EFFECT OF PLASTICIZER ON THE DRYING OF POLY (STYRENE) - *p*-XYLENE POLYMERIC COATINGS

A Dissertation submitted in partial fulfillment

for the award of degree

of

Master of Science in Chemistry

By

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July 2019

Certificate

This is to certify that the dissertation work Entitled **"Effect of plasticizer on the drying of poly (styrene) - *p*-xylene polymeric coatings"** submitted by **Harmandeep Kaur (301702011)** in partial fulfilment for the award of degree of **Master of Science in Chemistry** from Thapar Institute of Engineering & Technology (TIET), Patiala, Punjab, is a genuine work done under the supervision of **Dr. Sanjeev Kumar Ahuja** and **Dr. Avinash Chandra, Associate Professors, Chemical Engineering Department.** This work has not been submitted partially or wholly to any other Institute or University for the award of this or any other degree or diploma.

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Decleration

I hereby declare that the work being presented in the dissertation report Entitled **"Effect of plasticizer on the drying of poly (styrene) – *p*-xylene polymeric coatings"** by me in the partial fulfilment of the requirements for the award of degree of **Master of Science in Chemistry** at School of Chemistry and Biochemistry, Thapar Institute of Engineering & Technology, Patiala, Punjab, is an authentic record of my work carried under the supervisions of **Dr. Sanjeev Kumar Ahuja** and **Dr. Avinash Chandra, Associate Professors, Department of Chemical Engineering, Thapar Institute of Engineering & Technology, Patiala.** The matter presented in this dissertation has not been submitted in any other Institute or University for the award of any other degree or diploma.

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Abstract

The residual solvent study in poly (styrene) (PS) – *p*-xylene (PX) based system has been carried out. The effect of plasticizer: triphenyl phosphate (TPP), on the drying time, residual solvent %, coating thickness, solid/solvent concentrations in coatings of nearly 2000 μm and nearly 1300 μm has been investigated. Plasticizer loadings were changed from 0.52% to 2%. The residual solvent left was 2.62%, 2.50% , 2.49%, 2.87% and 1.35% in coatings having 0%, 0.52%, 1.02%, 1.51% and 2% TPP, respectively. The effect of plasticizer loading on the drying time was also investigated. Solutions with higher plasticizer concentrations took more time for drying but effective reduction in % residual PX was observed.

Table of Contents

List of Tables

List of Figures

Chapter 1

Introduction

1.1 Background

Polymers are macromolecules created by polymerization of many small molecules called monomers [1]. Polymeric coatings are thin layers of polymers that can be made by dissolving polymers in organic or inorganic solvents and are primarily used to protect the underlying substrate [2]. For functional coatings, most polymers are not water soluble and so organic solvents are used [3]. The solvent chosen should be cheap, abundantly available, and non-toxic. It should be able to completely dissolve the polymer, and should not allow any manufacturing defects like wrinkles, vesicles, crevices etc., because these factors influence the drying step [4, 5, 6]. Mostly volatile solvents are used in order to reduce the cost.

Pure polymers are affected adversely by environmental factors such as mechanical stress, corrosion, cracks, weathering, heat or flames, UV radiations etc. [7]. The additives makes a superb accompaniment to polymers as they improve basic polymer characteristics such as flexibility, extensibility, thermo-plasticity and increases flow by decreasing the glass transition temperature (T_g), melting temperature (T_m) and viscosity of polymer [8].

Plasticizers are one of the major class of additives that increases the plasticity or fluidity of polymers due to strong interactions between polymer subunits and plasticizer molecule [10]. Only a small amount of plasticizer can effectively improve the basic properties of polymer. The properties of brittle polymers can be improved by using plasticizer such as triphenyl phosphate (TPP) and as a result the rigid polymer can become flexible [9, 11].

1.2 Polystyrene applications

Polystyrene being a thermoplastic is of high significance as it can be easily injection moulded and then can be reprocessed frequently [10]. Poly (styrene) solid foam find applications in medical devices like diagnostic equipment due to ease of sterilization and its clarity. In other laboratory ware to form test tubes, petri dishes, flasks, and pipettes [13]. Expanded polystyrene (EPS) and extruded polystyrene (XPS) are embedded in materials to impart insulating and cushioning properties. Because this kind of insulation bring reduction in energy used within buildings by controlling indoor temperature. Rigid foam form of polystyrene can be more than 95% air and is used as lightweight protective packaging. It is

mostly used in appliance and home insulation, and solid and foam forms of polystyrene are used in CD and DVD cases, ovens, microwaves, blenders, refrigerators, air conditioners . Because of their inertness, durability, and water resistance, they are cost effective and long lasting in making automobile parts, gardening pots, in child protective seats, in roadways, and road bank stabilization systems [12,14].

1.3 Preparation of polymeric coatings

Polymeric coatings can be prepared by dissolving a polymer in a solvent using various methods depending on the requirement:

- **a)** solution casting method [15],
- **b)** spin casting method [16],
- **c)** drop casting method [17],
- **d)** film casting method [18].

Among these methods, the solution casting method is the easiest to operate for polymer coating preparation at industrial scale as well as on laboratory scale. In this method, the homogeneous solution with low viscosity is prepared by dissolving the polymer in one or more volatile solvents. Also it includes simplified incorporation of additives. Additionally, it is a convenient method for the production of high temperature resistant films even when processing at low temperatures.

This method provides greater film thickness uniformity, with extremely low haze, excellent flatness, dimensional stability, and maximum optical purity [19]. A schematic representation of the solution casting technique is shown in Figure 1.

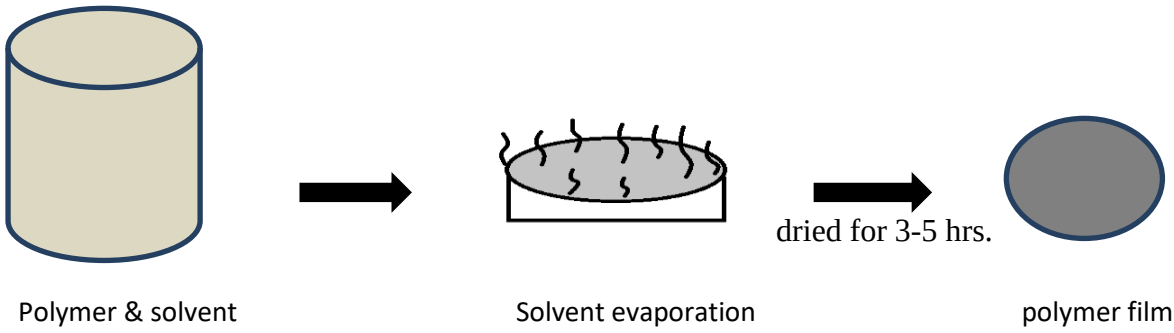


Figure 1.1: Schematic representation of solution casting technique.

1.4 Polymer coating drying

Drying is the ultimate and quality controlling step, which brings about essential changes in coating properties [19]. Although the drying of polymer solutions is a complex process involving heat and mass transfer yet it plays an important role in the manufacture of synthetic fibres, paint coatings, functional films and other polymeric products [20]. During the course of drying physical and chemical changes such as crystallization, shrinking, glass transition, texture, order and colour takes place along with change in phase of polymeric solution, which is wet in the beginning, but at the end of drying, a solid polymeric coating is generated. It is necessary to dry the polymeric coatings in controlled drying conditions to get excellent polymer coatings. Otherwise, due to improper drying, some unwanted changes like cracks, blisters and insufficient removal of solvent may occur [21].

1.5 Plasticizers applications in polymeric coatings

Plasticizers can be used to amend different properties of polymer coatings. Plasticizers, due to their compatibility with the polymer, penetrate into it and occupy the free volume around polymer chains [22]. Polystyrene is brittle and hard enough but it become rubbery when they are plasticized with solvents or other additives with low volatility, which in return reduces glass transition temperature by embedding themselves between polymer subunits or chains. In this way, plasticizer helps in pushing the polymer chains apart to make them more flexible, because there is increase in the plasticity, free volume of polymer, and this results in decrease in the viscosity, tensile strength, elastic modulus, and, thus, the glass transition temperature is lowered down [24]. Low molecular weight non-volatile plasticizer's primary purpose is to improve the workability, process-ability, toughness and flexibility of polymers, and, hence, lower thermal processing temperatures can be applied [14].

Polystyrene is flammable, but with the addition of an additive triphenyl phosphate (TPP), the flame resistance can be imparted to polystyrene. TPP can decompose to phosphoric acid on migrating to the surface and could form a protective layer to protect the polymer substrate from oxygen and flame [23]. Hence, TPP can act both as a flame retardant and plasticizer. Also, to produce flexible and successive polymeric coating, the residual solvent content should be minimum in the coating. Plasticizers influence the drying significantly. It has been found that only a small amount of plasticizer can alter the behaviour of polymeric coatings. Only little increase in concentration of plasticizer can enhance the drying rate along with

adequate removal of solvent. Therefore, aryl phosphates being thermally stable and due to their good plasticization and compatibility with many polymers helping to produce flexible films by improving the mechanical properties of coating, enhancing drying rate and responsible for the significant removal of solvent at the end of drying operations [25].

Chapter 2

Literature Review

This chapter includes literature of polymer-plasticizer system and solvent based polymeric coatings.

Jang and Wilkie [23] worked on the thermally stable triphenyl phosphate (TPP) and resorcinol bis(diphenyl-phosphate) (RDP), non halogenated fire retardants. They used TGA\FTIR and GC\MS techniques to study how the blends of the (PC\RDP) and (PC\TPP) were thermally degraded in air. They analysed the thermal degradation of both PC\RDP and PC\TPP blends and confirmed that both RDP and TPP can significantly reduce bisphenol A evolution, which is, in general, a product of alcoholysis/hydrolysis of carbonate linkage. Bisphenol A is evolved when the alcohol products produced through alcoholysis during polycarbonate (PC) thermal degradation reacts with some amount of phosphate. This leads to the formation of branched phosphate structures with the PC chain, which inhibits heat and mass transfer of degraded products. They concluded that in the case of polymers which can be thermally degraded, both TPP and RDP provide effective fire retardancy in spite of having different volatilization temperature by delaying degradation of polymers as they both possess phosphate group which form branched structures with polymers.

Sharma et al. [26] studied poly (styrene) – poly (methyl methacrylate) – tetrahydrofuran (PS-PMMA-THF) polymeric coatings. By using gravimetric weight loss data, they calculated average concentration of THF, PS, PMMA and variation in coating thickness with time. They observed that on doubling the PMMA mass fraction, the drying process slowed down due to very slow diffusion process within these coatings. But when polystyrene content was doubled within these coatings, there was no significant change in the drying mechanism. Hence, the residual solvent content did not change significantly on changing the PS content in system having 10% PS, but on doubling the PMMA content, very small reduction in residual solvent content was observed in nearly 5% PS systems. Therefore, the drying mechanism in the coating studied was greatly influenced by PMMA but was not a strong function of PS.

Jarray et al. [22] predicted the polymer - plasticizer compatibility during coating formulation for the hydroxypropyl-methylcellulose - polyethylene glycol (HPMC-PEG), microcrystalline cellulose-polyethylene glycol (MCC-PEG), and polyvinylpyrrolidone - polyethylene glycol

(PVP-PEG) systems using different methods including differential scanning calorimetry (DSC), molecular charge density using conductor-like screening model (COSMO), mesoscale simulation using dissipative particle dynamics (DPD) and molecular dynamics to calculate solubility parameter. They observed that all the different methods showed similar results. In case of HPMC and PVP polymers, the PEG plasticizer diffused well into the polymers because there was better interaction between these polymers and plasticizer. But MCC surrounded PEG and there was no diffusion of plasticizer because PEG and MCC were not miscible. Hence, compatibility of the plasticizer with the polymer led to high miscibility of polymer and plasticizer and the diffusion of plasticizer into the coating during film formation. Thus, it helps in producing stable and homogeneous coating film.

Arya [19] studied on the poly(methyl methacrylate)–tetrahydrofuran (PMMA-THF), poly (styrene)–tetrahydrofuran (PS-THF) and poly (styrene) – *p*-xylene (PS-PX) systems to measure the concentrations of polymer and solvent by using Confocal Raman spectroscopy. They observed that in case of high volatile solvent such as in PMMA-THF and PS-THF systems, the profiles measured using confocal Raman Spectroscopy are in accordance with free volume predicted profiles. But when the less volatile solvent system was studied which comprised PS-PX system, then it was observed that free volume model was incapable to envisage the complete drying behaviour.

Bhargava and Arya [27] studied the designing of several binary coatings of PS-THF and PS-PX with the aim to lessen the residual solvent. They performed experiments under quiescent drying conditions without any air flow. They made coatings with different poly (styrene) concentrations ranging from 5 wt.% to 15 wt.% approximately and performed numerous experiments for different coating thickness. They observed that in thick polymeric coating, the residual solvent left was minimum. Besides, the thinner coatings took less drying time in comparison to the thicker coatings due to the presence of smaller amount of initial solvent in the beginning of the polymeric coating. They concluded that it was advantageous to apply thicker coating once rather than layer by layer as it helped in minimizing the residual solvent.

Liang et al. [24] studied the effect of *o*-terphenyl (OTP) plasticizer on the T_g of PS using Fourier transform infrared spectroscopy. They studied the peak areas versus temperature curves for four conformation insensitive bands in the spectrum of PS in which two bands

were allocated to the modes of vibrations of the main chain and the other two to the side groups of PS. They observed that when PS was mixed with OTP, then for the main chain, due to cohesional entanglements, the reorientation relaxation temperature was lower than that of the side groups. This was happened because the side groups reorientation relaxation region was nearly same as the glass transition region of PS which was macroscopically observed. It pointed out that the glass transition process of PS was greatly influenced by reorientation of side groups.

Wang et al. [28] studied a mathematical model based on free volume theory to predict solvent self-diffusion coefficients in case of amorphous glassy polymers. They analysed how solvents such as ethyl benzene, benzene, methyl acetate, methyl ethyl ketone, and toluene helped in plasticization to accurately determine the fluctuation in the hole-free volume above and below the T_g. They used free volume parameters to calculate the solvent mutual-diffusion coefficients. On comparing values calculated using mathematical model with the experimental data already available on solvents blended in PS and PMMA, the measured results were in agreement with the predicted values.

Chapter 3

Materials and Methods

3.1 Materials

Table 3.1. Listing of Materials Used

Name of Chemical	Name of Supplier	Molecular weight, ($g\ mol^{-1}$)	Density, ($g\ cm^{-3}$)
Poly(styrene) (PS)	Sigma Aldrich, (USA)	192000	1.04
Triphenyl phosphate (TPP)	Sigma Aldrich, Germany	326.28	1.18
p-xylene (PX)	Loba Chemie	106.17	0.861

All the chemicals were used in pure form without purifying further.

3.2 Methodology

In the present work, five different kind of polymeric solutions with different concentrations of PS-TPP-PX were prepared for the polymeric coating preparations. By using semi-micro analytical weighing balance (222M DR, Precisa) having least count ±0.0001g, a required amount of solvent, plasticizer and polymer were weighed. These prepared polymeric solutions were decanted carefully into closely sealed bottles. After this to get the homogeneous solution, these sample bottles were kept in shaker for mechanical shaking at 200 rpm for 2 hours.

For the preparation of polymeric coatings, the solution casting technique was used. To get the desired initial coating thickness, a required amount of polymeric solution was taken from the sample bottle and decanted with micropipette into the sample holder which is of stainless steel and is circular in shape with 14.75 mm diameter and with depth 2000 µm. Several type of coatings with different initial thickness were prepared using different polymer solutions. The solvent evaporated immediately after the solution was decanted in the circular sample holder, therefore the loss in mass of the polymeric coating was recorded at an interval of 5 s

by using semi micro analytical weighing balance. The readings were taken until the polymeric coating dried completely. This was ensured when for a sufficient long time gap, there was no change recorded in two consecutive weight data. The polymeric coatings dried completely within 3-5 hours approximately. Then these coatings were considered dried for practical purposes. All the experiments were carried out at 26±1ºC. The different coating solution compositions are represented in Table 3.2. By using standard volumetric methods given in previous literature, different coating variables like % of residual solvent, concentration of PS, concentration of PX, coating thickness, solid (PS + TPP) concentration, and non dimensional thickness were calculated.

Table 3.2. Different Type of Coating Solutions

Solution type	PS (wt.%)	TPP (wt.%)	PX (wt.%)
A	4.95	0	95.05
B	5.02	0.52	94.46
C	5.03	1.02	93.95
D	5.02	1.51	93.47
E	5	2	93

3.1.3 Calculations

Sample calculations are shown for a particular coating. Let "*m*" be the initial mass of polymer solution comprising of 5.02% PS and 94.46% PX, and 0.52% TPP

Mass of PS, $M_{PS} = m \times (5.02/100)$

Mass of TPP, $M_{TPP} = m \times (0.52/100)$

Initial mass of PX, $M_{PX} = m \times (94.46/100)$

Volume of PS, $V_{PS} = M_{PS}/density\ of\ PS$

Volume of TPP, $V_{TPP} = M_{TPP}/density\ of\ TPP$

Volume of PX, $V_{PX} = M_{PX} / density\ of\ PX$

Total volume, $V_T = V_{PS} + V_{TPP} + V_{PX}$

Concentration of PS = M_{PS}/V_T

Concentration of TPP = M_{TPP}/V_T

Concentration of PX = M_{PX}/V_T

% Residual Solvent = *final mass of PX / initial mass of PX*

Coating thickness = *total volume / area of sample holder* = $V_T / \pi r^2$

Radius of the sample holder = 7.38 mm

Chapter 4

Results and Discussion

4.1 Case 1: Coatings of Nearly 2000 µm Initial Coating Thickness

4.1.1 Effect of Plasticizer Loading on Residual Solvent %, Drying time, Coating Thickness, and Solvent/Solid Concentrations.

Figure 4.1 shows the residual solvent versus time in case of poly (styrene) (PS)-triphenylphosphate (TPP) - *p*-xylene (PX) polymeric coatings. These coatings were prepared by varying the mass percentages of TPP, namely, 0%, 0.52%, 1.02%, 1.51% and 2% as given in Table 3.2. Table 4.1 shows the residual solvent content left at the end of drying process corresponding to different coating compositions. These results indicate that the amount of residual solvent is decreasing with the increase in plasticizer wt.% within the coating. At the end of drying, up to 97.38%, 97.5%, 97.51%, 97.13% and 98.65% PX has been removed and the remaining 2.62%, 2.50%, 2.49%, 2.87% and 1.35% PX is permanently trapped in these polymeric coatings, respectively.

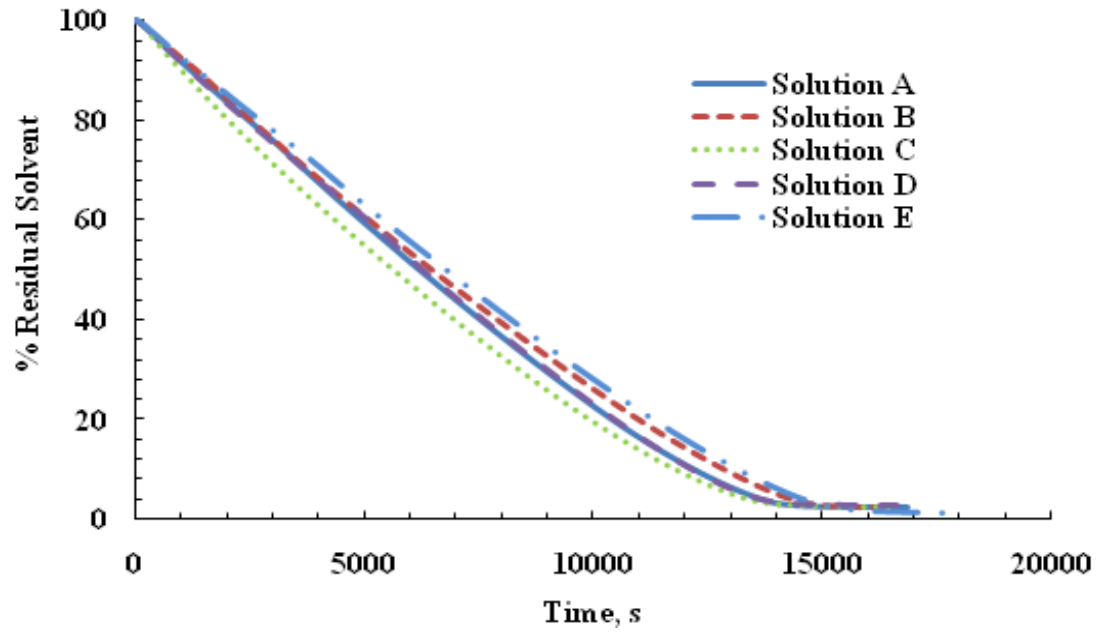


Figure 4.1: % Residual Solvent as a function of time, (s) for various TPP loading for nearly 2000 µm initial coating thickness.

Table 4.1 Drying Data of PS-TPP-PX Coatings of Nearly 2000µm Initial Thickness

Solution type	Coating thickness, (µm)		Final residual solvent, (%)	Solvent concentration, (g cm^{-3})		Solid concentration, (g cm^{-3})		Drying time, (s)	
	Initial	Final		Initial	Final	Initial	Final	Evaporation time, (s)	Constant time, (s)
A	2021	134	2.62	0.825	0.325	0.043	0.647	0-13650	13650-16839
B	2011	140	2.50	0.821	0.294	0.048	0.691	0-14310	14310-16305
C	1999	147	2.49	0.818	0.277	0.053	0.719	0-13179	13179-16571
D	2005	161	2.87	0.815	0.291	0.057	0.708	0-13500	13500-16630
E	2009	140	1.35	0.812	0.158	0.061	0.880	0-15520	15520-17966

The residual PX decreases linearly up to 227 min 5 s, 238 min 5 s, 219 min 65 s, 225 min and 258 min 68 s in the respective polymeric coatings having initial thickness 2021 µm, 2011 µm, 1999 µm, 2005 µm and 2009 µm, respectively. In the beginning, drying process was externally controlled and large amount of PX present evaporates at a very fast rate from the top surface of polymeric coatings. As a consequence, % of residual PX decreases linearly at a very fast rate. The rate of PX removal decreases with time because the mass transfer process becomes diffusion controlled. The least amount of residual solvent is left in the coating containing 2% TPP. It can be seen in Table 4.1, in general there is decrease in the residual solvent content with increase in the TPP wt.% with the exception of 1.5% TPP solution that exhibits maximum value of the residual solvent content. This indicates that the plasticizer reduces the polymer-polymer interaction by penetrating into the polymer matrix and increases the free volume. Also, there is increase in the evaporation time with increase in TPP wt.% with the exception of 1% TPP solution that exhibits minimum value of the evaporation time, as it can be seen in Table 4.1 and Figure 4.2.

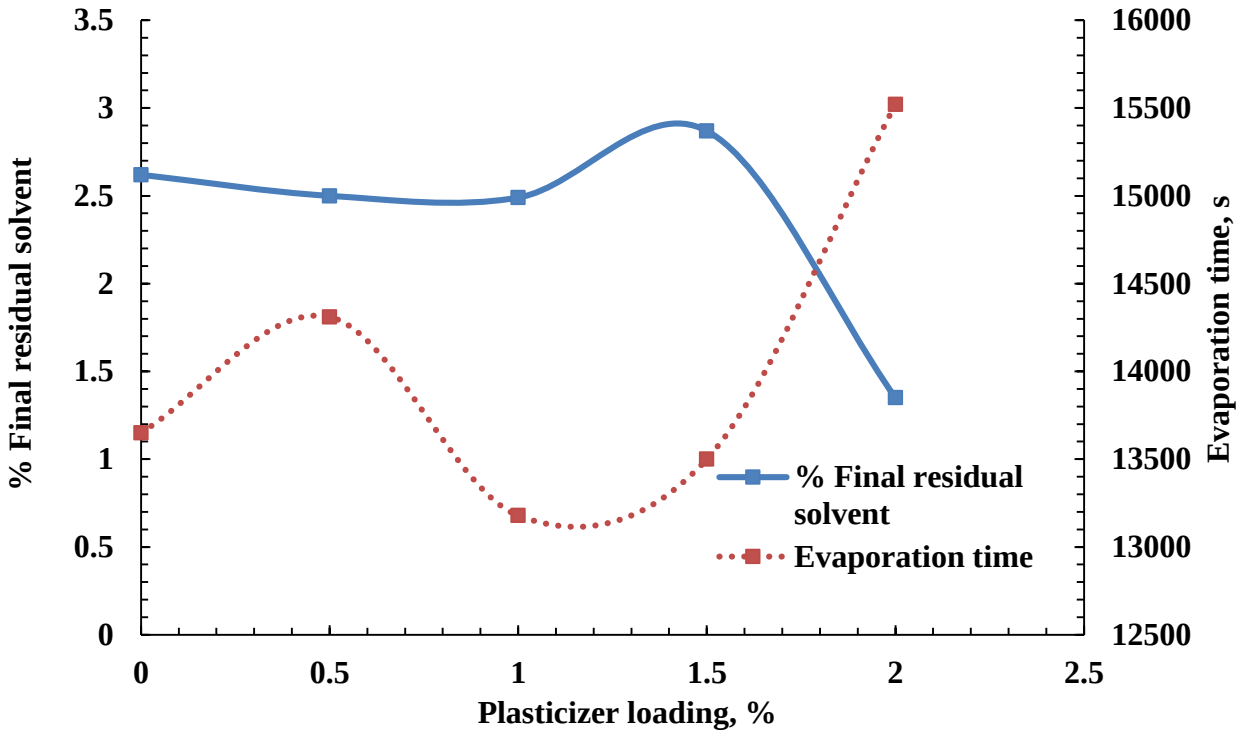


Figure 4.2: % Residual solvent and evaporation time, (s) as a function of plasticizer loading in case of polymeric coatings of nearly 2000 µm.

Figure 4.3 shows the coating thickness versus time in case of poly (styrene) (PS)-triphenyl phosphate (TPP) - *p*-xylene (PX) polymeric coatings. During the course of drying, coating thickness is decreasing because the solvent is evaporating from the polymeric coating into the surroundings. In all the cases, the coating thickness decreases linearly up to 225 min 30s, 234 min 73 s, 218 min 48 s, 223 min 16 s and 262 min 43 s, respectively and then it becomes constant. The initial and final coating thicknesses are shown in Table 4.1.

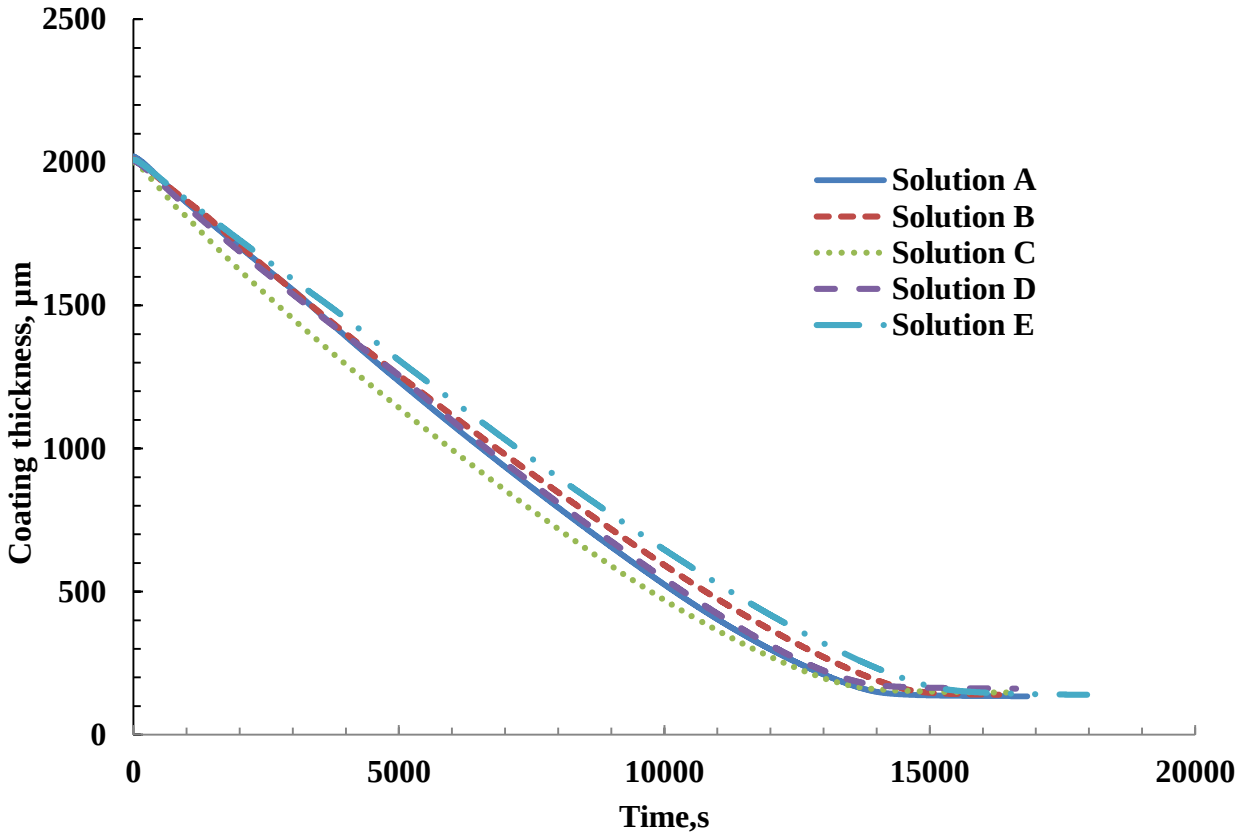


Figure 4.4 shows the concentration of solvent versus time in case of poly (styrene) (PS)-triphenyl phosphate (TPP) - *p*-xylene (PX) polymeric coatings. In the starting and at the end of drying process, the solvent concentrations are given in Table 4.1. In all the cases studied, there is an exponential decrease in the solvent concentration which indicates slow diffusion of solvent within the polymeric coating. In the case of polymeric coatings having initial coating thickness of 2021 µm, 2011 µm, 1999 µm, 2005 µm and 2009 µm, respectively, the concentration of PX decreases exponentially up to 246 min 63 s, 255 min 33 s, 242 min 83 s, 243 min 91 s and 293 min 18 s, respectively, and after this it becomes constant. In Table 4.1,

it is clearly shown that the solvent concentration is decreasing with the increase in plasticizer concentration.

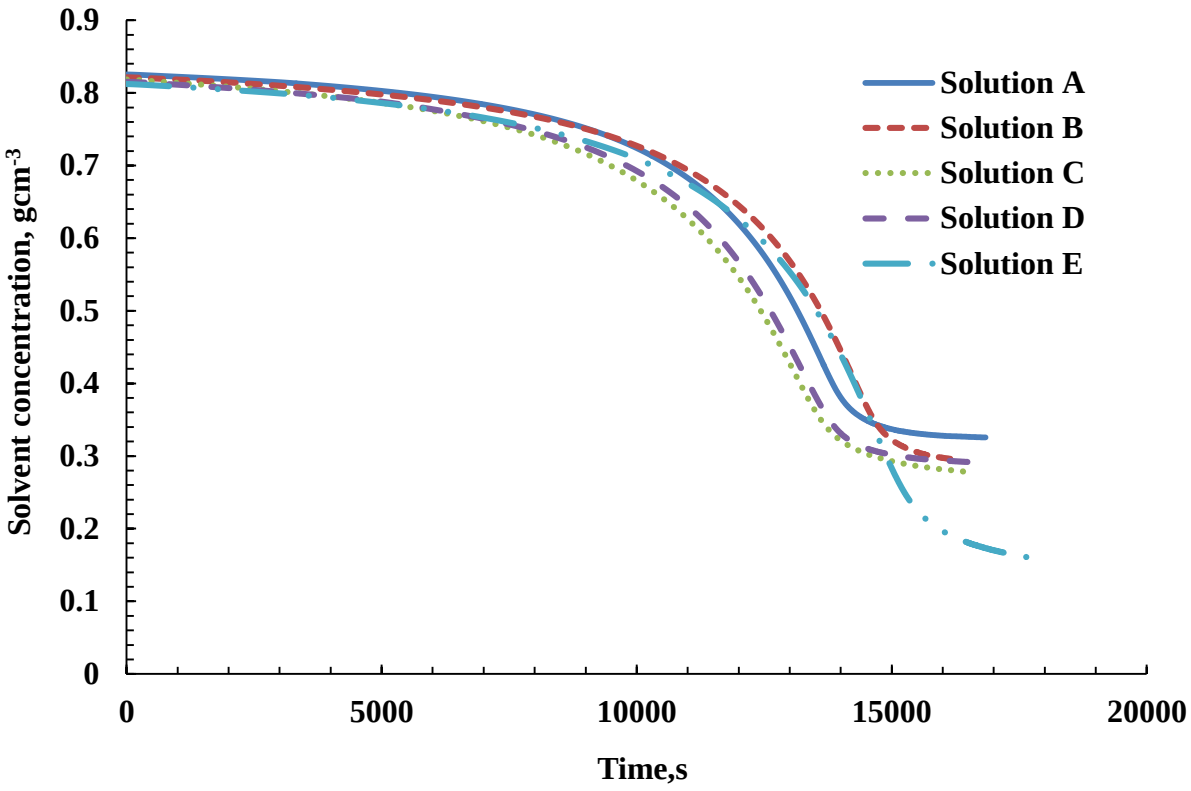


Figure 4.4: Solvent concentration, (g cm^{-3}) as a function of time, (s) for various TPP loading for nearly 2000 µm initial coating thickness.

Figure 4.5 shows the total solid (PS+TPP) concentration versus time in case of poly (styrene) (PS) – triphenyl phosphate (TPP) - *p*-xylene (PX) polymeric coatings. The initial and final solid concentrations are as provided in Table 4.1. It is clear from these results that solid concentration is increasing exponentially with increasing TPP wt.%, in all the different polymeric coatings with the initial coating thickness 2021 µm, 2011 µm, 1999 µm, 2005 µm and 2009 µm respectively. In polymeric coating with 2 wt.% TPP, the highest solid concentration is achieved as shown in Table 4.1 and Figure 4.5. Also, the polymeric coating containing 2 % TPP, contains minimum amount of residual solvent.

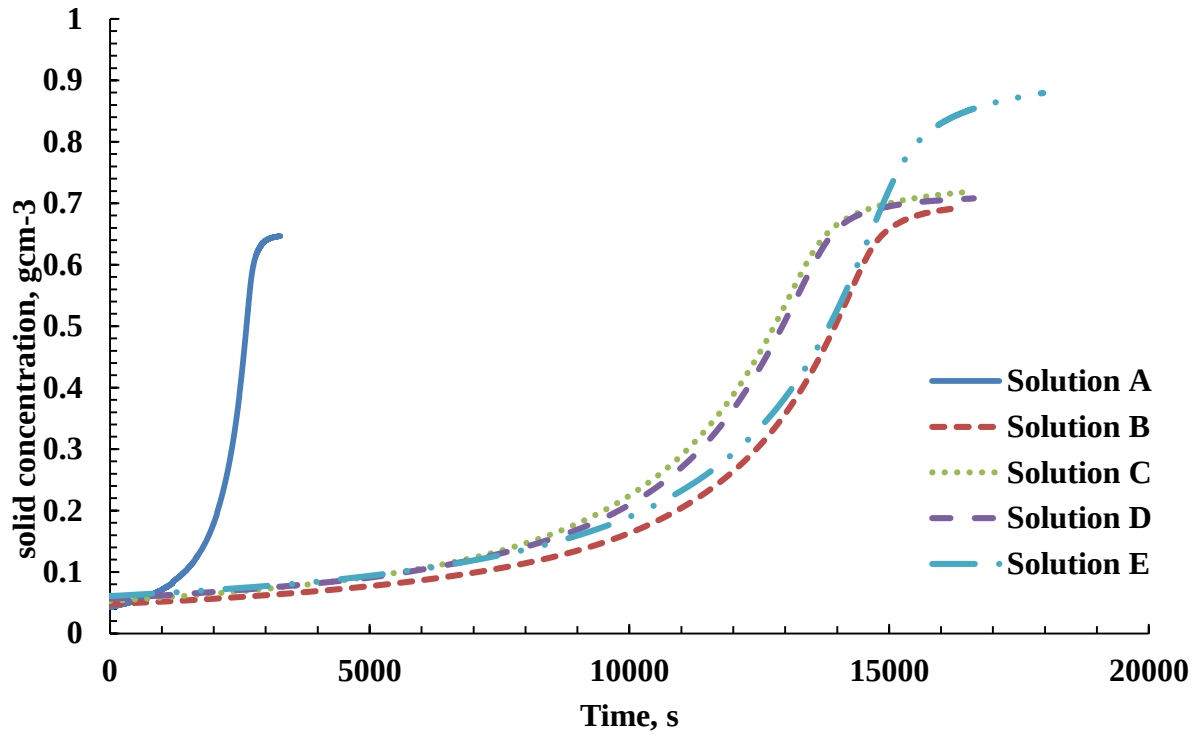


Figure 4.5: Solid concentration, (gcm^{-3}) as a function of time, (s) for various TPP loading for nearly 2000 µm initial coating thickness.

4.2 Case 2: Coatings of Nearly 1300 µm Initial Coating Thickness

4.2.1. Effect of Plasticizer Loading on Residual Solvent %, Drying Time, Coating Thickness, and Solid/Solvent Concentrations.

Figure 4.6 shows the residual solvent versus time in poly (styrene) (PS)-triphenylphosphate (TPP) - *p*-xylene (PX) polymeric coatings. Table 4.2 shows the residual solvent content remaining at the end of the drying process corresponding to different coating compositions. It is clear from the results that the residual solvent content is decreasing with the increase in plasticizer wt.% within the coating.

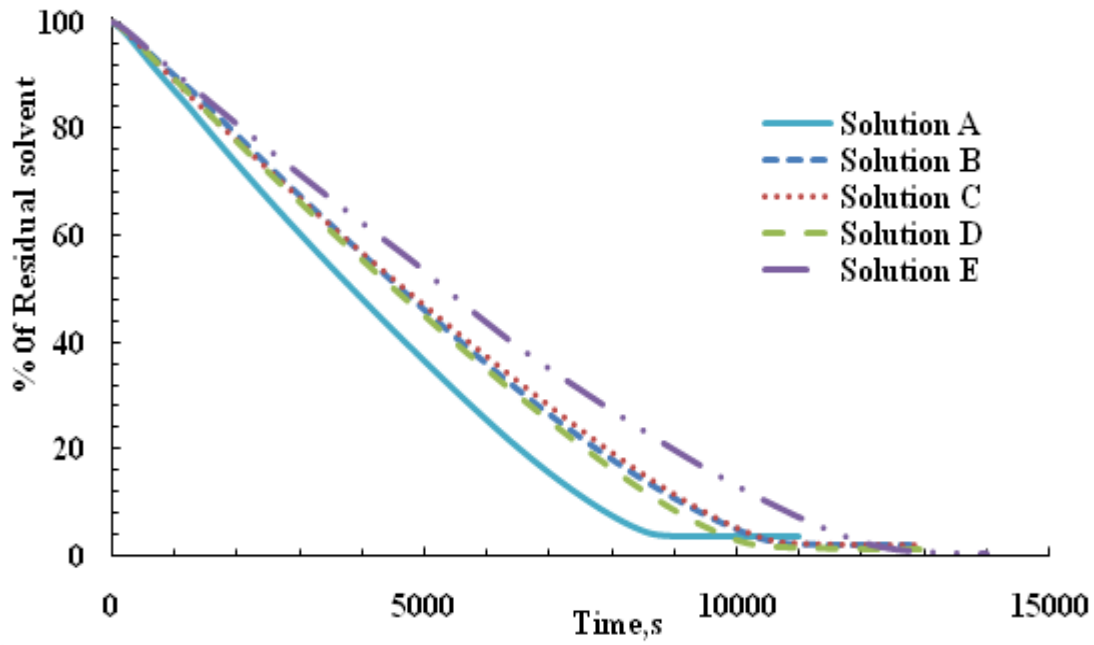


Figure 4.6: % Residual Solvent as a function of time, (s) for various TPP loading for nearly 1300 µm initial coating thickness.

At the end of drying, up to 96.08%, 97.92%, 97.93%, 98.52% and 99.97%, PX has been removed and the remaining 3.92%, 2.08%, 2.07%, 1.48% and 0.34% PX is permanently trapped in the polymeric coatings, respectively. The residual PX decreases linearly up to 141 min 86 s, 172 min 98 s, 173 min 25s, 167 min 46 s and 215 min 33s, respectively, in the polymeric coatings having initial thickness 1351 µm, 1342 µm, 1335 µm, 1330 µm, 1341 µm, respectively. In the beginning, drying process was externally controlled and large amount of PX present evaporates at a very fast rate from the top surface of polymeric coatings. As a consequence, % of residual PX decreases linearly at a very fast rate. The rate of PX removal decreases with time because mass transfer process becomes diffusion controlled. The amount of residual solvent is decreasing on increasing the plasticizer concentration within the polymeric coating. This indicates that the plasticizer reduces the polymer-polymer interaction by penetrating into the polymer matrix and increases the free volume. Also, there is increase in the evaporation time with increase in TPP wt.% , it can be seen in Table 4.2 and Figure 4.7.

Table 4.2 Drying data of PS-TPP-PX Coatings of Nearly 1300μm Initial Thickness

Solution type	Coating thickness, (μm)		Final residual solvent, (%)	Solvent concentration, (g cm^{-3})		Solid concentration, (g cm^{-3})		Drying time, (s)	
	Initial	Final		Initial	Final	Initial	Final	Evaporation time, (s)	Constant time, (s)
A	1351	107	3.92	0.825	0.410	0.043	0.545	0-8512	8512-12139
B	1342	88	2.08	0.821	0.259	0.048	0.734	0-10379	10379-12785
C	1335	93	2.07	0.818	0.244	0.053	0.760	0-10395	10395-12920
D	1330	89	1.48	0.815	0.179	0.057	0.846	0-10048	10048-13094
E	1341	80	0.34	0.812	0.046	0.061	1.019	0-12920	12920-14011

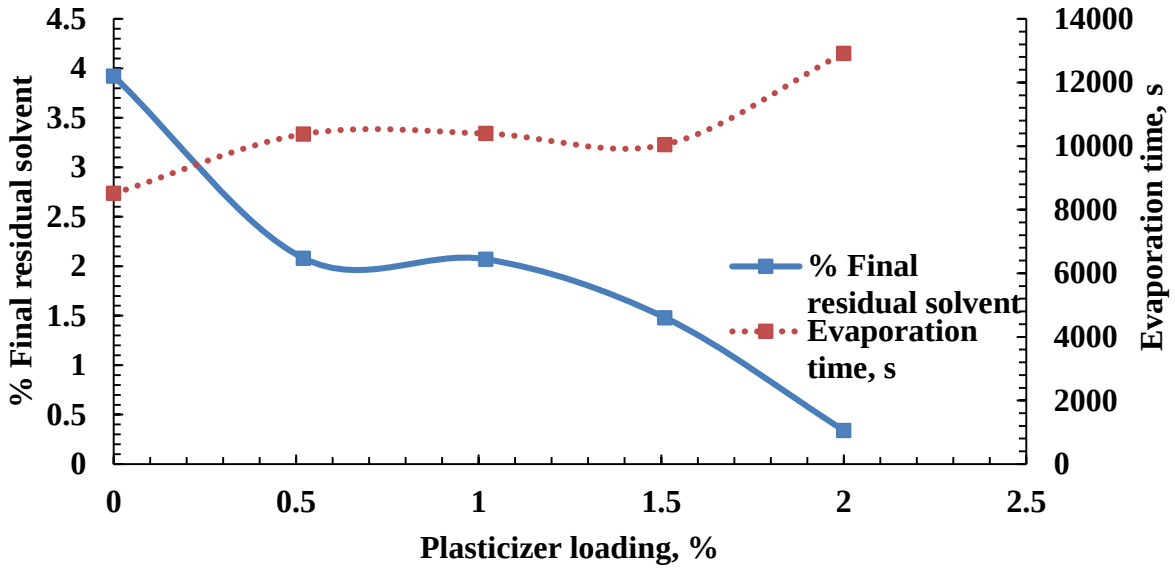


Figure 4.7: % Residual solvent and evaporation time, (s) as a function of plasticizer loading in case of polymeric coatings of nearly 1300 µm.

Figure 4.8 shows the coating thickness versus time in case of poly (styrene) (PS)-triphenyl phosphate (TPP) - *p*-xylene (PX) polymeric coatings of nearly 1300 µm initial coating thickness. During the course of drying, coating thickness is decreasing because the solvent is evaporating from the polymeric coating into the surroundings. In all cases, the coating thickness decreases linearly upto 141 min 7s, 173 min 23 s, 173 min 33 s, 168 min 46 s and 209 min 16 s, respectively and then it becomes constant. The initial and final coating thicknesses are shown in Table 4.2.

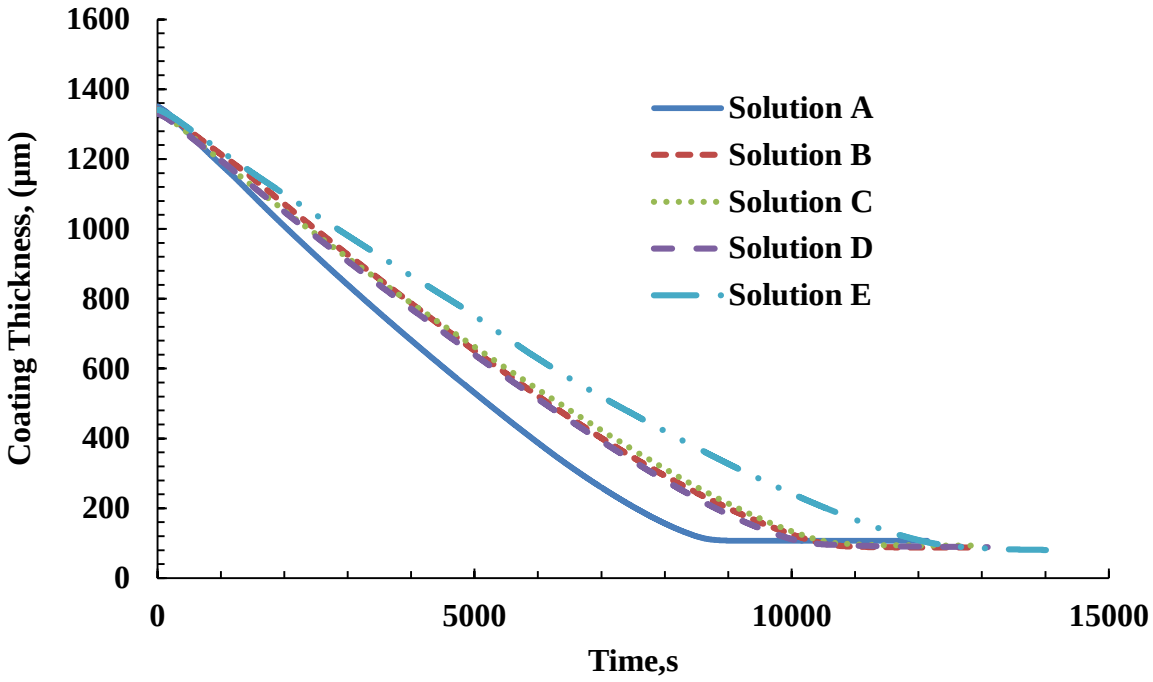


Figure 4.8: Coating thickness, (µm) as a function of time, (s) for various TPP loading for nearly 1300 µm initial coating thickness.

Figure 4.9 shows the solvent concentration versus time in different type of poly (styrene) (PS)-triphenyl phosphate (TPP) - *p*-xylene (PX) polymeric coatings of nearly 1300 µm initial coating thickness. In the starting and at the end of drying process, the solvent concentrations are given in Table 4.2. In all the cases, there is an exponential decrease in the solvent concentration which indicates slow diffusion of solvent within the polymeric coating. In the case of polymeric coatings having initial coating thickness of 1351 µm, 1342 µm, 1335 µm, 1330 µm, 1341 µm, respectively, the concentration of PX decreases exponentially up to 148 min 61 s, 196 min 81 s, 185 min 58 s, 184 min 30 s and 229 min 93 s, respectively and after this it becomes constant. From Table 4.2, it is clear that the solvent concentration is

decreasing with the increase in plasticizer concentration.

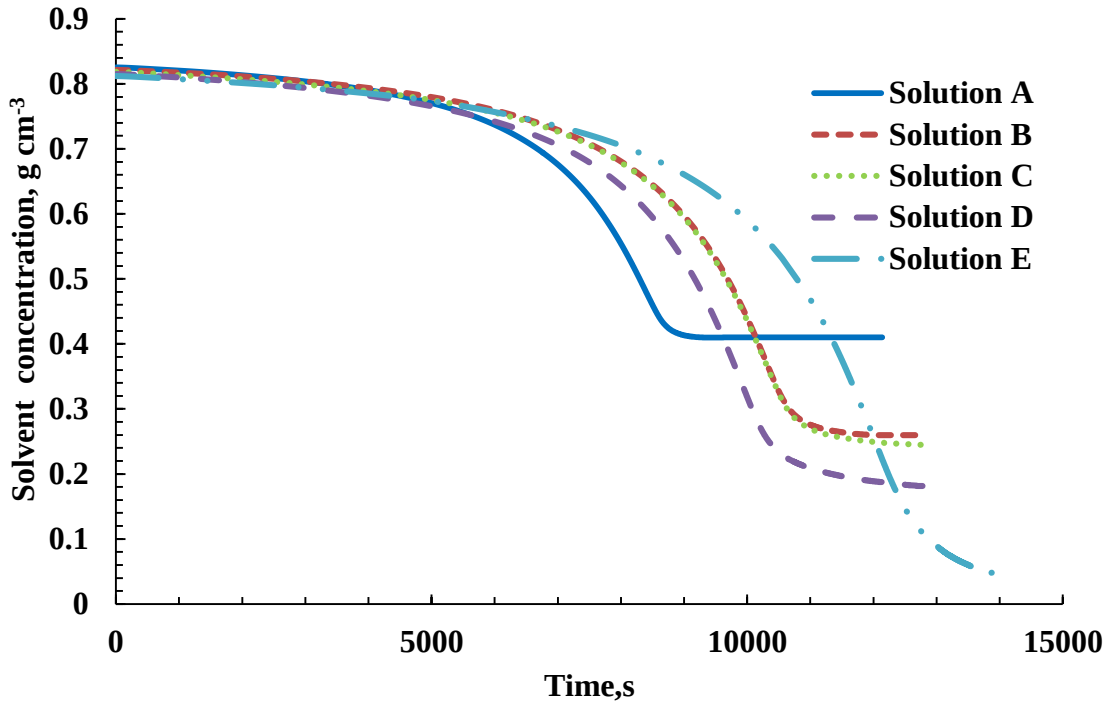


Figure 4.9: Solvent concentration, (g cm^{-3}) as a function of time, (s) for various TPP loading for nearly 1300 µm initial coating thickness.

Figure 4.10 shows the total solid (PS+TPP) concentration versus time in case of poly (styrene) (PS)-triphenyl phosphate (TPP) - *p*-xylene (PX) polymeric coatings. The initial and final solid concentrations are given in Table 4.2. It is clear from these results that the solid concentration is increasing exponentially with increasing TPP wt.% in all the different type of polymeric coatings with initial coating thickness 1351 µm, 1342 µm, 1335 µm, 1330 µm, 1341 µm, respectively. In polymeric coating with 2% TPP, the highest solid concentration is achieved as shown in Table 4.2 and Figure 4.10. Also, the polymeric coating containing 2% TPP, contains minimum amount of residual solvent.

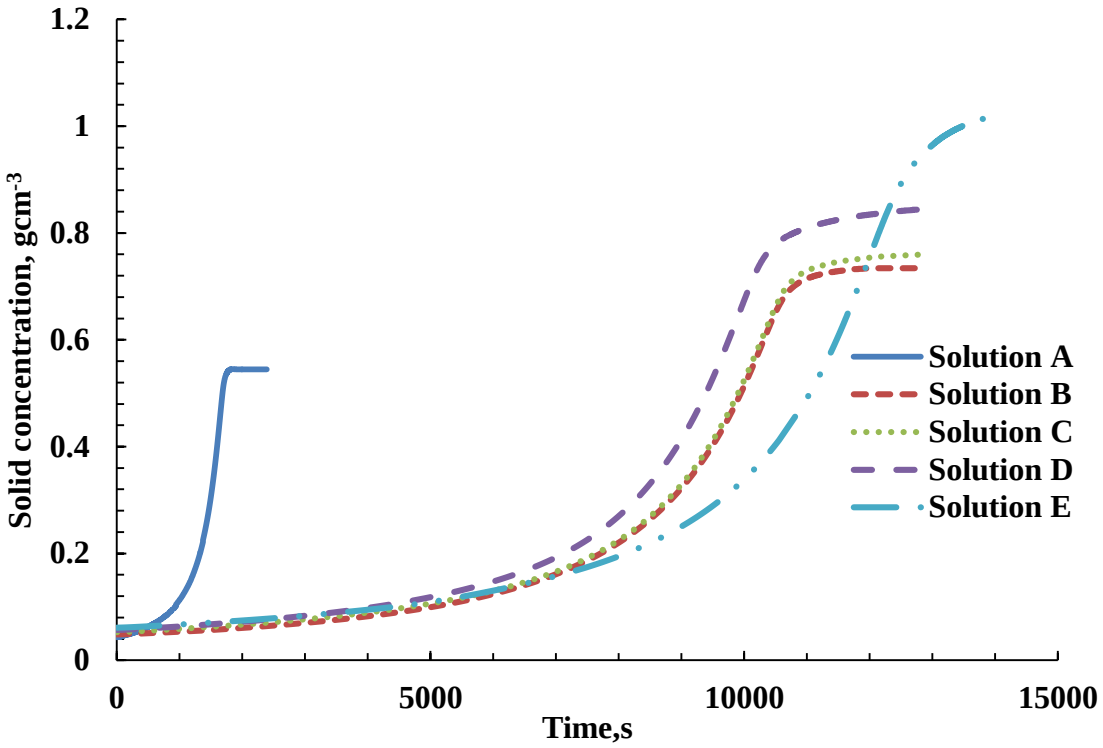
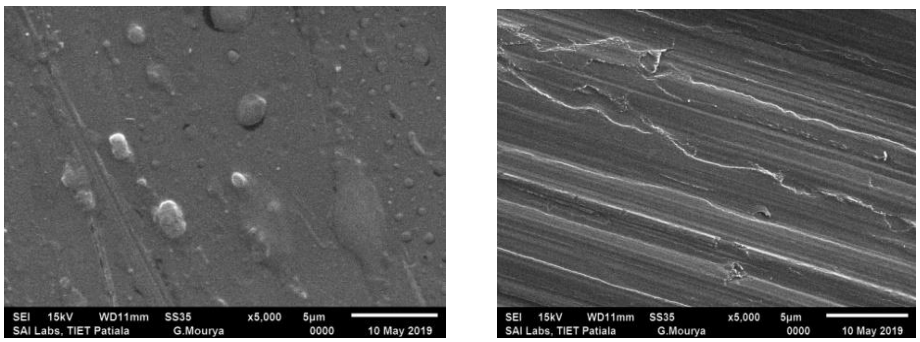


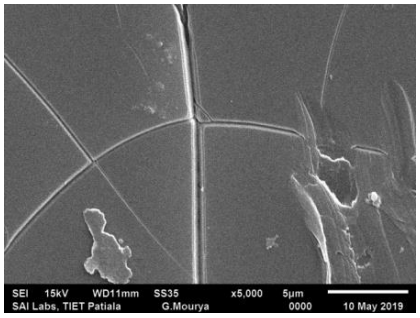
Figure 4.10. Solid concentration, gcm^{-3} as a function of time, (s) for various TPP loading for nearly 1300 µm initial coating thickness.

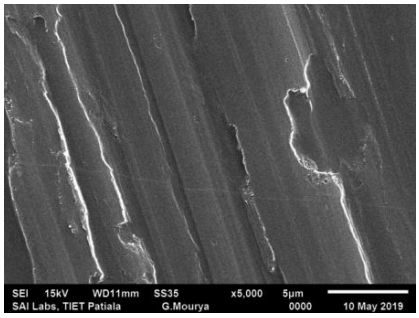
4.3 Surface Morphology for Coatings of Nearly 2000µm Initial Coating Thickness

To determine the surface morphology of different type of polymeric coatings, scanning electron microscopy (SEM) was used. In this technique, an accelerating voltage of 15 KV is used. Figure 4.11 shows the surface morphology for different type of polymeric coatings of nearly 2000µm initial coating thickness.



(a) **(Front)** **(Back)**





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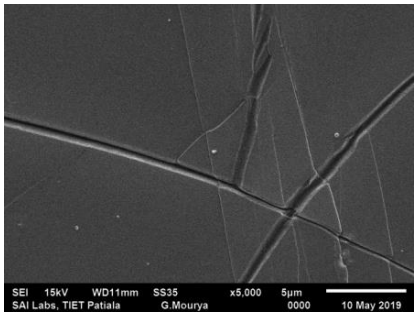

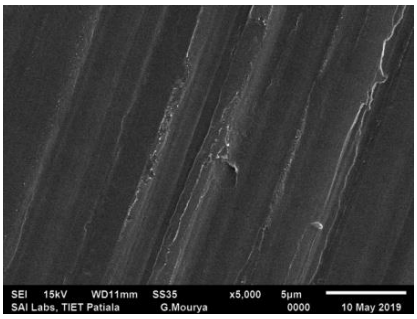

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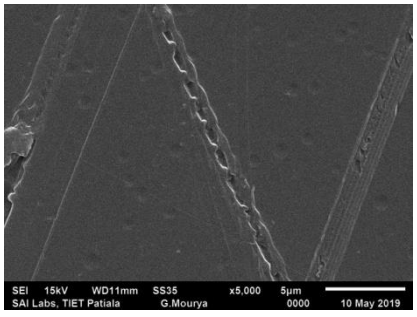

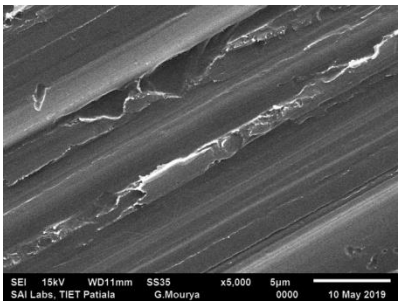

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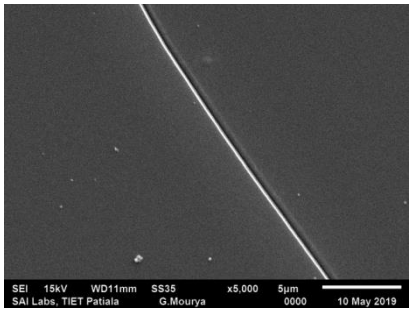

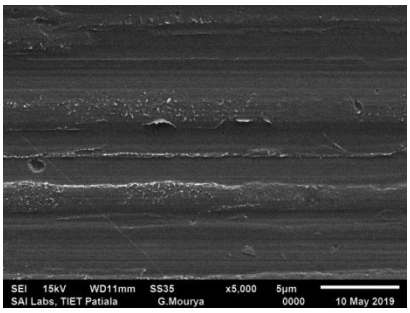

(e) (Front) (Back)

Figure 4.11 SEM images of different type of polymeric coatings, (a): Coating of 4.95% poly (styrene), 0% triphenyl phosphate and 95.05 % *p*-xylene (initial coating thickness: 2021 µm), (b): Coating of 5.02% poly (styrene), 0.52% triphenyl phosphate and 94.46% *p*-xylene (initial coating thickness: 2011 µm), (c): Coating of 5.03% poly (styrene), 1.02% triphenyl phosphate and 93.95% *p*-xylene (initial coating thickness: 1999 µm), (d): Coating of 5.02% poly (styrene), 1.51% triphenyl phosphate and 93.47% *p*-xylene (initial coating thickness: 2005 µm), (e): Coating of 5% poly (styrene), 2% triphenyl phosphate and 93% *p*-xylene (initial coating thickness: 2009 µm).

Figure 4.11 shows the surface morphology of the polymer coatings of nearly 2000 µm initial coating thickness**.** In Figure 4.11(a)(Front), the surface appears uneven with some rounded particles of variable size and shape; (b)(Back), the surface is irregular because of abrasion of polymeric coating. In Figure 4.1(b)(Front), the surface is dense and irregular; (b)(Back), the surface appears rough due to scratching of polymeric coating. In Figure 4.11(c)(Front), the surface appears even and dense along with appearance of some thin lines; (c)(Back), the surface of coating is rough because of scratching. In Figure 4.11(d)(Front), the surface is dense with pores into it which are responsible for its irregularity; (d)(Back) the surface of coating is uneven because of abrasion. In Figure 4.11(e)(Front), the surface appears very much dense and even; (e)(Back), the coating surface is irregular because of scratching of coating. By and large, all the coatings appear smooth and completely dense with no cracks or defects.

Chapter 5

Conclusions

The effect of plasticizer TPP on various PS-PX coatings is studied. In various polymeric coatings studied, it was observed that the percentage of residual solvent remaining at the end of drying process is highly influenced by the concentration of plasticizer. Overall, with the increase in concentration of plasticizer, effective reduction in residual solvent percentage in dry polymeric coating is observed. In the case of the polymeric coating with initial coating thickness 2000 µm in which plasticizer concentration is varied in the range of 0% to 2%, the residual solvent decreased from 2.62 % to 1.35 %, respectively, with one exception. However, the evaporation time increases with increase in TPP wt.% with only one exception. Again, when polymeric coatings having initial coating thickness 1300 µm were studied, with plasticizer concentration ranging from 0% to 2%, the residual solvent decreased from 3.92% to 0.34%. Also, the evaporation time, however, increases with increase in TPP wt.% with one exception. The SEM images show smooth and dense coating with little defects.

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Thesis

by Harman Harman

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Chapter 1

Introduction

1.1 Background

Polymers are macromolecules created by polymerization of many small molecules called monomers [1]. Polymeric coatings are thin layers of polymers that can be made by dissolving polymers in organic or inorganic solvents and are primarily used to protect the underlying substrate [2]. For functional coatings, most polymers are not water soluble and so organic solvents are used [3]. The solvent chosen should be cheap, abundantly available, and non-toxic. It should be able to completely dissolve the polymer, and should not allow any manufacturing defects like wrinkles, vesicles, crevices etc., because these factors influence the drying step [4, 5, 6]. Mostly volatile solvents are used in order to reduce the cost.

Pure polymers are affected adversely by environmental factors such as mechanical stress, corrosion, cracks, weathering, heat or flames, UV radiations etc. [7]. The additives makes a superb accompaniment to polymers as they improve basic polymer characteristics such as flexibility, extensibility, thermo-plasticity and increases flow by decreasing the glass transition temperature (T_g), melting temperature (T_m) and viscosity of polymer [8].

Plasticizers are one of the major class of additives that increases the plasticity or fluidity of polymers due to strong interactions between polymer subunits and plasticizer molecule [10]. Only a small amount of plasticizer can effectively improve the basic properties of polymer. The properties of brittle polymers can be improved by using plasticizer such as triphenyl phosphate (TPP) and as a result the rigid polymer can become flexible [9,11].

1.2 Polystyrene Applications

Polystyrene being a thermoplastic is of high significance as it can be easily injection moulded and then can be reprocessed frequently [10]. Poly (styrene) solid foam find applications in medical devices like diagnostic equipment due to ease of sterilization and its clarity. In other laboratory ware to form test tubes, petri dishes, flasks, and pipettes [13]. Expanded polystyrene (EPS) and extruded polystyrene (XPS) are embedded in materials to impart insulating and cushioning properties. Because this kind of insulation bring reduction in energy used within buildings by controlling indoor temperature. Rigid foam form of polystyrene can be more than 95% air and is used as lightweight protective packaging. It is

mostly used in appliance and home insulation, and solid and foam forms of polystyrene are used in CD and DVD cases, ovens, microwaves, blenders, refrigerators, air conditioners. Because of their inertness, durability, and water resistance, they are cost effective and long lasting in making automobile parts, gardening pots, in child protective seats, in roadways, and road bank stabilization systems [12,14].

1.3 Preparation of Polymeric Coatings

Polymeric coatings can be prepared by dissolving a polymer in a solvent using various methods depending on the requirement:

a) solution casting method [15],
b) spin casting method [16],
c) drop casting method [17],
d) film casting method [18].

Among these methods, the solution casting method is the easiest to operate for polymer coating preparation at industrial scale as well as on laboratory scale. In this method, the homogeneous solution with low viscosity is prepared by dissolving the polymer in one or more volatile solvents. Also it includes simplified incorporation of additives. Additionally, it is a convenient method for the production of high temperature resistant films even when processing at low temperatures.

This method provides greater film thickness uniformity, with extremely low haze, excellent flatness, dimensional stability, and maximum optical purity [19]. A schematic representation of the solution casting technique is shown in Figure 1.

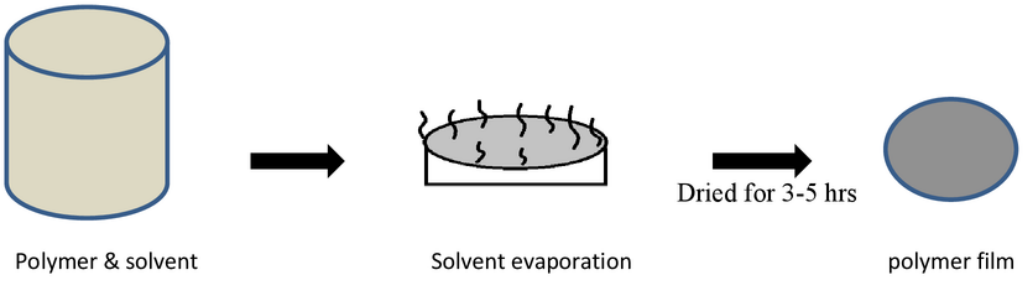


Figure 1.1: Schematic representation of solution casting technique.

1.4 Polymer Coating Drying

Drying is the ultimate and quality controlling step, which brings about essential changes in coating properties [19]. Although the drying of polymer solutions is a complex process involving heat and mass transfer yet it plays an important role in the manufacture of synthetic fibres, paint coatings, functional films and other polymeric products [20]. During the course of drying physical and chemical changes such as crystallization, shrinking, glass transition, texture, order and colour takes place along with change in phase of polymeric solution, which is wet in the beginning, but at the end of drying, a solid polymeric coating is generated. It is necessary to dry the polymeric coatings in controlled drying conditions to get excellent polymer coatings. Otherwise, due to improper drying, some unwanted changes like cracks, blisters and insufficient removal of solvent may occur [21].

1.5 Plasticizers Applications In Polymeric Coatings

Plasticizers can be used to amend different properties of polymer coatings. Plasticizers, due to their compatibility with the polymer, penetrate into it and occupy the free volume around polymer chains [22]. Polystyrene is brittle and hard enough but it become rubbery when plasticized with solvents or other additives with low volatility, which in return reduces glass transition temperature by embedding themselves between polymer subunits or chains. In this way, plasticizer helps in pushing the polymer chains apart to make them more flexible, because there is increase in the plasticity, free volume of polymer, and this results in decrease in the viscosity, tensile strength, elastic modulus, and, thus, the glass transition temperature is lowered down [24]. Low molecular weight non-volatile plasticizer's primary purpose is to improve the workability, process-ability, toughness and flexibility of polymers, and, hence, lower thermal processing temperatures can be applied [14].

Polystyrene is flammable, but with the addition of an additive triphenyl phosphate (TPP), the flame resistance can be imparted to polystyrene. TPP can decompose to phosphoric acid on migrating to the surface and could form a protective layer to protect the polymer substrate from oxygen and flame [23]. Hence, TPP can act both as a flame retardant and plasticizer. Also, to produce flexible and successive polymeric coating, the residual solvent content should be minimum in the coating. Plasticizers influence the drying significantly. It has been found that only a small amount of plasticizer can alter the behaviour of polymeric coatings. Only little increase in concentration of plasticizer can enhance the drying rate along with adequate

removal of solvent. Therefore, aryl phosphates being thermally stable and due to their good plasticization and compatibility with many polymers helping to produce flexible films by improving the mechanical properties of coating, enhancing drying rate and responsible for the significant removal of solvent at the end of drying operations [25].

Chapter 2

Literature Review

This chapter includes literature of polymer-plasticizer system and solvent based polymeric coatings.

Jang and Wilkie [23] worked on the thermally stable triphenyl phosphate (TPP) and resorcinol bis(diphenyl-phosphate) (RDP), non halogenated fire retardants. They used TGA\FTIR and GC\MS techniques to study how the blends of the (PC\RDP) and (PC\TPP) were thermally degraded in air. They analysed the thermal degradation of both PC\RDP and PC\TPP blends and confirmed that both RDP and TPP can significantly reduce bisphenol A evolution, which is, in general, a product of alcoholysis/hydrolysis of carbonate linkage. Bisphenol A is evolved when the alcohol products produced through alcoholysis during polycarbonate (PC) thermal degradation reacts with some amount of phosphate. This leads to the formation of branched phosphate structures with the PC chain, which inhibits heat and mass transfer of degraded products. They concluded that in the case of polymers which can be thermally degraded, both TPP and RDP provide effective fire retardancy in spite of having different volatilization temperature by delaying degradation of polymers as they both possess phosphate group which form branched structures with polymers.

Sharma et al. [26] studied poly (styrene) – poly (methyl methacrylate) – tetrahydrofuran (PS-PMMA-THF) polymeric coatings. By using gravimetric weight loss data, they calculated average concentration of THF, PS, PMMA and variation in coating thickness with time. They observed that on doubling the PMMA mass fraction, the drying process slowed down due to very slow diffusion process within these coatings. But when polystyrene content was doubled within these coatings, there was no significant change in the drying mechanism. Hence, the residual solvent content did not change significantly on changing the PS content in system having 10% PS, but on doubling the PMMA content, very small reduction in residual solvent content was observed in nearly 5% PS systems. Therefore, the drying mechanism in the coating studied was greatly influenced by PMMA but was not a strong function of PS.

Jarray et al. [22] predicted the polymer - plasticizer compatibility during coating formulation for the hydroxypropyl-methylcellulose - polyethylene glycol (HPMC-PEG), microcrystalline cellulose-polyethylene glycol (MCC-PEG), and polyvinylpyrrolidone - polyethylene glycol

(PVP-PEG) systems using different methods including differential scanning calorimetry (DSC), molecular charge density using conductor-like screening model (COSMO), mesoscale simulation using dissipative particle dynamics (DPD) and molecular dynamics to calculate solubility parameter. They observed that all the different methods showed similar results. In case of HPMC and PVP polymers, the PEG plasticizer diffused well into the polymers because there was better interaction between these polymers and plasticizer. But MCC surrounded PEG and there was no diffusion of plasticizer because PEG and MCC were not miscible. Hence, compatibility of the plasticizer with the polymer led to high miscibility of polymer and plasticizer and the diffusion of plasticizer into the coating during film formation. Thus, it helps in producing stable and homogeneous coating film.

Arya [19] studied on the poly(methyl methacrylate)–tetrahydrofuran (PMMA-THF), poly (styrene)–tetrahydrofuran (PS-THF) and poly (styrene) – *p*-xylene (PS-PX) systems to measure the concentrations of polymer and solvent by using Confocal Raman spectroscopy. They observed that in case of high volatile solvent such as in PMMA-THF and PS-THF systems, the profiles measured using confocal Raman Spectroscopy are in accordance with free volume predicted profiles. But when the less volatile solvent system was studied which comprised PS-PX system, then it was observed that free volume model was incapable to envisage the complete drying behaviour.

Bhargava and Arya [27] studied the designing of several binary coatings of PS-THF and PS-PX with the aim to lessen the residual solvent. They performed experiments under quiescent drying conditions without any air flow. They made coatings with different poly (styrene) concentrations ranging from 5 wt.% to 15 wt.% approximately and performed numerous experiments for different coating thickness. They observed that in thick polymeric coating, the residual solvent left was minimum. Besides, the thinner coatings took less drying time in comparison to the thicker coatings due to the presence of smaller amount of initial solvent in the beginning of the polymeric coating. They concluded that it was advantageous to apply thicker coating once rather than layer by layer as it helped in minimizing the residual solvent.

Liang et al. [24] studied the effect of *o*-terphenyl (OTP) plasticizer on the T_g of PS using Fourier transform infrared spectroscopy. They studied the peak areas versus temperature curves for four conformation insensitive bands in the spectrum of PS in which two bands were allocated

to the modes of vibrations of the main chain and the other two to the side groups of PS. They observed that when PS was mixed with OTP, then for the main chain, due to cohesional entanglements, the reorientation relaxation temperature was lower than that of the side groups. This was happened because the side groups reorientation relaxation region was nearly same as the glass transition region of PS which was macroscopically observed. It pointed out that the glass transition process of PS was greatly influenced by reorientation of side groups.

Wang et al. [28] studied a mathematical model based on free volume theory to predict solvent self-diffusion coefficients in case of amorphous glassy polymers. They analysed how solvents such as ethyl benzene, benzene, methyl acetate, methyl ethyl ketone, and toluene helped in plasticization to accurately determine the fluctuation in the hole-free volume above and below the T_g. They used free volume parameters to calculate the solvent mutual-diffusion coefficients. On comparing values calculated using mathematical model with the experimental data already available on solvents blended in PS and PMMA, the measured results were in agreement with the predicted values.

Chapter 3

Materials and Methods

3.1 Materials

Table 3.1. Listing of Materials Used

Name of Chemical	Name of Supplier	Molecular weight, ($g\ mol^{-1}$)	Density, ($g\ cm^{-3}$)
Poly(styrene) (PS)	Sigma Aldrich, (USA)	192000	1.04
Triphenyl phosphate (TPP)	Sigma Aldrich, Germany	326.28	1.18
p-xylene (PX)	Loba Chemie	106.17	0.861

All the chemicals were used in pure form without purifying further.

3.2 Methodology

In the present work, five different kind of polymeric solutions with different concentrations of PS-TPP-PX were prepared for the polymeric coating preparations. By using semi-micro analytical weighing balance (222M DR, Precisa) having least count ±0.0001g, a required amount of solvent, plasticizer and polymer were weighed. These prepared polymeric solutions were decanted carefully into closely sealed bottles. After this to get the homogeneous solution, these sample bottles were kept in shaker for mechanical shaking at 200 rpm for 2 hours.

For the preparation of polymeric coatings, the solution casting technique was used. To get the desired initial coating thickness, a required amount of polymeric solution was taken from the sample bottle and decanted with micropipette into the sample holder which is of stainless steel and is circular in shape with 14.75 mm diameter and with depth 2000 µm. Several type of coatings with different initial thickness were prepared using different polymer solutions. The solvent evaporated immediately after the solution was decanted in the circular sample holder, therefore the loss in mass of the polymeric coating was recorded at an interval of 5 s

by using semi micro analytical weighing balance. The readings were taken until the polymeric coating dried completely. This was ensured when for a sufficient long time gap, there was no change recorded in two consecutive weight data. The polymeric coatings dried completely within 3-5 hours approximately. Then these coatings were considered dried for practical purposes. All the experiments were carried out at 26±1°C. The different coating solution compositions are represented in Table 3.2. By using standard volumetric methods given in previous literature, different coating variables like % of residual solvent, concentration of PS, concentration of PX, coating thickness, solid (PS + TPP) concentration, and non dimensional thickness were calculated.

Table 3.2. Different Type of Coating Solutions

Solution type	PS (wt.%)	TPP (wt.%)	PX (wt.%)
A	4.95	0	95.05
B	5.02	0.52	94.46
C	5.03	1.02	93.95
D	5.02	1.51	93.47
E	5	2	93

3.1.3 Calculations

Sample calculations are shown for a particular coating. Let "m" be the initial mass of polymer solution comprising of 5.02% PS and 94.46% PX, and 0.52% TPP

Mass of PS, $M_{PS} = m \times (5.02/100)$

Mass of TPP, $M_{TPP} = m \times (0.52/100)$

Initial mass of PX, $M_{PX} = m \times (94.46/100)$

Volume of PS, $V_{PS} = M_{PS}/density\ of\ PS$

Volume of TPP, $V_{TPP} = M_{TPP}/density\ of\ TPP$

Volume of PX, $V_{PX} = M_{PX}/\ density\ of\ PX$

Total volume, $V_T = V_{PS} + V_{TPP} + V_{PX}$

Concentration of PS = M_{PS}/V_T

Concentration of TPP = M_{TPP}/V_T

Concentration of PX = M_{PX}/V_T

% Residual Solvent = *final mass of PX / initial mass of PX*

Coating thickness = *total volume / area of sample holder* = $V_T / \pi r^2$

Radius of the sample holder = 7.38 mm

Chapter 4

Results and Discussion

4.1 Case 1: Coatings of Nearly 2000 µm Initial Coating Thickness

4.1.1 Effect of Plasticizer Loading on Residual Solvent %, Drying time, Coating Thickness, and Solvent/Solid Concentrations.

Figure 4.1 shows the residual solvent versus time in case of poly (styrene) (PS)-triphenylphosphate (TPP) - *p*-xylene (PX) polymeric coatings. These coatings were prepared by varying the mass percentages of TPP, namely, 0%, 0.52%, 1.02%, 1.51% and 2% as given in Table 3.2. Table 4.1 shows the residual solvent content left at the end of drying process corresponding to different coating compositions. These results indicate that the amount of residual solvent is decreasing with the increase in plasticizer wt.% within the coating. At the end of drying, up to 97.38%, 97.5%, 97.51%, 97.13% and 98.65% PX has been removed and the remaining 2.62%, 2.50%, 2.49%, 2.87% and 1.35% PX is permanently trapped in these polymeric coatings respectively.

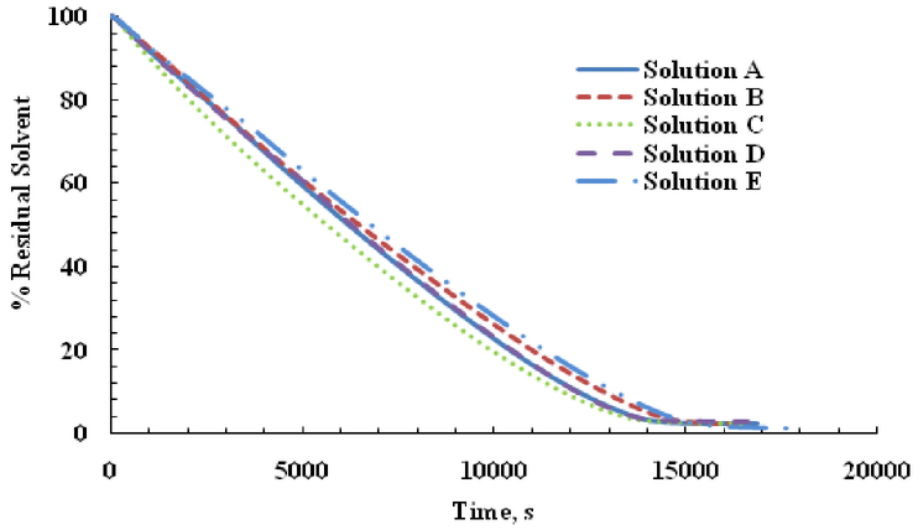


Figure 4.1: % Residual Solvent as a function of time, (s) for various TPP loading for nearly 2000 µm initial coating thickness.

Table 4.1 Drying Data of PS-TPP-PX Coatings of Nearly 2000µm Initial Thickness

Solution type	Coating thickness, (µm)		Final residual solvent, (%)	Solvent concentration, ($g\ cm^{-3}$)		Solid concentration, ($g\ cm^{-3}$)		Drying time, (s)	
	Initial	Final		Initial	Final	Initial	Final	Evaporation time, (s)	Constant time, (s)
A	2021	134	2.62	0.825	0.325	0.043	0.647	0-13650	13650-16839
B	2011	140	2.50	0.821	0.294	0.048	0.691	0-14310	14310-16305
C	1999	147	2.49	0.818	0.277	0.053	0.719	0-13179	13179-16571
D	2005	161	2.87	0.815	0.291	0.057	0.708	0-13500	13500-16630
E	2009	140	1.35	0.812	0.158	0.061	0.880	0-15520	15520-17966

The residual PX decreases linearly up to 227 min 5 s, 238 min 5 s, 219 min 65 s, 225 min and 258 min 68 s in the respective polymeric coatings having initial thickness 2021 µm, 2011 µm, 1999 µm, 2005 µm and 2009 µm, respectively. In the beginning, drying process was externally controlled and large amount of PX present evaporates at a very fast rate from the top surface of polymeric coatings. As a consequence, % of residual PX decreases linearly at a very fast rate. The rate of PX removal decreases with time because the mass transfer process becomes diffusion controlled. The least amount of residual solvent is left in the coating containing 2% TPP. It can be seen in Table 4.1, in general there is decrease in the residual solvent content with increase in the TPP wt.% with the exception of 1.5% TPP solution that exhibits maximum value of the residual solvent content. This indicates that the plasticizer reduces the polymer-polymer interaction by penetrating into the polymer matrix and increases the free volume. Also, there is increase in the evaporation time with increase in TPP wt.% with the exception of 1% TPP solution that exhibits minimum value of the evaporation time, as it can be seen in Table 4.1 and Figure 4.2.

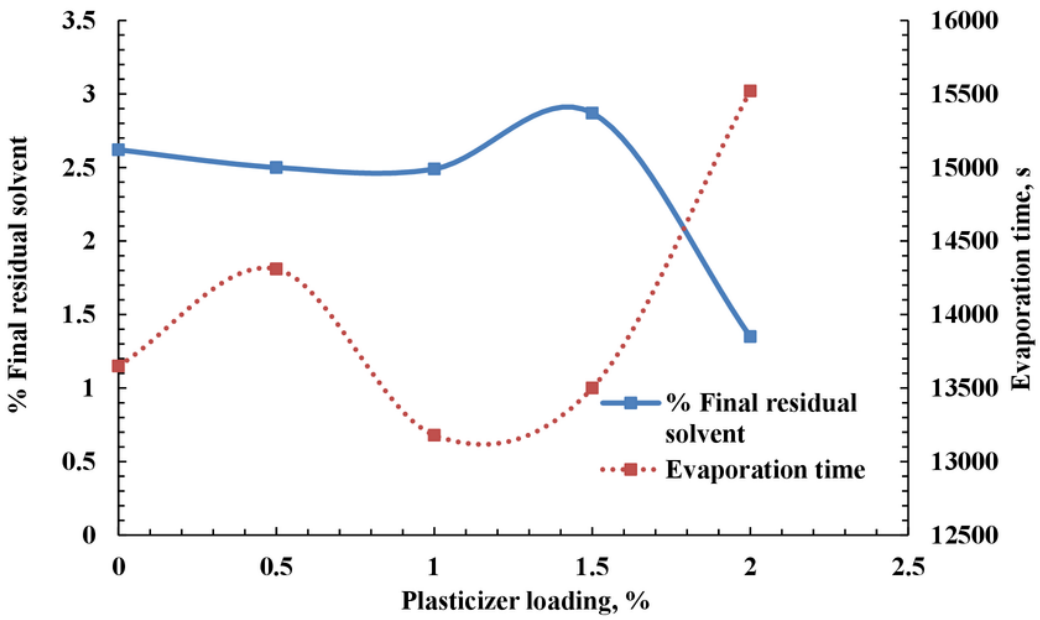


Figure 4.2: % Residual solvent and evaporation time, (s) as a function of plasticizer loading in case of polymeric coatings of nearly 2000 µm.

Figure 4.3 shows the coating thickness versus time in case of poly (styrene) (PS)-triphenyl phosphate (TPP) - *p*-xylene (PX) polymeric coatings. During the course of drying, coating thickness is decreasing because the solvent is evaporating from the polymeric coating into the surroundings. In all the cases, the coating thickness decreases linearly up to 225 min 30s, 234 min 73 s, 218 min 48 s, 223 min 16 s and 262 min 43 s, respectively and then it becomes constant. The initial and final coating thicknesses are shown in Table 4.1.

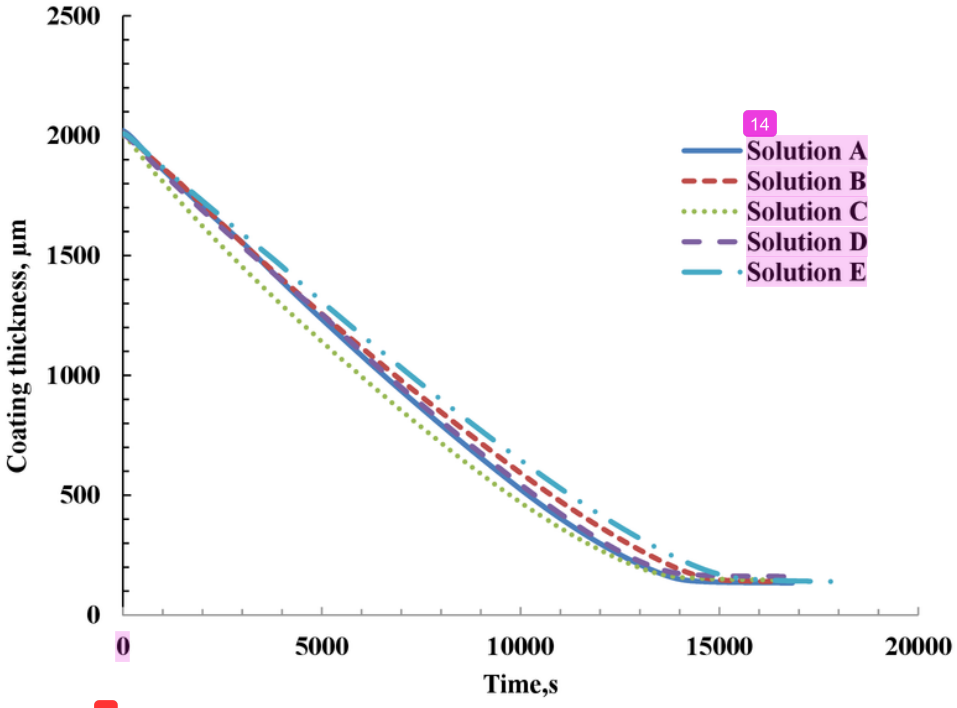


Figure 4.3: Coating thickness, (µm) as a function of time, (s) for various TPP loading for nearly 2000 µm initial coating thickness.

Figure 4.4 shows the concentration of solvent versus time in case of poly (styrene) (PS)-triphenyl phosphate (TPP) - *p*-xylene (PX) polymeric coatings. In the starting and at the end of drying process, the solvent concentrations are given in Table 4.1. In all the cases studied, there is an exponential decrease in the solvent concentration which indicates slow diffusion of solvent within the polymeric coating. In the case of polymeric coatings having initial coating thickness of 2021 µm, 2011 µm, 1999 µm, 2005 µm and 2009 µm, respectively, the concentration of PX decreases exponentially up to 246 min 63 s, 255 min 33 s, 242 min 83 s, 243 min 91 s and 293 min 18 s, respectively, and after this it becomes constant. In Table 4.1,

it is clearly shown that the solvent concentration is decreasing with the increase in plasticizer concentration.

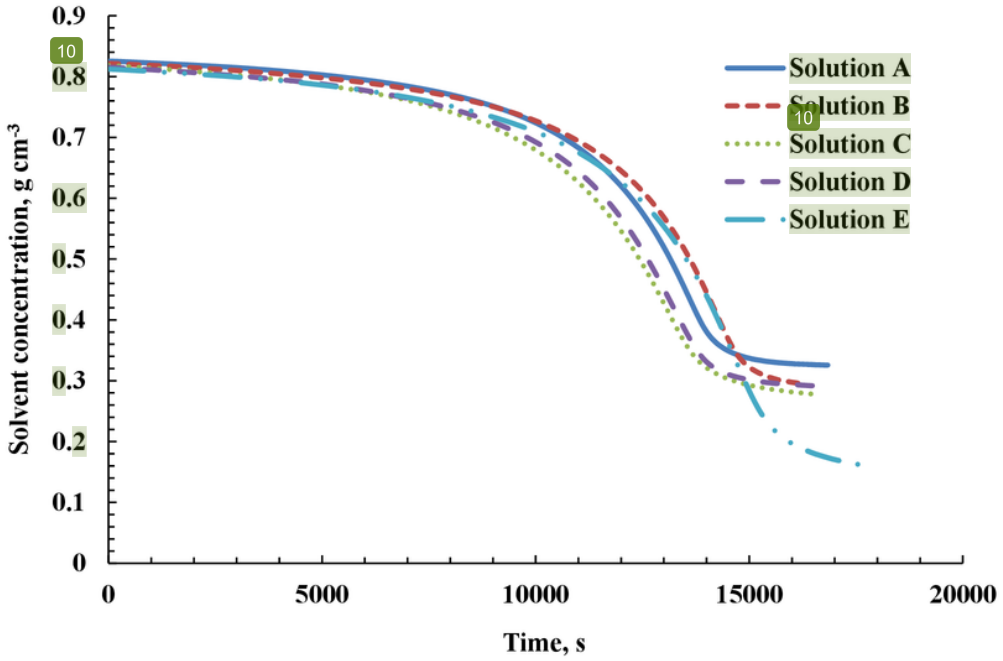


Figure 4.4: Solvent concentration, (g cm^{-3}) as a function of time, (s) for various TPP loading for nearly 2000 µm initial coating thickness.

Figure 4.5 shows the total solid (PS+TPP) concentration versus time in case of poly (styrene) (PS) - triphenyl phosphate (TPP) - *p*-xylene (PX) polymeric coatings. The initial and final solid concentrations are as provided in Table 4.1. It is clear from these results that solid concentration is increasing exponentially with increasing TPP wt.%, in all the different polymeric coatings with the initial coating thickness 2021 µm, 2011 µm, 1999 µm, 2005 µm and 2009 µm, respectively. In polymeric coating with 2 wt.% TPP, the highest solid concentration is achieved as shown in Table 4.1 and Figure 4.5. Also, the polymeric coating containing 2 % TPP, contains minimum amount of residual solvent.

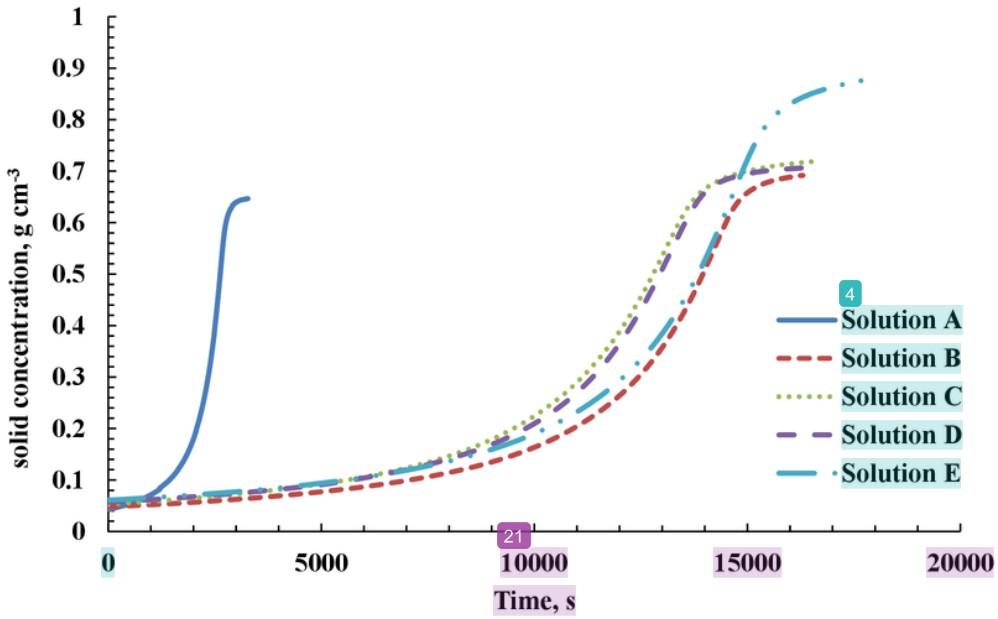


Figure 4.5: Solid concentration, (g cm^{-3}) as a function of time, (s) for various TPP loading for nearly 2000 µm initial coating thickness.

4.2 Case 2: Coatings of Nearly 1300 µm Initial Coating Thickness

4.2.1. Effect of Plasticizer Loading on Residual Solvent %, Drying Time, Coating Thickness, and Solid/Solvent Concentrations.

Figure 4.6 shows the residual solvent versus time in poly (styrene) (PS) - triphenylphosphate (TPP) - *p*-xylene (PX) polymeric coatings. Table 4.2 shows the residual solvent content remaining at the end of the drying process corresponding to different coating compositions. It is clear from the results that the residual solvent content is decreasing with the increase in plasticizer wt.% within the coating.

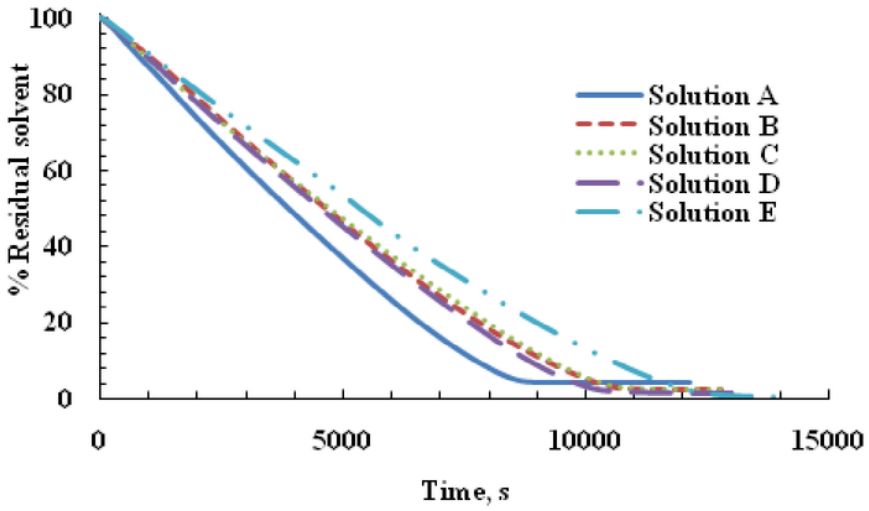


Figure 4.6: % Residual Solvent as a function of time, (s) for various TPP loading for nearly 1300 µm initial coating thickness.

At the end of drying, up to 96.08%, 97.92%, 97.93%, 98.52% and 99.97%, PX has been removed and the remaining 3.92%, 2.08%, 2.07%, 1.48% and 0.34% PX is permanently trapped in the polymeric coatings, respectively. The residual PX decreases linearly up to 141 min 86 s, 172 min 98 s, 173 min 25s, 167 min 46 s and 215 min 33s, respectively, in the polymeric coatings having initial thickness 1351 µm, 1342 µm, 1335 µm, 1330 µm, 1341 µm, respectively. In the beginning, drying process was externally controlled and large amount of PX present evaporates at a very fast rate from the top surface of polymeric coatings. As a consequence, % of residual PX decreases linearly at a very fast rate. The rate of PX removal decreases with time because mass transfer process becomes diffusion controlled. The amount of residual solvent is decreasing on increasing the plasticizer concentration within the polymeric coating. This indicates that the plasticizer reduces the polymer-polymer interaction by penetrating into the polymer matrix and increases the free volume. Also, there is increase in the evaporation time with increase in TPP wt.% , it can be seen in Table 4.2 and Figure 4.7.

Table 4.2 Drying data of PS-TPP-PX Coatings of Nearly 1300µm Initial Thickness

Solution type	Coating thickness, (µm)		Final residual solvent, (%)	Solvent concentration, ($g\ cm^{-3}$)		Solid concentration, ($g\ cm^{-3}$)		Drying time, (s)	
	Initial	Final		Initial	Final	Initial	Final	Evaporation time, (s)	Constant time, (s)
A	1351	107	3.92	0.825	0.410	0.043	0.545	0-8512	8512-12139
B	1342	88	2.08	0.821	0.259	0.048	0.734	0-10379	10379-12785
C	1335	93	2.07	0.818	0.244	0.053	0.760	0-10395	10395-12920
D	1330	89	1.48	0.815	0.179	0.057	0.846	0-10048	10048-13094
E	1341	80	0.34	0.812	0.046	0.061	1.019	0-12920	12920-14011

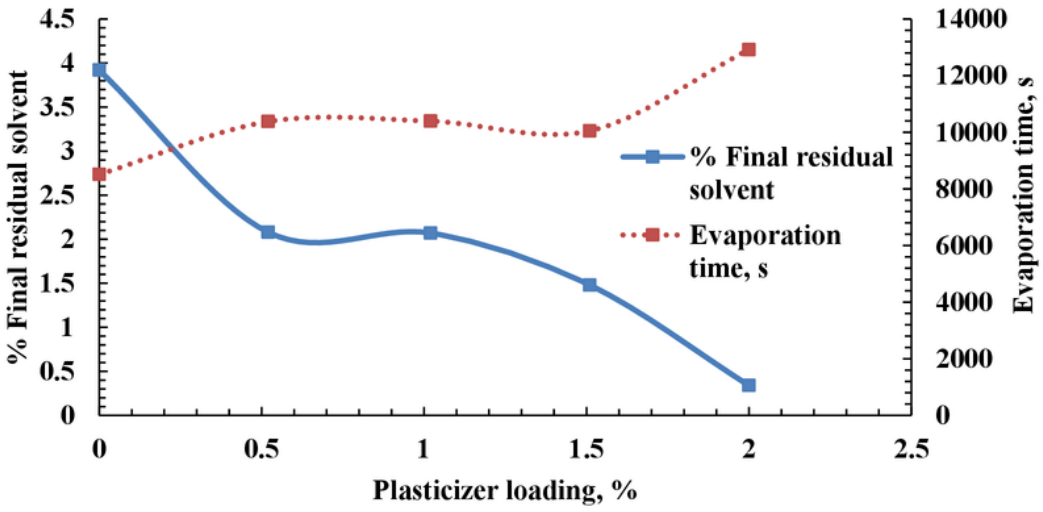


Figure 4.7: % Final residual solvent and evaporation time, (s) as a function of plasticizer loading in case of polymeric coatings of nearly 1300 µm.

Figure 4.8 shows the coating thickness versus time in case of poly (styrene) (PS) - triphenyl phosphate (TPP) - *p*-xylene (PX) polymeric coatings of nearly 1300 µm initial coating thickness. During the course of drying, coating thickness is decreasing because the solvent is evaporating from the polymeric coating into the surroundings. In all cases, the coating thickness decreases linearly upto 141 min 7s, 173 min 23 s, 173 min 33 s, 168 min 46 s and 209 min 16 s, respectively and then it becomes constant. The initial and final coating thicknesses are shown in Table 4.2.

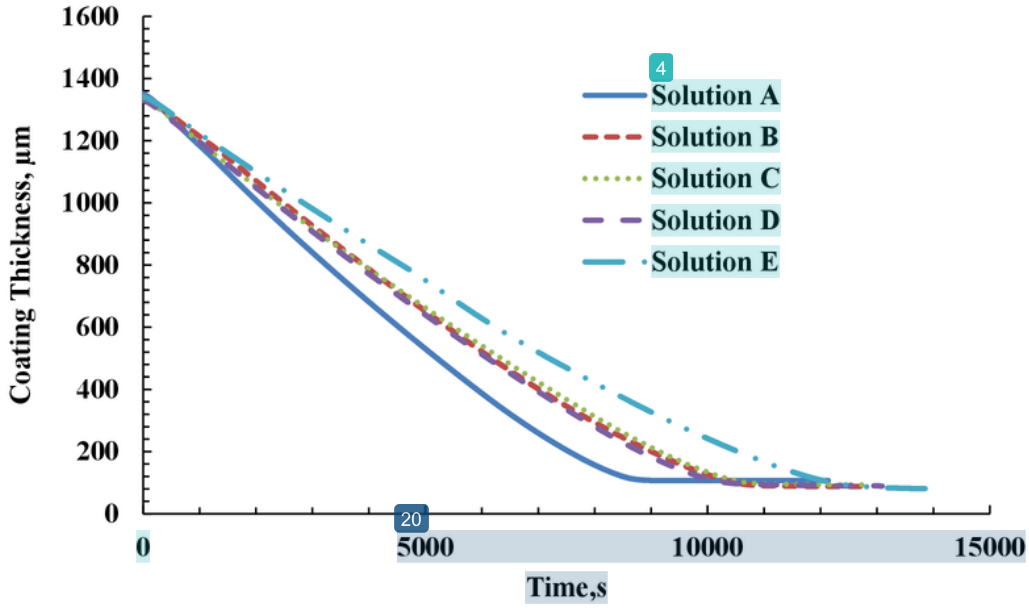


Figure 4.8: Coating thickness, (µm) as a function of time, (s) for various TPP loading for nearly 1300 µm initial coating thickness.

Figure 4.9 shows the solvent concentration versus time in different type of poly (styrene) (PS) - triphenyl phosphate (TPP) - *p*-xylene (PX) polymeric coatings of nearly 1300 µm initial coating thickness. In the starting and at the end of drying process, the solvent concentrations are given in Table 4.2. In all the cases, there is an exponential decrease in the solvent concentration which indicates slow diffusion of solvent within the polymeric coating. In the case of polymeric coatings having initial coating thickness of 1351 µm, 1342 µm, 1335 µm, 1330 µm, 1341 µm, respectively, the concentration of PX decreases exponentially up to 148 min 61 s, 196 min 81 s, 185 min 58 s, 184 min 30 s and 229 min 93 s, respectively and after this it becomes constant. From Table 4.2, it

is clear that the solvent concentration is decreasing with the increase in plasticizer concentration.

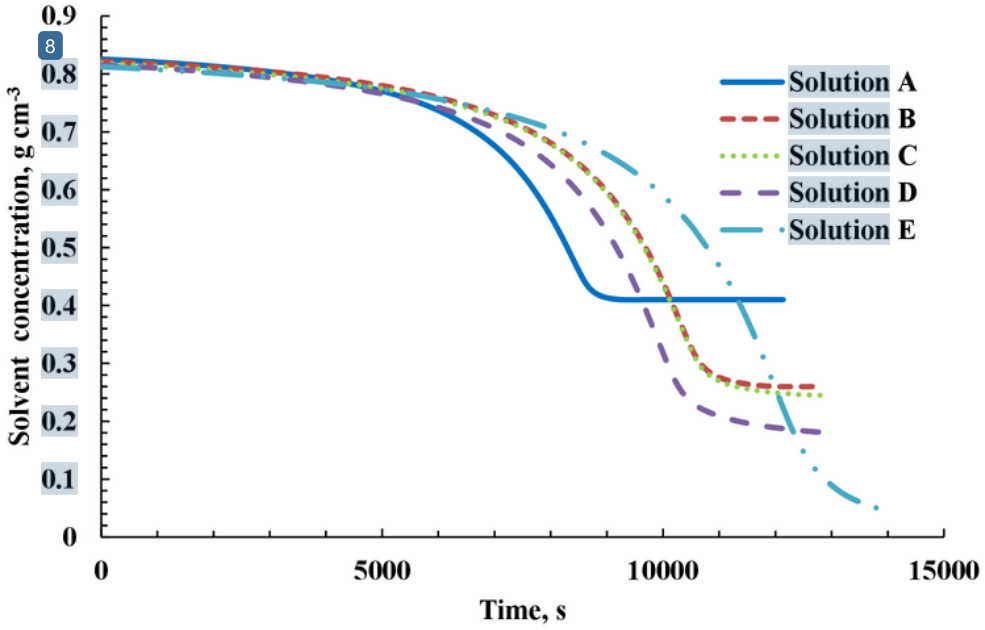


Figure 4.9: Solvent concentration, (g cm^{-3}) as a function of time, (s) for various TPP loading for nearly 1300 µm initial coating thickness.

Figure 4.10 shows the total solid (PS+TPP) concentration versus time in case of poly (styrene) (PS) - triphenyl phosphate (TPP) - *p*-xylene (PX) polymeric coatings. The initial and final solid concentrations are given in Table 4.2. It is clear from these results that the solid concentration is increasing exponentially with increasing TPP wt.% in all the different type of polymeric coatings with initial coating thickness 1351 µm, 1342 µm, 1335 µm, 1330 µm and 1341 µm, respectively. In polymeric coating with 2% TPP, the highest solid concentration is achieved as shown in Table 4.2 and Figure 4.10. Also, the polymeric coating containing 2% TPP, contains minimum amount of residual solvent.

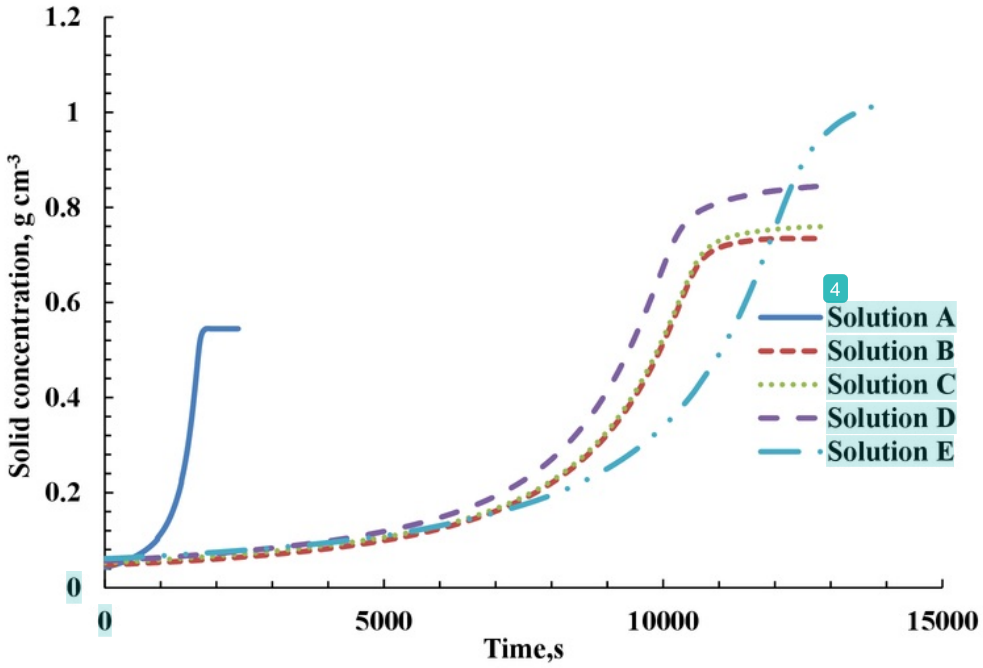
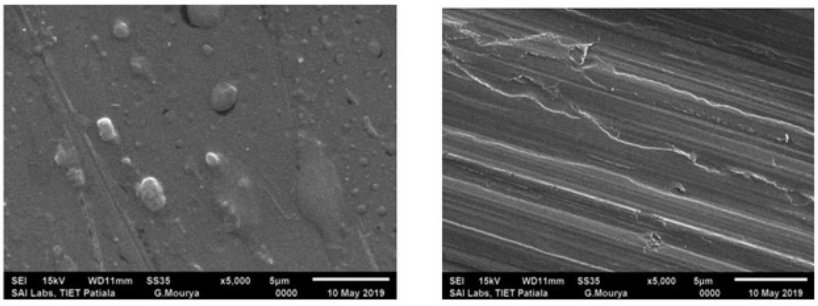


Figure 4.10. Solid concentration, (g cm^{-3}) as a function of time, (s) for various TPP loading for nearly 1300 µm initial coating thickness.

4.3 Surface Morphology for Coatings of Nearly 2000µm Initial Coating Thickness

To determine the surface morphology of different type of polymeric coatings, scanning electron microscopy (SEM) was used. In this technique, an accelerating voltage of 15 KV is used. Figure 4.11 shows the surface morphology for different type of polymeric coatings of nearly 2000µm initial coating thickness.



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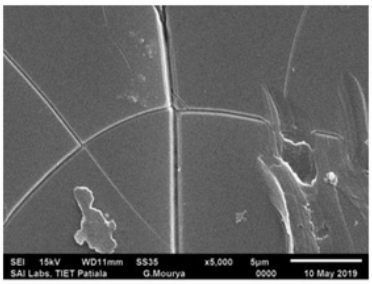

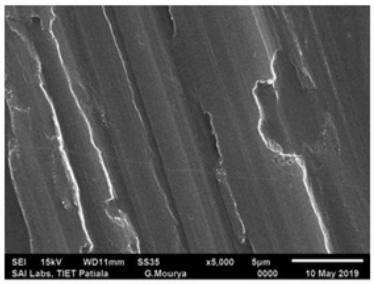

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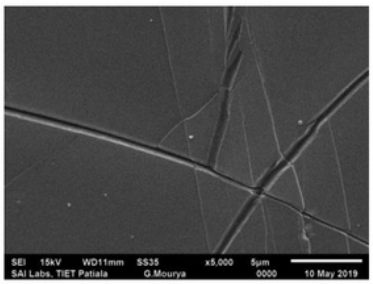

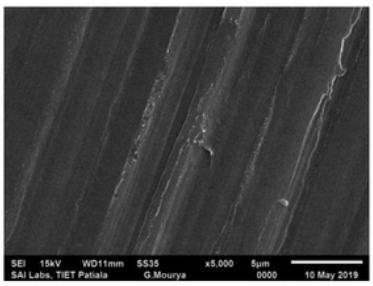

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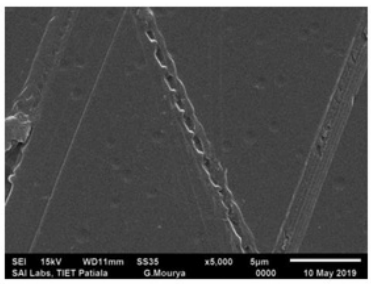

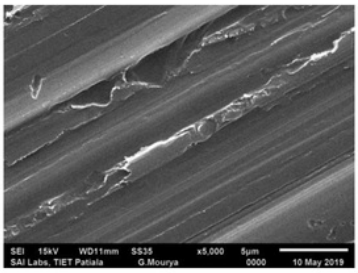

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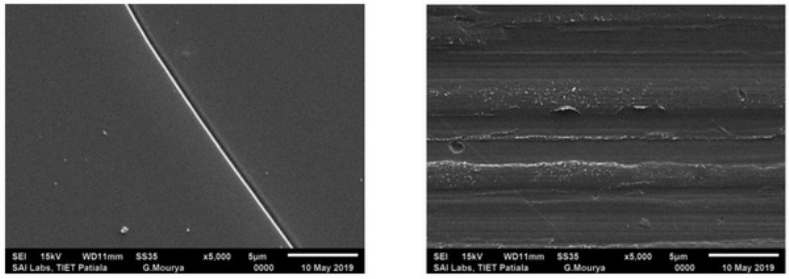

(e) (Front) (Back)

Figure 4.11 SEM images of different type of polymeric coatings, (a): Coating of 4.95% poly (styrene), 0% triphenyl phosphate and 95.05 % *p*-xylene (initial coating thickness: 2021 µm), (b): Coating of 5.02% poly (styrene), 0.52% triphenyl phosphate and 94.46% *p*-xylene (initial coating thickness: 2011 µm), (c): Coating of 5.03% poly (styrene), 1.02% triphenyl phosphate and 93.95% *p*-xylene (initial coating thickness: 1999 µm), (d): Coating of 5.02% poly (styrene), 1.51% triphenyl phosphate and 93.47% *p*-xylene (initial coating thickness: 2005 µm), (e): Coating of 5% poly (styrene), 2% triphenyl phosphate and 93% *p*-xylene (initial coating thickness: 2009 µm).

Figure 4.11 shows the surface morphology of the polymer coatings of nearly 2000 µm initial coating thickness**.** In Figure 4.11(a)(Front), the surface appears uneven with some rounded particles of variable size and shape; (b)(Back), the surface is irregular because of abrasion of polymeric coating. In Figure 4.11(b)(Front), the surface is dense and irregular; (b)(Back), the surface appears rough due to scratching of polymeric coating. In Figure 4.11(c)(Front), the surface appears even and dense along with appearance of some thin lines; (c)(Back), the surface of coating is rough because of scratching. In Figure 4.11(d)(Front), the surface is dense with pores into it which are responsible for its irregularity; (d)(Back) the surface of coating is uneven because of abrasion. In Figure 4.11(e)(Front), the surface appears very much dense and even; (e)(Back), the coating surface is irregular because of scratching of coating. By and large, all the coatings appear smooth and completely dense with no cracks or defects.

Chapter 5

Conclusions

The effect of plasticizer TPP on various PS-PX coatings is studied. In various polymeric coatings studied, it was observed that the percentage of residual solvent remaining at the end of drying process is highly influenced by the concentration of plasticizer. Overall, with the increase in concentration of plasticizer, effective reduction in residual solvent percentage in dry polymeric coating is observed. In the case of the polymeric coating with initial coating thickness 2000 µm in which plasticizer concentration is varied in the range of 0% to 2%, the residual solvent decreased from 2.62 % to 1.35 %, respectively, with one exception. However, the evaporation time increases with increase in TPP wt.% with only one exception. Again, when polymeric coatings having initial coating thickness 1300 µm were studied, with plasticizer concentration ranging from 0% to 2%, the residual solvent decreased from 3.92% to 0.34%. Also, the evaporation time, however, increases with increase in TPP wt.% with one exception. The SEM images show smooth and dense coating with little defects.

Thesis

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