 minutes with initial thicknesses of 675µm, 740µm and 672µm respectively. The final concentration of solutions 1, 2, 3 and 4 were 0.427g cm^{-3}, 0.438g cm^{-3}, 0.328g cm^{-3} and 0.059g cm^{-3} with initial concentrations of 0.958g cm^{-3}, 0.948g cm^{-3}, 0.947g cm^{-3} and 0.917g cm^{-3} respectively.

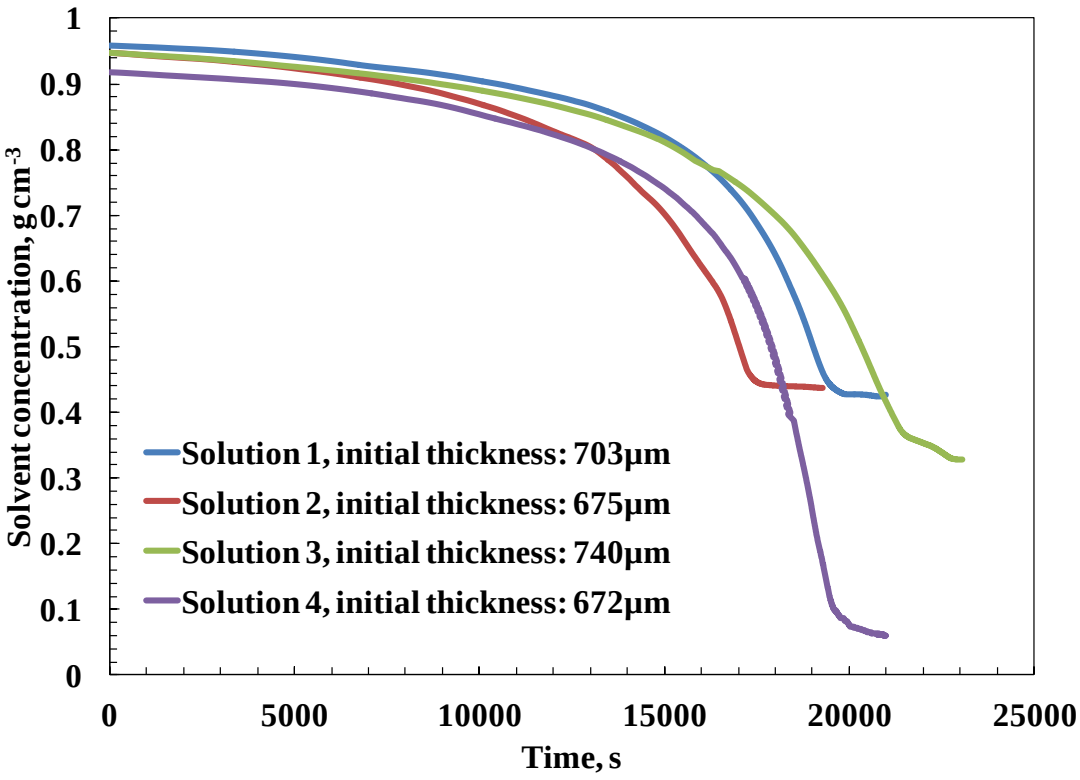

Figure 4.7: Solvent concentration as a function of time.

4.1.8 Average concentration of solid

The average concentration of solid [poly(vinyl alcohol) and surfactant] change with time is shown in Figure 4.8. The concentration increases exponentially and then plateaus off. In solution 1, the concentration increases linearly up to 5 hr 31 minutes having an initial thickness of 703µm. The final concentration of the coating was 0.682g cm^{-3} where the initial concentration was 0.499g cm^{-3}. Solution 2, 3 and 4 also decreased exponentially up to 4 hr 54 minutes, 5 hr 59 minutes and 5 hr 31 minutes having initial thicknesses of 675µm, 740µm and 672µm respectively. The initial concentration of solution 2, 3 and 4 were 0.061g cm^{-3}, 0.061g cm^{-3} and 0.060g cm^{-3} reaching to a final concentration of 0.657g cm^{-3}, 0.779g cm^{-3} and 1.047 g cm^{-3} respectively. The coating which has least percentage of residual solvent will have highest concentration of solid. In this case solution 4 had the highest amount of solid concentration present amongst all solutions. The close comparison of Figure 4.1 and 4.5 shows completely different drying behaviour. However, the only change in the condition is the change initial thickness from 600µm to 700µm respectively. This change is just a physical change which is affecting the drying behaviour to a larger extent. It implies that thicker coating may be more viscous on the top due to evaporation of solvent but not able to stop the solvent diffusion into it by a larger extent. Therefore, the drying trends of all solutions are same for a longer period of time as shown in Figure 4.8. However, solvent has been removed from solution 4 is 99.97%. But, 99.44% solvent was removed in case of coating having initial thickness of 600µm as can be seen in Figure 4.1. This shows that recovery of solvent is almost same in both thinner and thicker case but is taking more time which is obvious due to high amount of solvent.

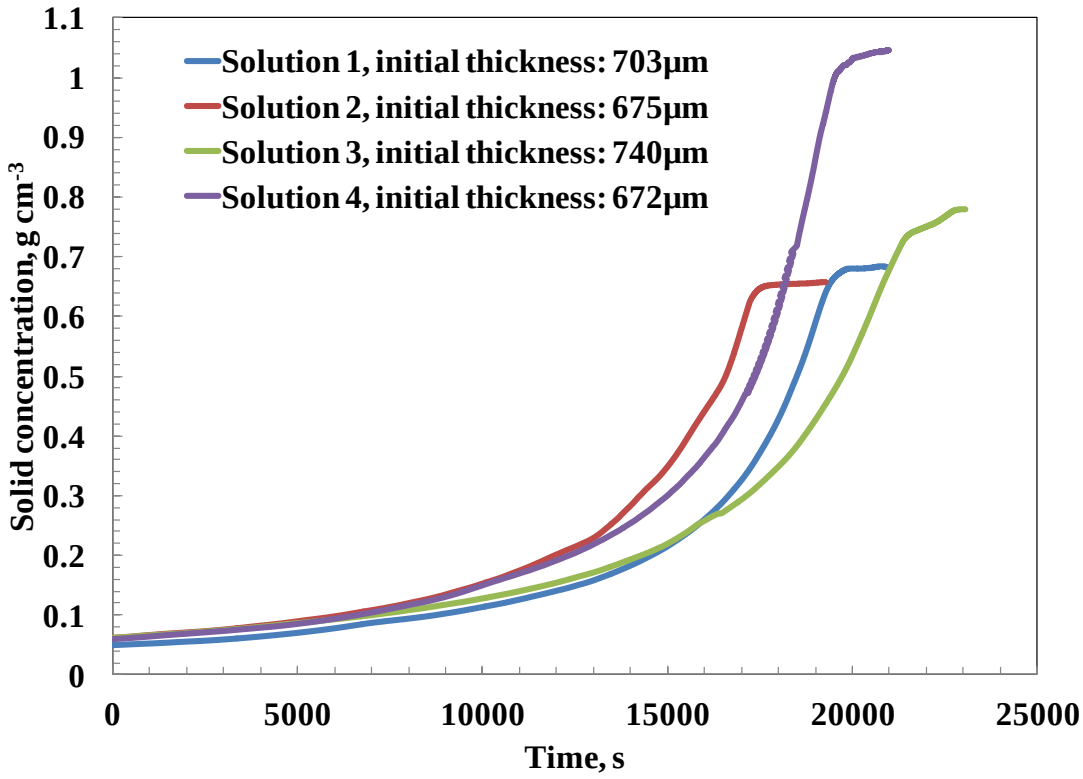

Figure 4.8: Solid concentration as a function of time.

4.2 Drying of coating of 10% poly(vinyl alcohol)

Four solutions of poly(vinyl alcohol) were prepared in double distilled water. The weight percentages of solutions above are given in Chapter 3.

Solution 5: poly(vinyl alcohol) and double distilled water

Solution 6: poly(vinyl alcohol), poly(ethylene glycol) and double distilled water

Solution 7: poly(vinyl alcohol), sodium dodecyl sulphate and double distilled water

Solution 8: poly(vinyl alcohol), Capstone FS-63 and double distilled water

4.2.1 Percentage of Residual Solvent

The change is percentage of residual solvent with time is described in Figure 4.9. The residual decreases linearly with time. In solution 5, the residual solvent linearly falls up to 2 hr 5 min having an initial thickness of 356µm. Solution 6, 7 and 8 followed the same trend, they linearly decreased up to 3 hr 59 minutes, 5 hr 26 minutes and 3 hr 1 minutes having initial thicknesses of 473µm, 637µm and 507µm respectively. In the four solutions from 1 to 4, the residual amount evaporated was

97.14%, 97.07%, 95.59% and 95.34% respectively left with 2.89%, 2.93%, 4.41% and 4.66% permanently trapped in the coatings. In the starting, the residual solvent is decreasing at a faster rate because there is a huge amount of solvent present on the top surface of the coating. As the time increases, the solvent drying rate becomes slower and then it becomes almost constant. The drying process shifts from being external transfer mass controlled to diffusion controlled. As observed in Figure 4.1 and 4.5, solution 4 which has a fluorosurfactant has least amount of percentage residual solvent present in it. However, in case of solution 8 with same components as solution 4 but different weight percentage of PVA, the observed result is not the same. This implies that for higher percentage of polymer percent in solution more amount of surfactant is needed to get required results. All the solutions have almost same amount of residual solvent present in it.

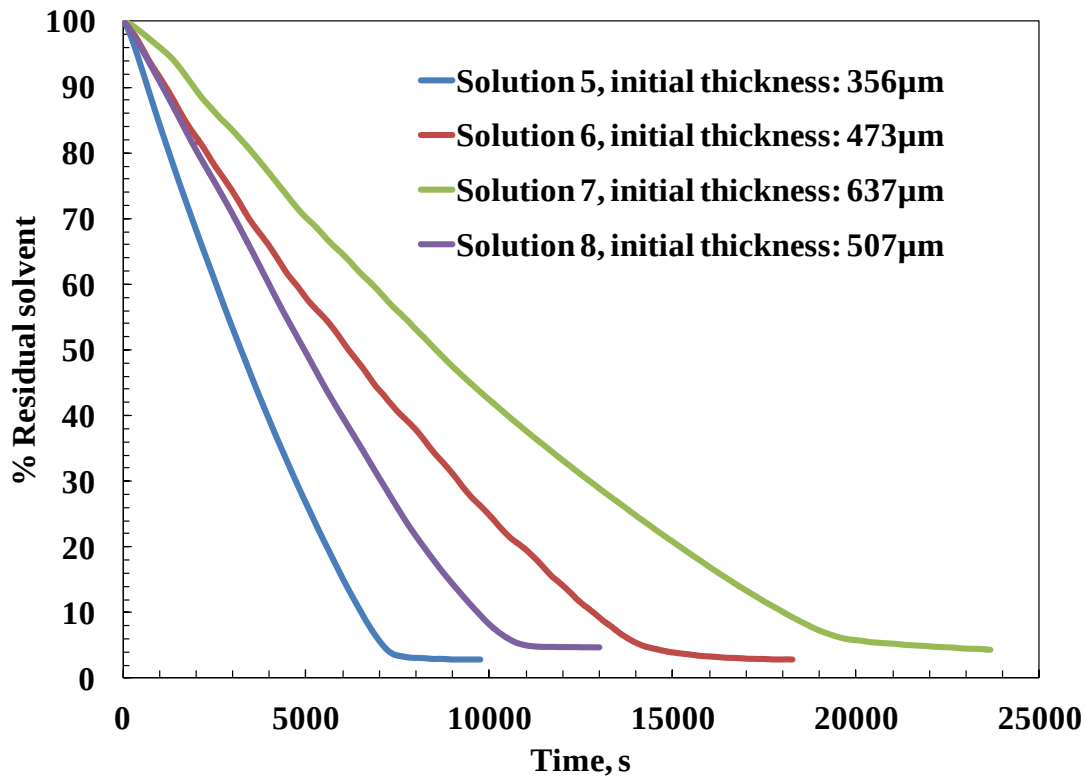

Figure 4.9: Residual solvent as a function of time.

4.2.2 Coating Thickness

Instantaneous coating thickness is shown in Figure 4.10. The coating thickness decreases with time. In solution 5, the thickness linearly decreases up to 2 hr 4

minutes having an initial thickness of 356µm. Solutions 6, 7 and follows the same trend and linearly decreases up to 3 hr 59 minutes, 5 hr 24 minutes and 3 hr 0 minutes having initial thicknesses of 473µm, 637µm and 507µm respectively. The final thicknesses of solution 5, 6, 7 and 8 were 40µm, 58µm, 87µm and 66µm. Solution 5 has least thickness but the initial thickness of the coating was comparatively very less to the other coatings. The solution with thickest coating will have high amount of residual solvent left in it. Solution 7 has highest initial coating thickness which implies that the solution is less viscous than other solutions but this still has high amount of residual solvent present in it.

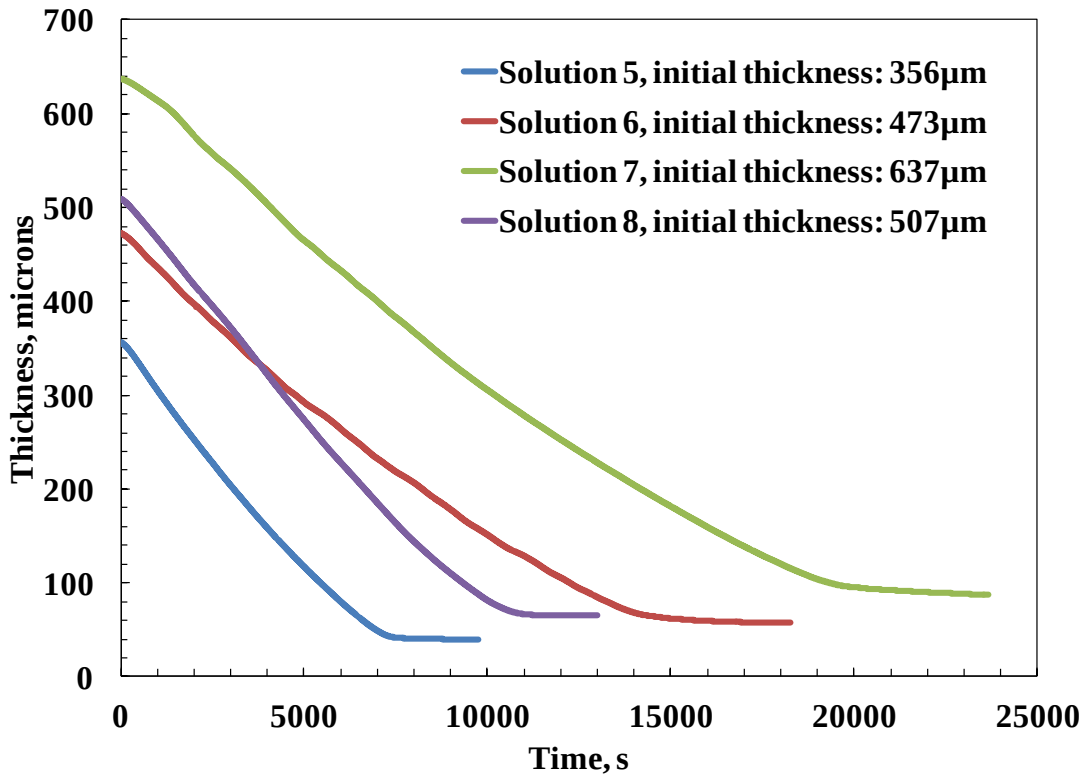

Figure 4.10: Coating thickness as a function of time.

4.2.3 Average Concentration of Double Distilled Water

Figure 4.11 shows the change of average concentration of double distilled water with time. The concentration of solvent exponentially decreases with time as it starts to evaporate. In solution 5, the concentration decreases up to 2 hr 7 minutes having an initial thickness of 356µm. Solution 6, 7 and 8 follows the same trend and exponentially decreases up to 4 hr 8 minutes, 5 hr 24 minutes and 3 hr 7 minutes

having initial thicknesses of 473µm, 637µm and 507µm. The final concentrations of solution 5, 6, 7 and 8 were 0.236g cm^{-3}, 0.219g cm^{-3}, 0.295g cm^{-3} and 0.318g cm^{-3} where their initial concentrations were 0.915g $cm^{-3,}$ 0.905g cm^{-3}, 0.905g cm^{-3} and 0.876g cm^{-3} respectively. Very little differences are observed in the final concentration of solvent in all the coatings.

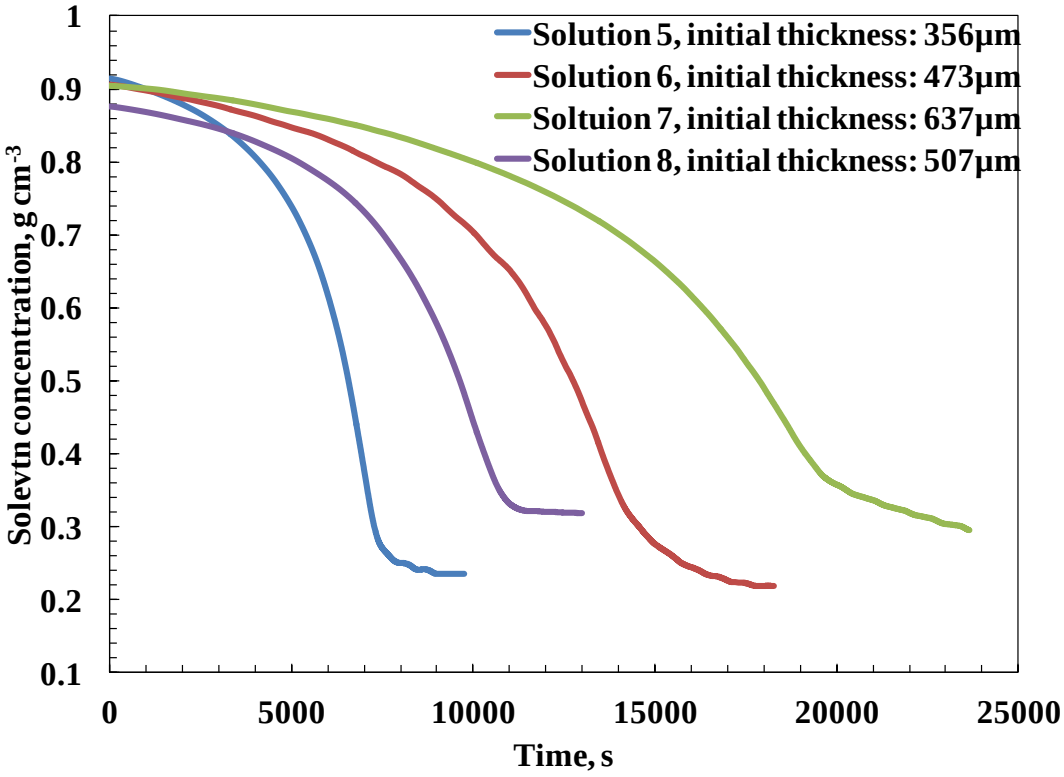

Figure 4.11: Solvent concentration as a function of time.

4.2.4 Average Concentration of Solid

Figure 4.12 shows the change in average concentration of solid [poly(vinyl alcohol) and surfactant] with time. The concentration of solid exponentially increases with time as the solvent evaporates from the coating. In solution 5, the concentration increases up to 2 hr 8 minutes having an initial thickness of 356µm. Solution 6, 7 and 8 follows the same trend and exponentially increases up to 4 hr 17 minutes, 5 hr 30 minutes and 3 hr 7 minutes having initial thicknesses of 473µm, 637µm and 507µm respectively. The final concentration of solution 5, 6, 7 and 8 are 0.909g cm^{-3}, 0.921g cm^{-3}, 0.827g cm^{-3} and 0.799g cm^{-3} where the initial concentrations were 0.102g cm^{-3}, 0.112g cm^{-3}, 0.112g cm^{-3} and 0.103g cm^{-3} respectively. In this case, it is very tough to

identify the best surfactant as the obtained results are same for all surfactants as shown in Figure 4.12.

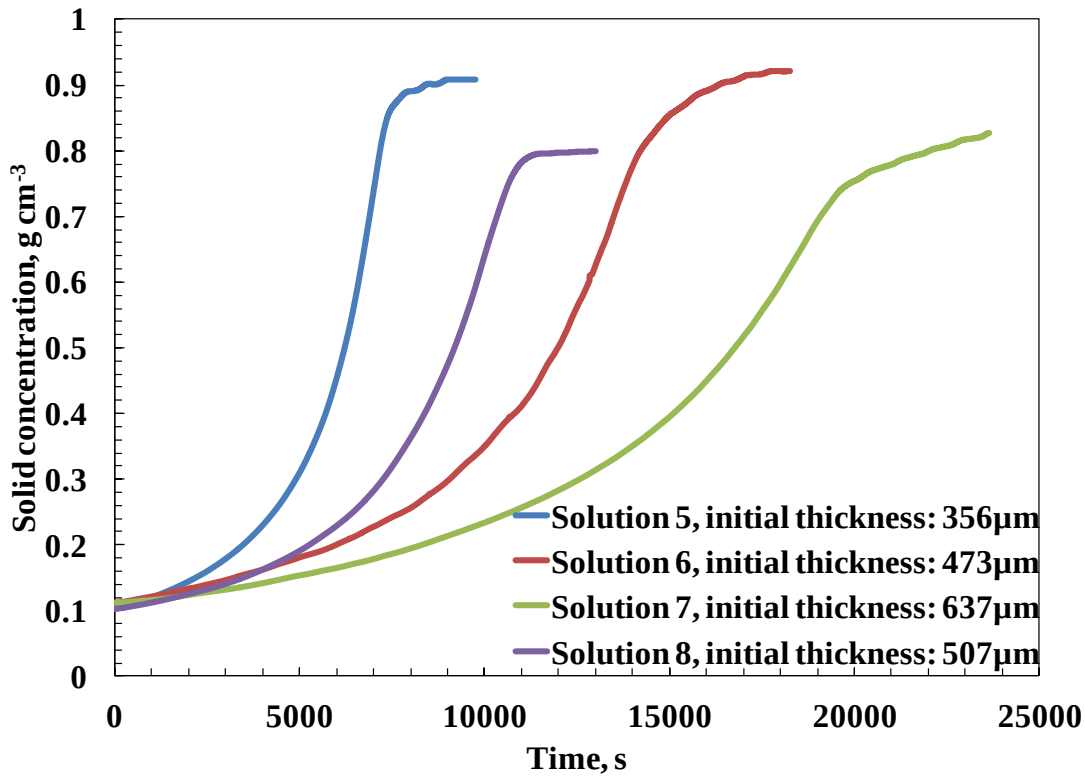

Figure 4.12 Solid concentration as a function of time.

Chapter 5

Conclusion

Drying of water based polymeric coatings has been studied. For this study, poly(vinyl alcohol)-water system has been studied. Effect of various coating parameters like thickness, concentration of solvent and polymer has been studied. The drying rate was very slow in this system due to very low evaporation rate of water from the polymeric coating. The drying rates were manipulated by using various ionic, non-ionic and fluoro based surfactants. Ionic surfactant could not change the drying mechanism. However, the non ionic has changed the drying behaviour to a small extent. The major change was observed by the use of fluoro based surfactants.

The fluoro based surfactant has reduced the viscosity of the coating solution. These coatings showed a very slow drying rate for a sufficiently long period of time. Hence, the recovery of residual solvent was more in the coatings. This effect was clearly observed in polymeric coatings having 5% poly(vinyl alcohol). These findings are in agreement with earlier published data [20]. However, there was no difference in residual solvent for coatings having 10% poly(vinyl alcohol). This could be due to the less plasticizer effect of the surfactant because the surfactant percentage was kept same in both the systems. By changing the percentage surfactant the residual solvent recovery can be enhanced as was observed in previous solutions.

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Chapter 1

Introduction

Polymeric coatings have become a major part of various industries. The different types of polymeric coatings are used in textile industry, electronic industry, automobile industry, food industry and many more [1-3]. The main purpose of polymer coatings is to increase the life span of the material or surface, protecting it from moisture, cracks and basically act as a shield.

1.1 Classification and Preparation of Polymeric Coatings

Polymer systems are generalised in two parts binary or multi-component polymeric systems. Polymeric coatings are prepared by using solvent or without solvents. They are being used as protective colloid, in corrosion protection, ink-jet printing technologies, LCD-panels, edible polymeric coatings and medical test strips [4].

Polymer coatings are prepared by using various techniques. Spin casting, solution casting, thermal spraying, dip casting and drop casting. The easiest and simplest method for the preparation of coatings is solvent casting technique especially in academic area. Solvent casting technique is unique technique for a blister free and uniform polymeric coating. It involves the formation of a homogeneous solution of polymer and solvent. The benefits of this technique are described below

- It can be processed at low temperature, beneficial for polymer coatings which are thermally active or which contain active ingredients sensitive to temperature.
- Easy addition of fillers and additives.
- Ability for production of high-temperature resistant films from non-thermoplastic but raw materials.
- Wider range of choice of materials, any solvent based coatings can be used either solvent or aqueous.

1.2 Drying of Polymeric Coatings

Several methods are used for drying of coatings such as thermal drying, condensation drying and controlled drying. The drying mechanism is explained on various levels of different component system. Controlling the drying conditions are maintaining to get good quality of polymeric coatings. Many researchers are working on reducing the residual solvent percentage to least amount because it gives defect free polymeric coatings. Residual solvent is the amount of solvent that is left in the dried polymeric coating which then diffuses into the coating at the later stage. Solvent transport in coatings is explained using free volume theory given by Vrentas and Duda [5, 6] in combination with Flory-Huggins theory of polymer solution thermodynamics. This theory speculates the drying behaviour of coatings which has been prepared by use of high volatile solvents. The observed drying rates are in accordance with predictions of model [7, 8] in case of high volatile solvents. However, for low volatile solvents the experimental results are not in such agreement with the model [8]. Price Jr and Cairncross [9] mathematically optimized the drying conditions in single zone dryers. A detailed drying model with automatic optimization is used to find optimal drying conditions to avoid the defects and minimize the residual solvent.

1.3 Green coatings

In industrial area, a huge of amount of organic solvents is used in the preparation of polymeric coatings which is not at all environmental friendly. Organic solvent damage nature and can end up being toxic. In present work, double distilled water is used as a solvent in the synthesis of polymeric coatings using PVA. These coatings can also be termed as green coatings due to their environment free nature. Many industries have been paying attention to the importance of green coatings because they do not cause pollution and they are cost effective. In water based coatings, the drying time is usually higher as compared to organic solvent based coatings because organic solvents are more volatile than water. Slow drying rate requires high energy for very long drying time of coatings which eventually needs higher amount of energy.

1.4 Surfactant in Polymeric Coatings

The introduction of a third component into a binary solution has shown promising results and enhancement in drying of the polymer solution by changing the solution structure at molecular level [10]. Now a days, Polymer-surfactant systems are high interest of the research because of their interactions, drying rate, film formation, wetting performances and other applications [11]. The surfactant plays a crucial role in drying and levelling of polymeric coatings [12]. Even a small amount of surfactant brings about an appreciable change in the polymeric films. The polymer/surfactant system in which the pairs are of opposite charges have been of special interest [13]. There are mainly three forces which are present in the polymer/surfactant system: hydrophobic, dipole-ion interactions, and strong columbic forces. The same charge polymer/surfactant has feeble association where as if they are of opposite charges they have strong electrical interaction. Hydrophobicity of the polymer can be a ruling factor in case opposite charges polymer/surfactant system [14]. The reactivity of the system is controlled by many factors. The surface tension of these systems has been studied a lot in order to reduce the surface tension of the solution and levelling effect. The surfactant head group determines surfactant properties and classification. The critical aggregation number (cac)/critical micelle aggregation (cmc) tells a lot about the binding of polymer to the surfactant. Below this critical micellation number, association is promoted and above this value there is found to a decrease in total aggregation number [12].

In spite of that it has essential properties to prevent coagulation, particle aggregation and foremost reducing the surface tension leading to reduction of residual solvent [15].

As described above surfactant based coatings are said to better than other type of coatings because of their drying characteristics.

1.5 Dissertation outlines

This thesis has been arranged as following:

Chapter 1: A brief introduction about the classification and preparation of coatings, use of surfactant, drying of polymeric coatings and green coatings is given in this chapter

Chapter 2: A detailed literature review regarding interactions of surfactant and polymer, drying of polymeric coatings, diffusion in polymeric coatings and research gap is given here.

Chapter 3: Methodology and materials used are given.

Chapter 4: Comparison between drying study of different coatings is given in this chapter.

Chapter 5: Conclusion and further scope of study is

Chapter 2

Literature Review

In this chapter, recent literature related to the residual solvent study in coatings has been reviewed. The literature review has been divided into following parts: interaction between surfactant and polymer, drying of polymeric coatings and other properties.

2.1 Interaction of surfactant and polymer

Anthony et al. [12] studied the interaction between two polymers and a surfactant which are, PS1: poly(maleic acid -*co*- methyl vinyl ether), PS4: poly(maleic acid -*co*- ethyl vinyl ether) and DTAC (dodecyltrimethylammonium chloride) respectively. The interactions are affected by the hydrophobicity of polymer. The aggregate number of polymer bounds was found to be independent of the bound surfactant concentration. The binding of surfactant with polyelectrolyte was found to be cooperative and further adding cooperative binding of PS1 with surfactant was in range $0<\alpha<1$ and for PS4 was $0.5<\alpha<1$. The difference in interaction is because of the hydrophobicity of PS4 with surfactant molecules whereas in PS1, surfactant operates through short range electrostatic interaction and the polymer is less hydrophobic. The polymer bound aggregates have larger fluorescence lifetime of pyrene and higher viscosity as compared to the polymer which are free of surfactant micelles. It is probably because of the binding of polymer and surfactant ion and also the tight binding of polymer-surfactant charged ion groups and polymer main chain. The surfactant counter ions were excluded from the surface of aggregate because of the binding.

Balaza et al. [16] studied the interaction of surfactant in dilute solutions as function of surfactant concentration. A critical surfactant concentration is required for surfactant – polymer interaction. Lower than this value, the addition of surfactant enhances the solution viscosity due to aggregation. Higher than this value, adding up surfactant causes stearic hindrance in the association leading to low aggregation number and viscosity from its optimal value. They used an algorithm similar to diffusion-limited aggregation (DLA) for simulation study. This shows that increasing

the surfactant by small fractions increases the average functionality because it exposes the end of polymer which is otherwise used in loops. As amount of surfactant (mono-functional units) is increased the average functionality decreases which in turn decreases the aggregation number. They used Carothers equations as given below

$$X_n = (1 - f_{avg})^{-1} \quad (1)$$

Where f_{avg} : average monomer functionality and X_n : degree of polymerization.

Meconi et al. [15] studied the adsorption and desorption of ionic and non-ionic surfactants on polymer surfaces. The surfactants used were sodium dodecyl sulphate (SDS) and polyethylene glycol-polyethylene block copolymer (PEG-PE) respectively. At low surfactant concentrations, non-ionic surfactants had higher adsorbing power, higher attractive forces, and lesser stability at the surface as compared to ionic surfactants and further adding they do not alter the final product significantly. Physio-chemical properties of head parts are responsible for this difference. Ionic surfactant formed a self-assembled structure while non-ionic formed a disordered layer as they had hydrophilic head groups which weaken the interaction with water molecules in aqueous medium. The reduction in surface tension relative to chemical potential change of surfactant was measured by Gibbs adsorption theorem as given by

$$\frac{d\gamma}{d\mu_{\text{surfactant}}} = -\Gamma \quad (2)$$

Where, $d\gamma$ = change in surface tension, $d\mu_{\text{surfactant}}$ = change in chemical potential and

Γ = surfactants molecules per unit area.

Ruckenstein et al. [17] studied about the aggregation of surfactants in presence of polymers. The surfactants used were SDS, dodecyltrimethylammonium chloride (DTAC) and triton X-100 in presence of polyethylene oxide. The changes of interfacial free energy between polymer and surfactant molecules, bound aggregates and microenvironment were calculated by developed model. Very small amount of surfactant headgroup was able to decrease overall surface energy and hence better aggregation. However, no micelle formation was observed in case of large headgroup surfactant due to enhancement in interfacial energy between microenvironment and micelles. In this case, the micelle bound to macromolecule form at a concentration below cmc of free micelles. On the other hand, if the headgroup is large the overall

interfacial energy increases between microenvironment and micelles leading to no micelle formation. This explained the fact that surfactant with smaller head trigger the formation of bound micelles and large headgroups do not stimulate the formation.

2.2 Drying of Polymeric Coatings

Kajiya et al. [10] studied the drying of the polymer solution droplets using small amounts of surfactant. They found that on adding small amount of surfactants, the polymer film become levelled instead of taking a concave shape. The polymer solution of monodispersed polystyrene was used in this work. The surfactants used were fluorosurfactant F470 and F489 which are oligomers with perfluoroalkyl hydrophobic and lipophobic groups. The main use of surfactant was to lower the surface tension of the polymer liquid which also affected the contact angle. They observed that without the surfactant, most of the polymer was found at the edge; there was ringlike profile formation. On the other side, while they added surfactants, the polymer instead of edge was at the centre and polymer film was flatter. The Marangoni force required was very small to restrain the outward flow. This behaviour was seen in some other cases too where the polymer concentration was very high. They found that a very small quantity of surfactant can cause levelling effect and enhanced the drying process.

Okazaki et al. [18] studied the drying mechanism of coated films of poly(vinyl alcohol) films. They focused on the diffusion process of water and the shrinkage of volume of the film. They measured the diffusion coefficients over a period of time using different methods like drying the film using hot air. Numerical solutions were obtained using transport equations for water and were compared with experimental results. The dependency of diffusion coefficient on concentration, dependency of equilibrium vapour pressure of water on concentration and effect of shrinking in the volume followed due to evaporation of water were considered to simulate the drying process of coated PVA film. The mutual diffusion was measured for low, intermediate and high concentration of PVA. The experimental and calculated results show that diffusion coefficient is a reliable factor between both results. They used Boltzmann's equation for calculating diffusion constant D as a function of concentration.

$$D = -\frac{1}{2t}\left(\frac{d_z}{d\Omega}\right)\int_0^{\Omega} z\,d\Omega \tag{3}$$

Cairncross et al. [19] studied the residual solvent in polymeric coatings. At constant temperature, they found that the rate of drying continuously falls and drops to zero and residual solvent plateaus. Their drying model predicted the dependency of residual solvent on temperature, diffusion properties and concentration of solution. There are different drying periods which shows the trend in residual solvent behaviour, drying rate, and temperature. In these periods the drying rapidly increases whereas the rate of drying is constrained by diffusion mass transport by keeping the uniform solvent concentration throughout the coating. Moving to other rate period, drying is diffusion controlled and drying rate approaches zero. Eventually, the rate of drying approached to zero which was termed as diffusional plateau and considerable amount of solvent left in the coating. The final residual solvent is controlled by the internal diffusion resistance to mass transfer in dried polymer coating.

Yamamura et al. [20] studied the effect of fluorosurfactant on drying of solvent of liquid film coatings . The use of fluorosurfactant has shown 10% increase in solvent evaporation within a certain range. They used CAB (Cellulose acetate butyrate) and MEK (methyl ethyl ketone) solution and a fluorine based surfactant. Continuous weighing showed that drying rates were initially increased and then afterwards decreased with increase in surfactant mass fraction. The enhanced solvent drying is ascribed to diffusion coefficient increasing rather than variation in vapour pressure.

Gu et al. [21] studied the drying of aqueous surfactant solutions. The block copolymers Pluronic F127 and Pluronic L64 were used. They studied equilibrium adsorption isotherm, surface evaporation, internal diffusion, degree of hydration and self assembled structure. It was observed that initially percentage of water loss was linearly increasing with drying time and then nonlinearly coming to a plateau. The drying rate was affected by relative humidity (RH), surface evaporation and nanostructure of polymer. Drying rate was relatively constant for all polymers and it changes differently for different polymer. Hydration levels of pluronic hydrogels played an important role in drying of solution rather than the self-assembled nanostructure.

2.3 Diffusion in Polymeric Coatings

Muller et al. [22] studied diffusion in thin films. They used non-volatile moieties as penetrant in thin films. The experiment showed that drying conditions were affecting the formation of non-volatile compound. It was distributed inhomogenously in the final step and influencing the required product. They observed the mobility of additive and concentration dependent diffusion coefficient using Infrared-Micro-Raman-Spectroscopy (IMRA). They analysed a multi-component system containing a polymer (cellulosetriacetate (TAC) for LCD-panel foils), a non-volatile component (triphenylphosphate (TPP) used as plasticizer) and methylenchlorid (MeCl) used as solvent. They noticed the formation of a distinctive layer because of inhomogeneous distribution of polymer and additive. They used the 'Two layer experiment': one consisted of a mixture of solvent, polymer, and non-volatile additive and second one with polymer, solvent only. The layers were put on the two thin glass plates and joined together. Diffusion of additive equalized the additive concentration gradient after the layers were in contact. The process of equalization was a function of time and with decrease in solvent loading there was significant increase of equilibrium-time. There was a thin film formation in case of slow loading of solvent. Slow loading is the only limitation of this procedure. To overcome this, other setup was used in which solvent partial on coating-air interface was used to check loading of solvent in the two layers.

Muller et al. [4] studied the effect of non-volatile plasticizer on solvent diffusion in polymers coatings. The drying curves were affected when the solvent loading was too slow and then plasticizer loading played the important role. The solvent having high plasticizer loading had higher drying rate. The solvent diffusion coefficient increased with the high amount of plasticizer loading which in turn decreased the drying time of polymers coatings. They used triphenylphsosphat (TPP), methylenchlorid (MeCl) and poly(vinyl acetate) (PVAc) as non-volatile plasticizer, solvent and polymers respectively. The small quantity of plasticizer had significant effect on the mutual diffusion coefficient. The accelerating effect of plasticizer was then observed for the description of drying curves of such solvent system. They used changed the plasticizer loading from 0 to 0.15 g_{TPP}/g_{PVAc} with an increment of 0.05. The initial solvent loading in each experiment was $X_{MeCl} = 0.9 g_{TPP}/g_{PVAc}$, with a

polymer coating of thickness 115µm keeping and other drying conditions were kept same. The drying curves were almost identical till the solvent loading of $X_{MeCl} = 0.2 g_{MeCl} / g_{PVAc}$ because the drying rate was controlled by gas phase transport resistance and not by solvent loading. With the solvent loading less than $X_{MeCl} = 0.2 g_{MeCl} / g_{PVAc}$ the drying rate was limited due to solvent diffusion. The solvent with high TPP had the highest drying rate and with no TPP had lowest. The diffusion coefficient became the function of plasticizer and solvent loadings and is given by

$$D = \exp\left(\frac{a + b.X_1}{1 + c.X_1}\right)\left[m^2.s^{-1}\right] \qquad (4)$$

Where D= mutual diffusion coefficient, X_1= solvent loading in $g_{solvent} / g_{TPP}$ and a, b, and c are parameters that had to be fitted to experimental data

Ravichandran et al. [23] used ultrasonic method to study the thermo acoustical properties of sodium dodecyl sulphate (SDS) in poly(vinyl alcohol) (PVA) solution. They measured density, viscosity and ultrasonic velocity over a range of composition. The factors increased linearly with the concentration of 0.25N surfactant at 2% PVA solution up to a certain value. A sudden decrease of velocity was seen at a particular concentration in both solutions, disconnection was velocity indicated critical micelle concentration. At low concentration, the solutions remained clear but as the concentration of surfactant increased, they were no longer clear. The increment in sodium dodecyl sulphate decreased ultrasonic velocity in 0.5N solution due to high hydrophobic nature of SDS and hydrophilic parts at higher concentration which form micelle rods.

Table 1 to 2 show residual solvent in various types of coatings: Single layer, multilayer, multi-component and binary coatings. Some amount of solvent has been left in all coatings and its percentage varies from system to system and the type of coating mechanism used. The residual solvent left in single layer was much lesser as compared of multilayer to get nearly same dried thickness. The residual solvent in layer by layer multilayer was much higher than simultaneous multilayer. Residual solvent was also dependent on the system order being coated. The coatings having on the system order being coated. The coatings having polymer of high glass transition

temperature retained much solvent when it was coated on the top as an be solvent when it was coated on the top as can be seen in PMMA-THF (top) and PS-THF (bottom) system in Table 1. PVAc-toluene coating retained 5-13% toluene even if they were dried at 70°C as can be seen in Table 2.

Table 1. Residual solvent in multilayer polymeric coatings[24].

S. No.	Top Layer	Bottom Layer	Coating Technique	% Residual Solvent
1	Poly(methyl methacrylate)(10.14%)– Tetrahydrofuran(89.86%)	Poly(styrene)(10.07%)- Tetrahydrofuran (89.93%)	Layer by Layer	12.79
2	Poly(styrene)(5%) – Tetrahydrofuran (95%)	Poly(methyl methacrylate)((10.14%)- Tetrahydrofuran (89.86%)	Layer by Layer	14.60
3	Poly(styrene)(10.07%)– Tetrahydrofuran (89.93%)	Poly(methyl methacrylate)(10.14%)– Tetrahydrofuran (89.86%)	Layer by Layer	11.07
4	Poly(styrene)(15.13%)– Tetrahydrofuran (84.87%)	Poly(methyl methacrylate)((10.14%)– Tetrahydrofuran (89.86%)	Layer by Layer	17.18
5	Poly(methyl methacrylate)(10.14%)– Tetrahydrofuran (89.86%)	Poly(styrene)(5%) – Tetrahydrofuran (95%)	Layer by Layer	16.79
6	Poly(methyl methacrylate)(10.14%)– Tetrahydrofuran (89.86%)	Poly(styrene)(15.13%)– Tetrahydrofuran (84.87%)	Layer by Layer	18.28
7	Poly(styrene)(15.13%)– Tetrahydrofuran (84.87%)	Poly(methyl methacrylate)(10.14%)– Tetrahydrofuran (89.86%)	Simultaneous	18.52
8	Poly(methyl methacrylate)(10.14%)– Tetrahydrofuran (89.86%)	Poly(styrene)(5%) – Tetrahydrofuran (95%)	Simultaneous	6.50
9	Poly(methyl methacrylate)(10.14%)– Tetrahydrofuran (89.86%)	Poly(styrene)(15.13%)– Tetrahydrofuran (84.87%)	Simultaneous	14.8
10	Poly(styrene)(5%)– Tetrahydrofuran (95%)	Poly(methyl methacrylate)(10.14%)– Tetrahydrofuran (89.86%)	Simultaneous	5.80
11	Poly(methyl methacrylate)(10.14%)– Tetrahydrofuran (89.86%)	Poly(styrene)(10.07%)– Tetrahydrofuran (89.93%)	Simultaneous	8.84

Table 2. Residual Solvent left in polymeric coatings.

S. No.	Coatings Method	Coating Composition	Initial Thickness, μm	Ultimate Thickness, μm	% Residual Solvent	Drying Time, s	Reference(s)
1.	Single Layer	PVAc: 30%–toluene:70% at 118°C	----	----	5.44	30	[9, 25]
2.	Layer by layer	PS:9.75% - *p*-xylene: 90.25% at 32°C	563	218	15.44	6480	[26]
3.	Layer by layer	PS:5.01% - THF: 94.99% at 32°C	533 each	120	9.98	2260	[26]
4.	Single Layer	PS:5.01% - THF: 94.99% at 32°C	1010	61	1.88	3240	[26]
5.	Single Layer	PVAc: 10%–toluene:90% at 40°C	-----	-----	10.60	5000	[19]
6.	Single Layer	Cellulose Acetate: 17.2%–Acetone:82.8% at 70°C	----	-----	3.17	100	[27]
7.	Layer by layer	PS:10.06% - THF: 89.94% at 32°C	525 each	229	19.71	3240	[26]
8.	Single Layer	PS:10.06% -THF: 89.94% at 32°C	1327	174	4.92	3472	[26]
9.	Single Layer	PVAc : 10%–toluene:90% at 100°C	-----	-----	2.38	5000	[19]
10.	Single Layer	PS:15.14% -THF: 84.86% at 32°C	1891	409	9.78	7144	[26]
11.	Single Layer	PVAc: 30%–toluene:70% at 120°C	135.29		1.716		[28]
12.	Single Layer	PVAc: 30%–toluene:70% at 118°C	----	----	5.44	30	[9, 25]
13.	Single Layer	Cellulose Acetate: 17.2%–Acetone:82.8% at 70°C	----	-----	3.17	100	[27]

2.4 Research gap

- In the earlier literature [4, 10, 12, 15-18, 20, 21, 23] mainly interactions of different polymers and surfactant have been studied and analyzed. Drying mechanism of polymer coating using a surfactant has caught less attention.
- Few researches [4, 22] have used plasticizer such as TPP and fluorine based surfactant to study the effect on the mutual diffusion coefficients, drying rate, levelling effect of polymer/surfactant solution. The results showed an enhancement in drying rate by almost 10-15%.
- Fluorine based surfactants has been studied by few researches [10, 20] in organic solvents and study has been referred in water based coatings.
- Table 1 and 2 listed above show that there is always a certain amount of residual solvent left in the polymeric coatings.
- In this work, application of various surfactants on residual solvent content in water based polymeric coatings has been studied. In this work water soluble anionic, non ionic and fluorosurfactant has been used to study the effect caused by them on the polymer coating. PVA-water system has been selected to study surfactant effect on drying behaviour

2.5 Objectives

i. To reduce the amount of residual solvent present in water base polymeric coatings: PVA-water system.
ii. To find the suitable surfactant for water based polymers.
iii. To find the optimum amount of surfactant to be used for maximum solvent recovery.

Chapter 3

Materials and methods

3.1 Chemicals used

Poly(vinyl alcohol) (PVA) was provided by Lobachemie, India (density: 1.19g cm^{-3}, molecular weight: 115,000), poly(ethylene glycol) 6000 (PEG 6000) was provided by Spectrochem, India (density: 1.08g cm^{-3}, molecular weight: 5000-7000), Sodium dodecyl sulphate (SDS) was provided by SD Fine Chemicals, India (density: 1.01g cm^{-3}, molecular weight: 238.33). The solvent used was double distilled water (DD water), fluorosurfactant CAPSTONE FS-63 (35% solids, 20% isopropyl alcohol and 45% water) was provided by Rishichem distributors Pvt. Ltd, India (density: 1.1g cm^{-3}).

3.2 Methodology

The polymeric coatings are prepared using solution casting technique. The solutions were prepared by using above chemicals in different weight percentage. The weighed chemicals were poured in reagent bottles. Afterwards, the bottles were kept in digital water bath (LWB 311D, Daihan Labtech India Pvt. Ltd., India) at a temperature of 95ºC to dissolve PVA. After complete dissolution of PVA the bottles were kept for shaking in a mechanical shaker for 4 hours. The solutions were left overnight. Known amount of solution was poured into the sample holder to get the desired initial coating thickness. The schematic representation of the process is given below in Figure 3.1. In this work, the coatings of poly(vinyl alcohol) and poly(ethylene glycol)6000, poly(vinyl alcohol) and sodium dodecyl sulphate and poly(vinyl alcohol) and CAPSTONE FS-63 were dissolved in double distilled water.

Several solutions were prepared having different polymer mass fractions. The polymer mass fractions were kept 5% and 10% respectively. In all solution, the surfactant mass fractions were also kept same but their type has been changed. Only one surfactant was used at a time.

Solution 1: PVA (polymer): 5.00%, DD water (solvent): 95.00%

Solution 2: PVA (polymer): 5.02% PEG 6000 (surfactant): 1.03% DD water (solvent): 93.95%

Solution 3: PVA (polymer): 5.05%, SDS (surfactant): 1.02%, DD water (solvent): 93.93%

Solution 4: PVA (polymer): 4.99%, CAPSTONE FS-63 (surfactant): 0.96%, DD water (solvent): 94.05%

Solution 5: PVA (polymer): 10.00%, DD water (solvent): 90.00%

Solution 6: PVA (polymer): 9.99%, PEG 6000 (surfactant): 1.00%, DD water (solvent): 89.01%

Solution 7: PVA (polymer): 10.00%, SDS (surfactant): 1.00%, DD water (solvent): 89.00%

Solution 8: PVA (polymer): 10.1%, CAPSTONE FS-63 (surfactant): 1.11% DD water (solvent): 88.79%

Various coatings were prepared of different initial thicknesses by pouring a known amount of polymer solution in the circular sample holder by the use of micropipette. The dimensions of circular sample holder are diameter: 12.24 mm, depth: 1000 µm as shown in the Figure 3.2. As the solution is poured into the circular sample holder, it spreads out into the entire area, the solvent starts to evaporate from the coating, resulting in weight loss of coating solution. The weight of sample was recorded as a function of time using Precisa analytical weighing balance (ES225SM-DR) having an accuracy of ± 0.0001 g. The method was continuous weighing until the weight of sample comes to a point where two or more consecutive weight becomes constant to confirm that drying process is stopped. For practical purposes drying of coatings was under natural convection. All the experiments were carried out at room temperature 27±1°C or as stated.

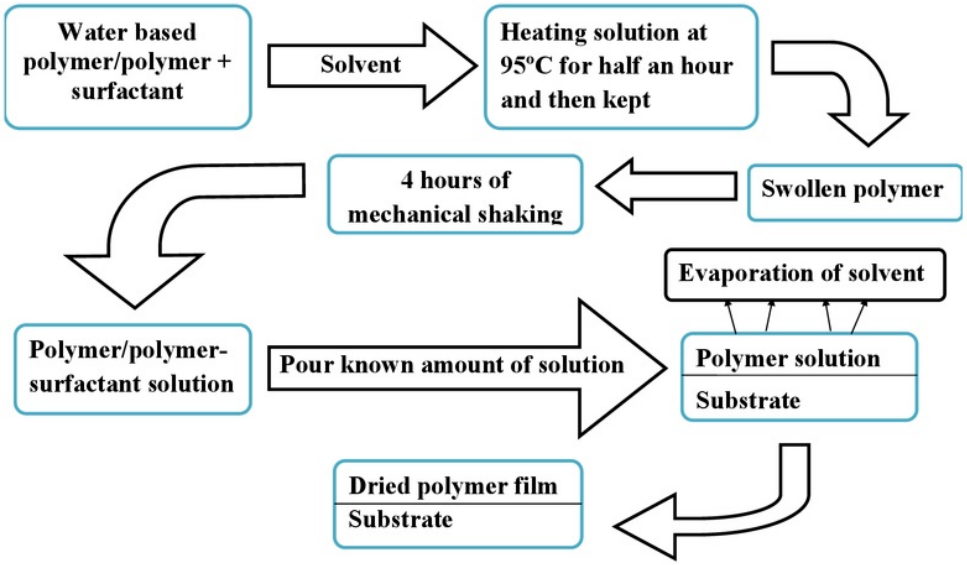

Figure 3.1: Schematic representation of polymer/polymer-surfactant solution for coating preparation

Figure 3.2: Circular sample holder

3.3 Calculations of various coating parameters:

Let the total mass of solution at 0 second is 3635.38 mg of polymer solution having 5.02% polymer and 94.97% solvent respectively.

Total mass of solution = 3635.38 mg

Weight of sample holder = 3558.24 mg

Exact mass of solution = 3635.38 – 3558.24 = 0.07714 g

Mass of polymer = $0.07714 \times \frac{5.02}{100} = 0.003872$ g

Mass of solvent = 0.07714 - 0.003872 = 0.07326 g

Density of polymer = 1.04 g cm^{-3}

Volume of polymer = $\frac{0.003872}{1.04} = 0.003723$ cm^3

Density of solvent = 0.866 g cm^{-3}

Volume of solvent = $\frac{0.07326}{0.866} = 0.084596$ cm^3

Total volume =0.003723 + 0.084596 = 0.088319 cm^3

Concentration of polymer = $\frac{0.003872}{0.088319} = 0.043846$ g cm^{-3}

Concentration of solvent = $\frac{0.07326}{0.088319} = 0.082949$ g cm^{-3}

Cross-sectional area of circular sample holder = 1.177 cm^2

Thickness = $\frac{0.088319 cm^3}{1.177\ cm^2} \times 10000 = 752 \mu m$

% Residual solvent = $100 \times \frac{0.07326g}{0.07326g} = 100\%$

Chapter 4

Results and Discussion

The effect of different types of surfactant on drying behaviour of poly(vinyl alcohol)-water coatings haven been studies and discussed here.

4.1 Drying study of Coating having 5% poly(vinyl alcohol)

Four solutions of poly(vinyl alcohol) were prepared in double distilled water.

Solution 1: poly(vinyl alcohol) and double distilled water

Solution 2: poly(vinyl alcohol), poly(ethylene glycol) and double distilled water

Solution 3: poly(vinyl alcohol), sodium dodecyl sulphate and double distilled water

Solution 4: poly(vinyl alcohol), Capstone FS-63 and double distilled water

The weight percentage of all the components in above solutions is given in Chapter 3.

Set 1: Drying study of 5% PVA coatings of nearly 600µm thickness

4.1.1 Percentage of Residual Solvent

The change is residual double distilled water in show in Figure 4.1. It shows that the percentage of double distilled water is decreasing with time. In solution 1, the residual DD water linearly decreases up to 2 hr 34 minutes having initial thickness 583µm. Up to 96.56% of solvent has evaporated and remaining 3.44% will be permanently trapped in the coating. The coating of solution 2, 3 and 4 have followed the same trend, the residual solvent is decreasing linearly upto 2 hr 14 minutes, 2 hr 29 minutes and 4 hr 51 minutes having initial thicknesses of 448µm, 592µm and 557µm respectively. Upto 98.67%, 93.12% and 99.44% solvent have evaporated, leaving 1.33%, 6.88% and 0.56% permanently trapped in the coatings. More amount of solvent has been removed in the large drying time. At first, it is decreasing linearly but at a fast rate due to presence of high amount of solvent at top surface. After a certain time, the rate decreases due to poor diffusion of solvent and also the process becomes diffusion controlled [19]. Least amount of residual solvent was left in

coatings having fluorosurfactant as can been seen in the solution 1 which is in agreement with the earlier findings about the effect of surfactant [20]. However, in solution 2 and solution 3, the percentage of residual solvent is lower and higher than solution 1 respectively. Solution 3 is having an anionic surfactant which forms a self assembled structure and holds tightly to solvent water molecules whereas in non ionic surfactant is solution 2 the hydrophobic part tries to stay away from water causing the water to evaporate easily.

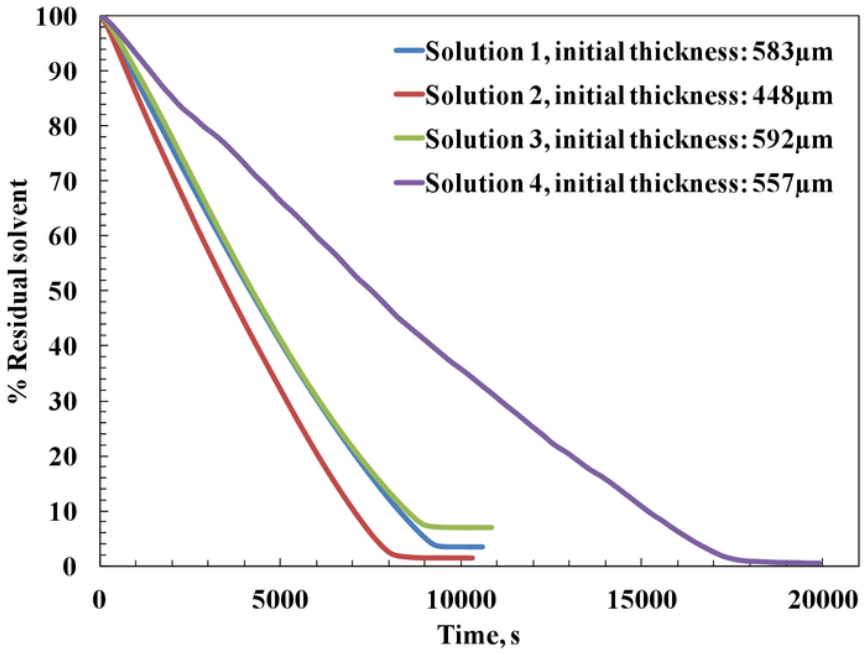

Figure 4.1: Residual solvent as a function of time.

4.1.2 Coating Thickness

The variation of coating thickness with respect to time is shown in Figure 4.2. It shows that the thickness of polymeric coating is decreasing with time. This is due to evaporation of solvent from the coatings. In solution 1, the thickness begins to decrease linearly till 2 hr 35 minutes having an initial thickness of 583µm. It decreases linearly as the solvent evaporates with time. Similarly in solution 2, 3 and 4 follows the same trend, the thickness decreases linearly up to 2 hr 14 minutes, 2 hr 28 minutes and 4 hr 50 minutes having initial thicknesses 448µm, 592µm and 557µm.

The coating left with more thickness has high amount of solvent trapped in them. The final thickness of solution 1, 2, 3 and 4 is 44µm, 30µm, 70µm and 28µm respectively. As it is clear from the values that coating of solution 3 is thickest of them all which imply that there is high amount of solvent left in the coating. However solution 2 has the minimum thickness but the initial thickness in that case was also lower as compared to the other solutions. Solution 4 has the lowest amount of residual present in the coating leaving it thin and completely dried. Coatings of solution 4 have least amount of solvent left due to presence of fluorosurfactant.

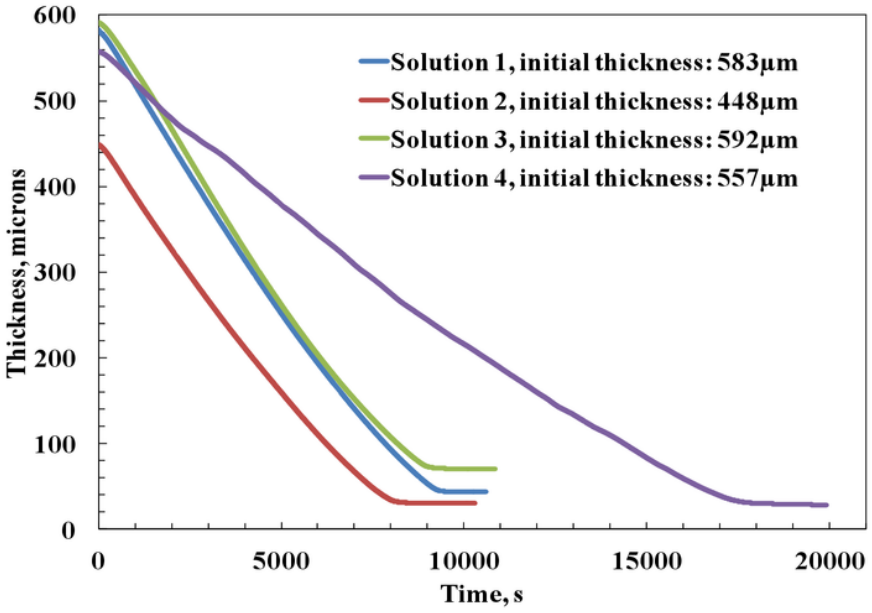

Figure 4.2: Coating thickness as a function of time.

4.1.3 Average Concentration of Double Distilled Water

The average concentration of double distilled water with respect to time is shown in Figure 4.3. It shows that concentration of double distilled water is decreases with time as it starts to evaporate. It decreases exponentially with time and levels off after a certain point. In solution 1 the solvent exponentially decreases up to 2 hr 40 minutes having an initial thickness of 583µm. Solution 2, 3 and 4 following the same trend decreases up to 2 hr 26 minutes, 2 hr 33 minutes and 4 hr 58 minutes having initial thicknesses of 448µm, 592µm and 557µm respectively. Solution 4 is having the

least concentration of double distilled water with a final concentration of 0.108g cm^{-3} where initial concentration was 0.955g cm^{-3}.It is observed that solution 4 coatings take more time for drying because of slow diffusion. The final concentration of solution 1, 2 and 3 are 0.440g cm^{-3}, 0.195g cm^{-3} and 0.551g cm^{-3} with initial concentrations of 0.958 g cm^{-3}, 0.948g cm^{-3} and 0.947g cm^{-3} respectively.

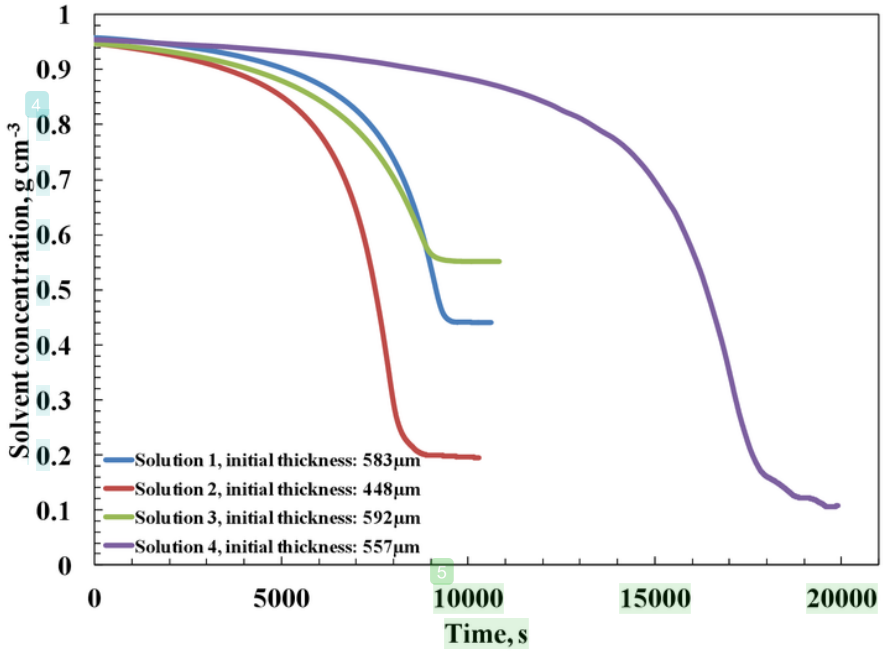

Figure 4.3: Solvent concentration as a function of time.

4.1.4 Average Concentration of Solid

Figure 4.4 shows the average concentration of solid [poly(vinyl alcohol) and surfactant] with time. Solid concentration increases exponentially with time and then levels off after a certain value. In solution 1, the solid concentration of coating exponentially increases up to 2 hr 39 minutes having initial thickness of 583µm. Other solution follows the same trend as described before, solution 2, 3 and 4 increases exponentially up to 2 hr 28 minutes, 2 hr 33 minutes, 4 hr 58 minutes having initial thicknesses 448µm, 592µm and 557µm respectively. The initial concentration of solution 1, 2, 3 and 4 were 0.050g cm^{-3}, 0.061g cm^{-3}, 0.061g cm^{-3} and 0.054g cm^{-3} and after evaporation of solvent the final concentration was 0.667g cm^{-3}, 0.942g cm^{-3},

0.518g cm^{-3} and 1.072g cm^{-3} respectively. The coatings with high solid concentration will have lowest percentage of residual solvent present in it. The solution with highest drying time and highest solid concentration is solution 4. It has low diffusion coefficient so solvent takes much time to evaporate but the final results are better than other solutions. The diffusion process in solution 4 is completely different than solution 1, 2, and 3 respectively. In solution 4, the evaporation of solvent is slow as compared to other solutions. The evaporation process is almost equal to the rate of diffusion of solvent within the polymer. Therefore, solution 4 is taking more time. The final concentration of solid is highest in this due to high amount of solvent removal. It may due to low glass transition of these coating and remains rubbery for longer period.

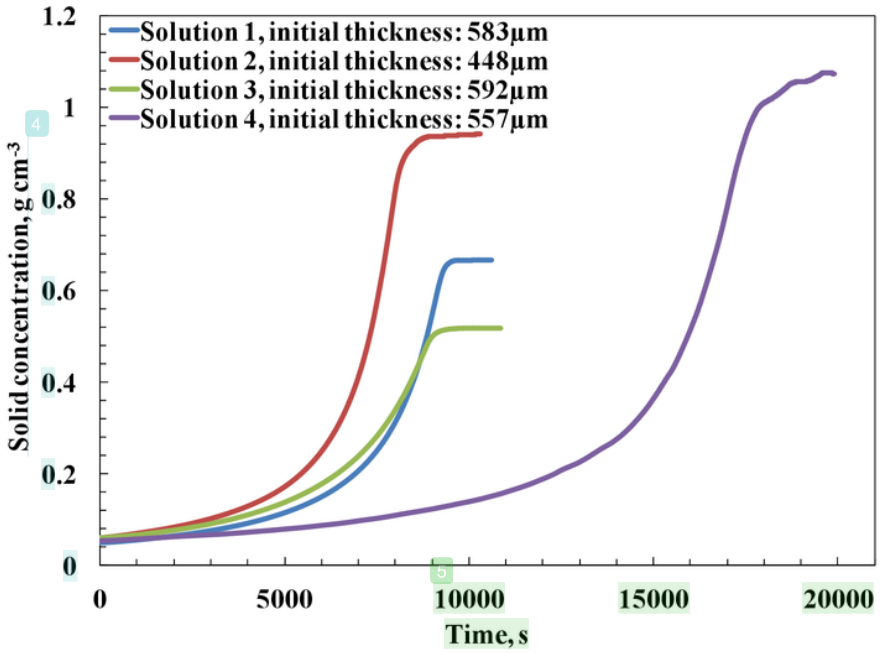

Figure 4.4: Solid concentration as a function of time.

Set 2: Drying study of 5% PVA coatings of nearly 700µm thickness

4.1.5 Percent of Residual Solvent.

Figure 4.5 depicts the change of residual double distilled water with time. It shows the percentage of residual solvent for all coatings is decreasing with time. In solution 1, the residual solvent linearly decreases up to 5 hr 24 minutes having an initial thickness of 703µm. Up to 91.96% of solvent has been evaporated and remaining 8.04% is remained trapped forever. Solution 2, 3 and 4 follow the same trend and linearly falls up to 4 hr 50 minutes, 5 hr 58 minutes and 5 hr 25 minutes having initial thicknesses of 675µm, 740µm and 672µm. In previous solutions 2, 3 and 4, the percentage of residual solvent evaporated is 95.72%, 97.28% and 99.97% leaving 4.28%, 2.72% and 0.30% permanently trapped in the coating. Solution 4 is having the least amount of percentage residual solvent left in the coating as compared to all the other coatings. Fluorosurfactant reduces the surface tension of the solution to a greater extent causing the solvent to move freely within the coating to the top surface and leaving less percentage behind.

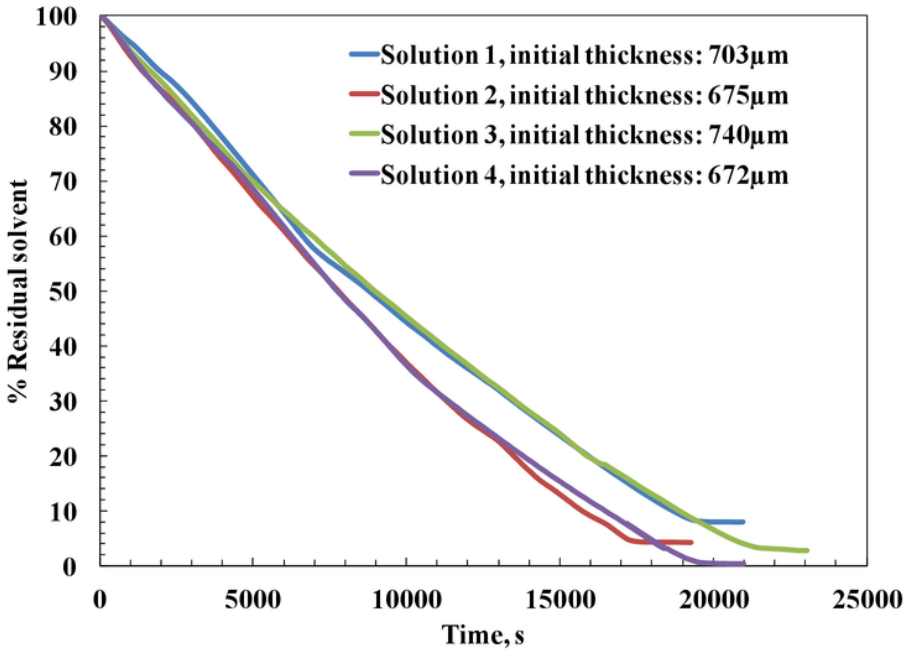

Figure 4.5: Residual solvent as a function of time.

4.1.6 Coating Thickness

Instantaneous coating thickness is shown in Figure 4.6. Coating thickness decreases linearly with time up to a certain point and then plateaus off. In solution 1 the thickness decreases linearly up to 5 hr 21 minutes and then reaches to a final value of 52µm, the initial thickness of the coating was 703µm. Solutions 2, 3 and 4 follows the same trend of linearly decreasing with time and levelling off; it decreases up to 4 hr 48 minutes, 5 hr 57 minutes and 5 hr 24 minutes reaching to a final thickness of 63µm, 100µm and 31µm respectively. The initial thicknesses of the solution were 675µm, 740µm and 672µm. The coating with more thickness will have a significant amount of percentage residual solvent left in it causing it to be thicker. However, the least thickness will have a very small amount of residual solvent present in it. The solution 4 has least thickness and is completely dried up with very less residual solvent content.

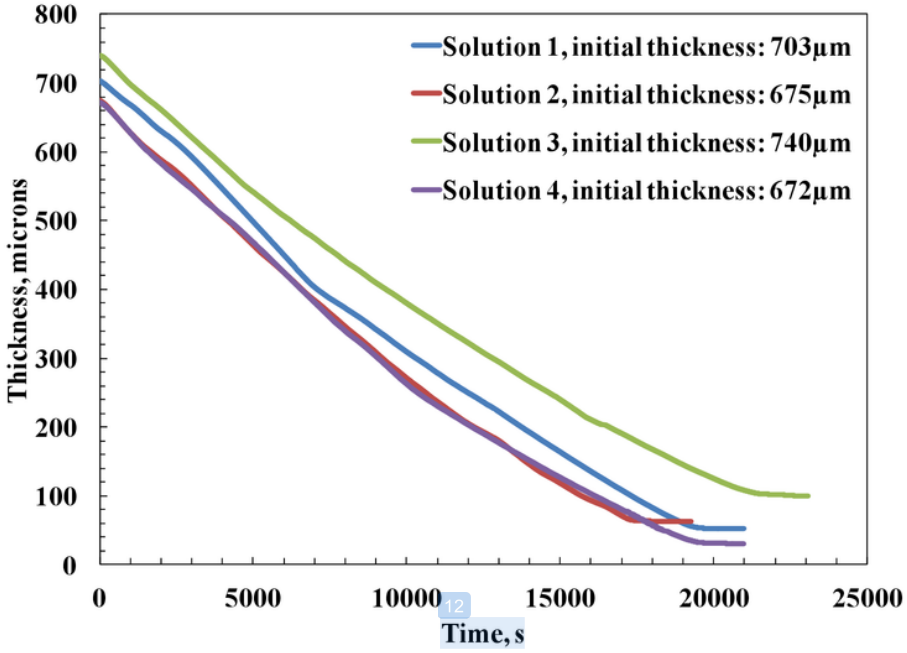

Figure 4.6: Coating thickness as a function of time.

4.1.7 Average Concentration of Double Distilled Water

Figure 4.7 describes the change in average concentration of double distilled water with time. The trend followed here is exponential decrease to a specific value and then levelling off. In solution 1, the solvent concentration decreases up to 5 hr 27 minutes having an initial thickness of 703µm. Solution 2, 3 and 4 followed the same trend and exponentially decreased up to a value of 4 hr 53 minutes, 5 hr 59 minutes and 5 hr 29 minutes with initial thicknesses of 675µm, 740µm and 672µm respectively. The final concentration of solutions 1, 2, 3 and 4 were 0.427g cm^{-3}, 0.438g cm^{-3}, 0.328g cm^{-3} and 0.059g cm^{-3} with initial concentrations of 0.958g cm^{-3}, 0.948g cm^{-3}, 0.947g cm^{-3} and 0.917g cm^{-3} respectively.

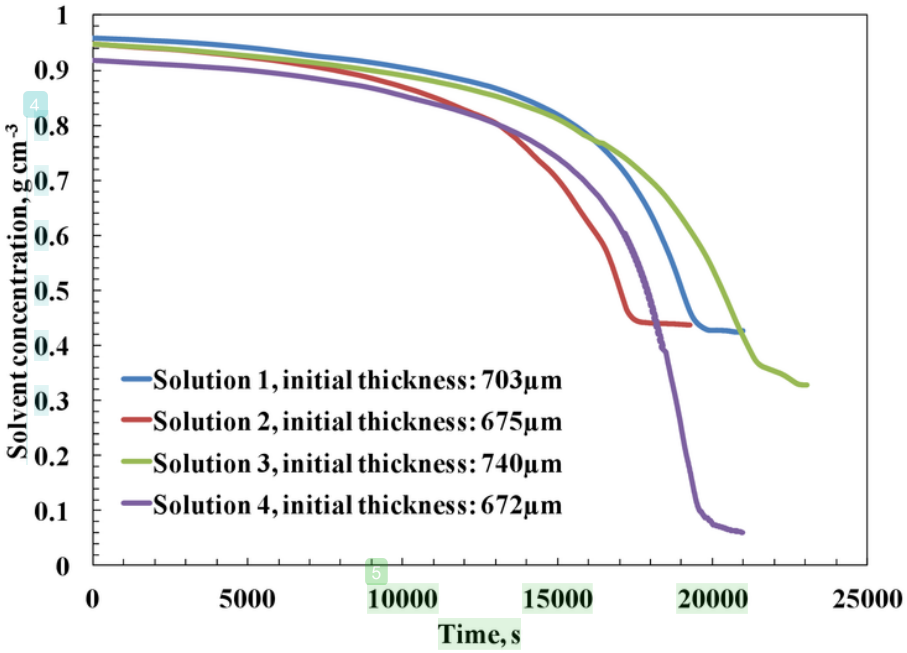

Figure 4.7: Solvent concentration as a function of time.

4.1.8 Average concentration of solid

The average concentration of solid [poly(vinyl alcohol) and surfactant] change with time is shown in Figure 4.8. The concentration increases exponentially and then plateaus off. In solution 1, the concentration increases linearly up to 5 hr 31 minutes

having an initial thickness of 703µm. The final concentration of the coating was 0.682g cm^{-3} where the initial concentration was 0.499g cm^{-3}. Solution 2, 3 and 4 also decreased exponentially up to 4 hr 54 minutes, 5 hr 59 minutes and 5 hr 31 minutes having initial thicknesses of 675µm, 740µm and 672µm respectively. The initial concentration of solution 2, 3 and 4 were 0.061g cm^{-3}, 0.061g cm^{-3} and 0.060g cm^{-3} reaching to a final concentration of 0.657g cm^{-3}, 0.779g cm^{-3} and 1.047 g cm^{-3} respectively. The coating which has least percentage of residual solvent will have highest concentration of solid. In this case solution 4 had the highest amount of solid concentration present amongst all solutions. The close comparison of Figure 4.1 and 4.5 shows completely different drying behaviour. However, the only change in the condition is the change initial thickness from 600µm to 700µm respectively. This change is just a physical change which is affecting the drying behaviour to a larger extent. It implies that thicker coating may be more viscous on the top due to evaporation of solvent but not able to stop the solvent diffusion into it by a larger extent. Therefore, the drying trends of all solutions are same for a longer period of time as shown in Figure 4.8. However, solvent has been removed from solution 4 is 99.97%. But, 99.44% solvent was removed in case of coating having initial thickness of 600µm as can be seen in Figure 4.1. This shows that recovery of solvent is almost same in both thinner and thicker case but is taking more time which is obvious due to high amount of solvent.

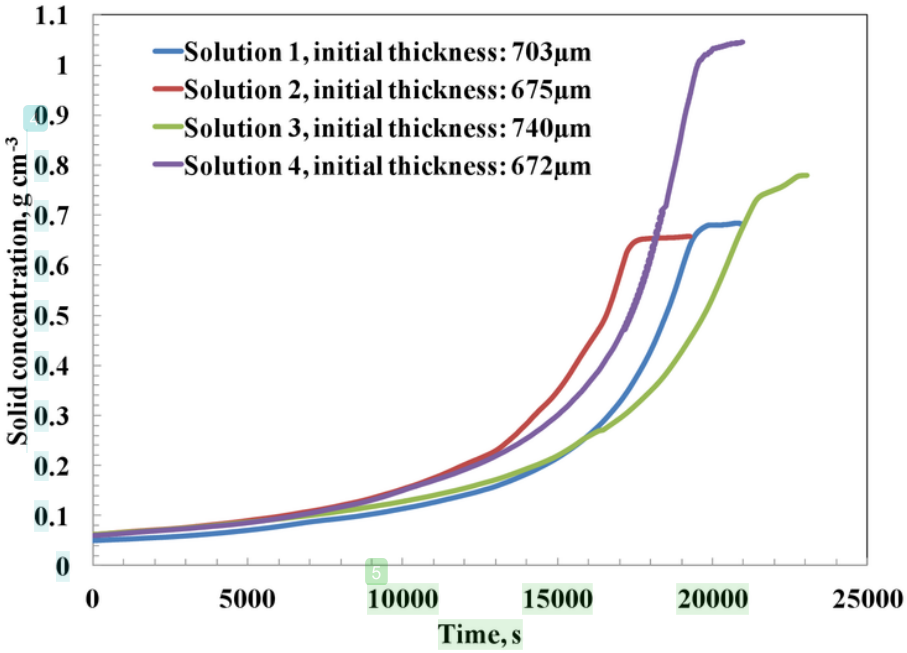

Figure 4.8: Solid concentration as a function of time.

4.2 Drying of coating of 10% poly(vinyl alcohol)

Four solutions of poly(vinyl alcohol) were prepared in double distilled water. The weight percentages of solutions above are given in Chapter 3.

Solution 5: poly(vinyl alcohol) and double distilled water

Solution 6: poly(vinyl alcohol), poly(ethylene glycol) and double distilled water

Solution 7: poly(vinyl alcohol), sodium dodecyl sulphate and double distilled water

Solution 8: poly(vinyl alcohol), Capstone FS-63 and double distilled water

4.2.1 Percentage of Residual Solvent

The change is percentage of residual solvent with time is described in Figure 4.9. The residual decreases linearly with time. In solution 5, the residual solvent linearly falls up to 2 hr 5 min having an initial thickness of 356µm. Solution 6, 7 and 8 followed the same trend, they linearly decreased up to 3 hr 59 minutes, 5 hr 26 minutes and 3 hr 1 minutes having initial thicknesses of 473µm, 637µm and 507µm respectively. In the four solutions from 1 to 4, the residual amount evaporated was

97.14%, 97.07%, 95.59% and 95.34% respectively left with 2.89%, 2.93%, 4.41% and 4.66% permanently trapped in the coatings. In the starting, the residual solvent is decreasing at a faster rate because there is a huge amount of solvent present on the top surface of the coating. As the time increases, the solvent drying rate becomes slower and then it becomes almost constant. The drying process shifts from being external transfer mass controlled to diffusion controlled. As observed in Figure 4.1 and 4.5, solution 4 which has a fluorosurfactant has least amount of percentage residual solvent present in it. However, in case of solution 8 with same components as solution 4 but different weight percentage of PVA, the observed result is not the same. This implies that for higher percentage of polymer percent in solution more amount of surfactant is needed to get required results. All the solutions have almost same amount of residual solvent present in it.

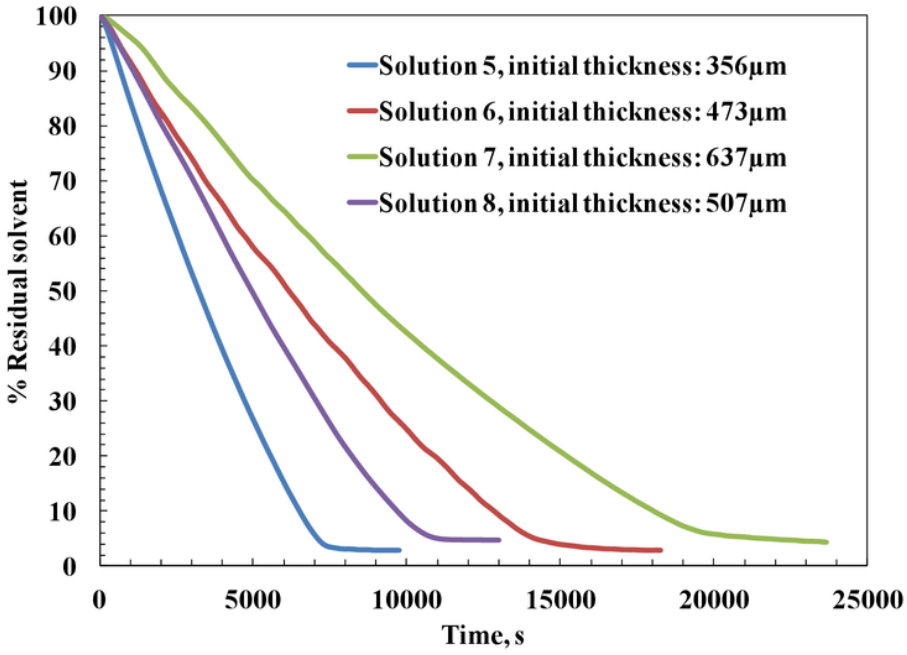

Figure 4.9: Residual solvent as a function of time.

4.2.2 Coating Thickness

Instantaneous coating thickness is shown in Figure 4.10. The coating thickness decreases with time. In solution 5, the thickness linearly decreases up to 2 hr 4

minutes having an initial thickness of 356µm. Solutions 6, 7 and follows the same trend and linearly decreases up to 3 hr 59 minutes, 5 hr 24 minutes and 3 hr 0 minutes having initial thicknesses of 473µm, 637µm and 507µm respectively. The final thicknesses of solution 5, 6, 7 and 8 were 40µm, 58µm, 87µm and 66µm. Solution 5 has least thickness but the initial thickness of the coating was comparatively very less to the other coatings. The solution with thickest coating will have high amount of residual solvent left in it. Solution 7 has highest initial coating thickness which implies that the solution is less viscous than other solutions but this still has high amount of residual solvent present in it.

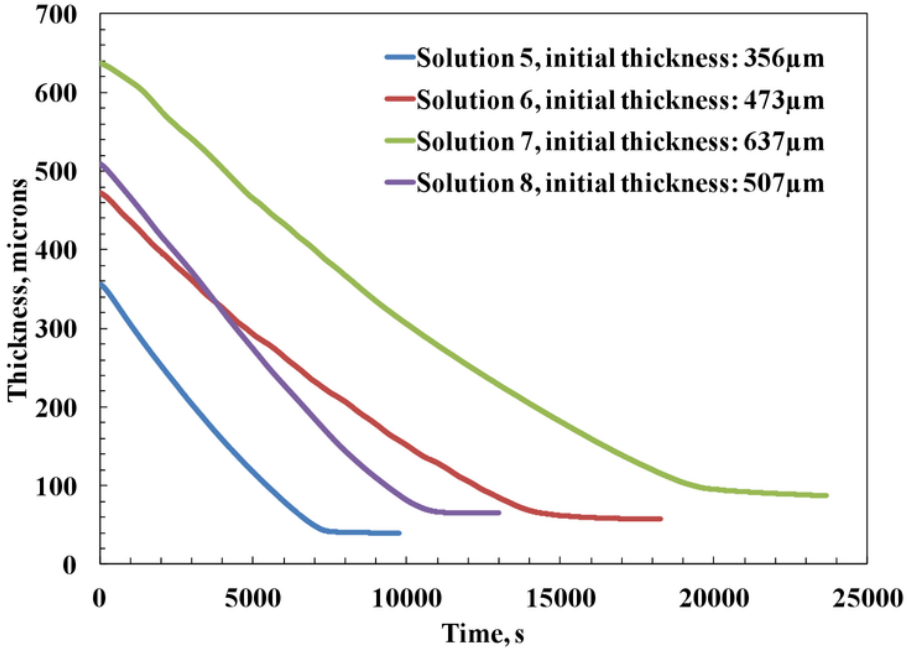

Figure 4.10: Coating thickness as a function of time.

4.2.3 Average Concentration of Double Distilled Water

Figure 4.11 shows the change of average concentration of double distilled water with time. The concentration of solvent exponentially decreases with time as it starts to evaporate. In solution 5, the concentration decreases up to 2 hr 7 minutes having an initial thickness of 356µm. Solution 6, 7 and 8 follows the same trend and exponentially decreases up to 4 hr 8 minutes, 5 hr 24 minutes and 3 hr 7 minutes

having initial thicknesses of 473µm, 637µm and 507µm. The final concentrations of solution 5, 6, 7 and 8 were 0.236g cm^{-3}, 0.219g cm^{-3}, 0.295g cm^{-3} and 0.318g cm^{-3} where their initial concentrations were 0.915g cm^{-3}, 0.905g cm^{-3}, 0.905g cm^{-3} and 0.876g cm^{-3} respectively. Very little differences are observed in the final concentration of solvent in all the coatings.

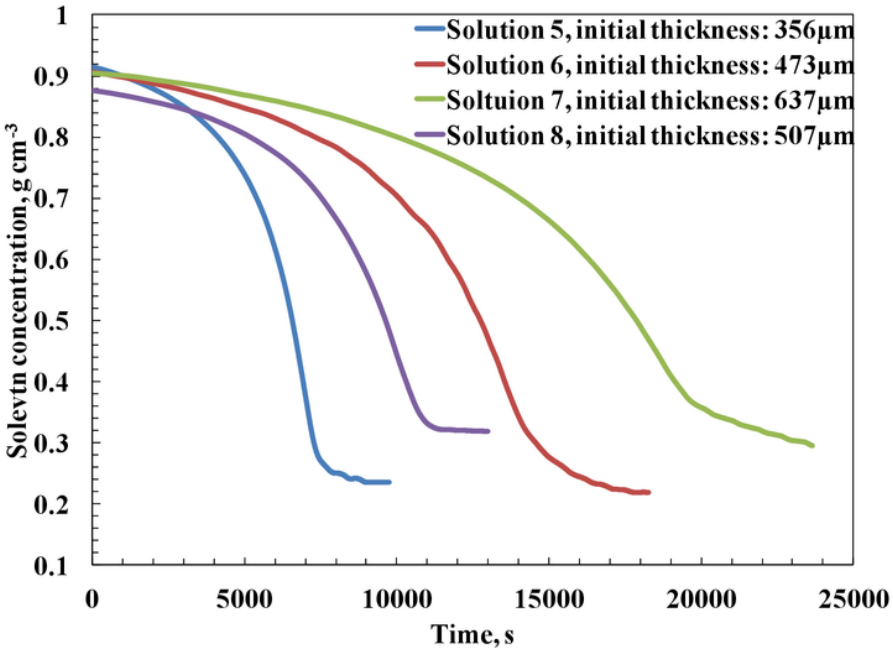

Figure 4.11: Solvent concentration as a function of time.

4.2.4 Average Concentration of Solid

Figure 4.12 shows the change in average concentration of solid [poly(vinyl alcohol) and surfactant] with time. The concentration of solid exponentially increases with time as the solvent evaporates from the coating. In solution 5, the concentration increases up to 2 hr 8 minutes having an initial thickness of 356µm. Solution 6, 7 and 8 follows the same trend and exponentially increases up to 4 hr 17 minutes, 5 hr 30 minutes and 3 hr 7 minutes having initial thicknesses of 473µm, 637µm and 507µm respectively. The final concentration of solution 5, 6, 7 and 8 are 0.909g cm^{-3}, 0.921g cm^{-3}, 0.827g cm^{-3} and 0.799g cm^{-3} where the initial concentrations were 0.102g cm^{-3}, 0.112g cm^{-3}, 0.112g cm^{-3} and 0.103g cm^{-3} respectively. In this case, it is very tough to

identify the best surfactant as the obtained results are same for all surfactants as shown in Figure 4.12.

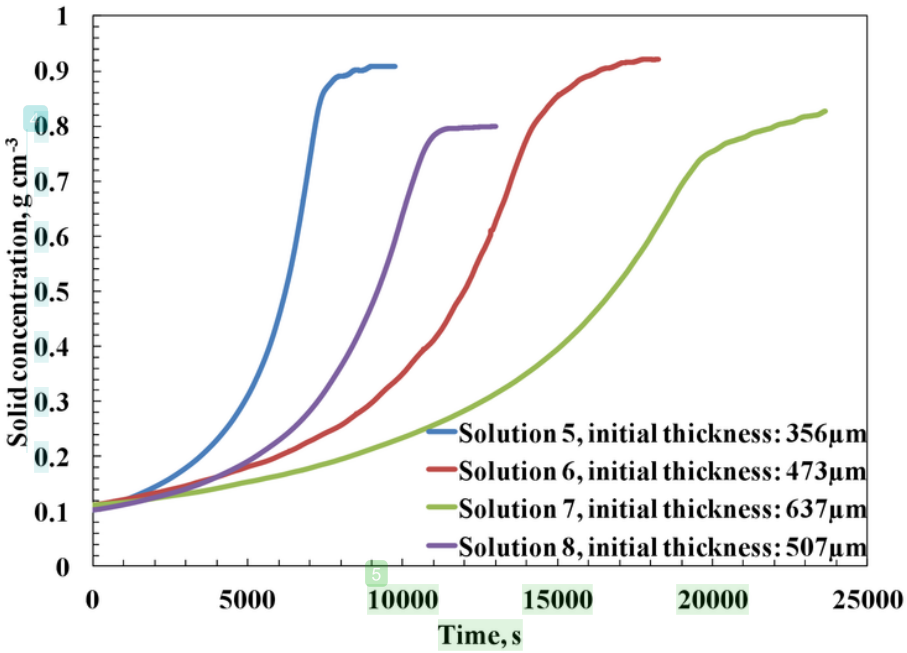

Figure 4.12 Solid concentration as a function of time.

Chapter 5

Conclusion

Drying of water based polymeric coatings has been studied. For this study, poly(vinyl alcohol)-water system has been studied. Effect of various coating parameters like thickness, concentration of solvent and polymer has been studied. The drying rate was very slow in this system due to very low evaporation rate of water from the polymeric coating. The drying rates were manipulated by using various ionic, non-ionic and fluoro based surfactants. Ionic surfactant could not change the drying mechanism. However, the non ionic has changed the drying behaviour to a small extent. The major change was observed by the use of fluoro based surfactants.

The fluoro based surfactant has reduced the viscosity of the coating solution. These coatings showed a very slow drying rate for a sufficiently long period of time. Hence, the recovery of residual solvent was more in the coatings. This effect was clearly observed in polymeric coatings having 5% poly(vinyl alcohol). These findings are in agreement with earlier published data [20]. However, there was no difference in residual solvent for coatings having 10% poly(vinyl alcohol). This could be due to the less plasticizer effect of the surfactant because the surfactant percentage was kept same in both the systems. By changing the percentage surfactant the residual solvent recovery can be enhanced as was observed in previous solutions.

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