

**DRYING OF QUATERNARY COATINGS OF POLY(STYRENE)
AND POLY(METHYL METHACRYLATE)**

M.Tech. Dissertation

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by

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Certificate

This is to certify that the dissertation work entitled “**Drying of Quaternary Coatings of Poly(styrene) and Poly(methyl methacrylate)**” submitted by **Anubhav Prashar (Roll. No. 601611001)** in partial fulfillment for the award of degree of Master of Technology in Chemical Engineering from Thapar Institute of Engineering and Technology, Patiala, Punjab, is a genuine work done under our guidance. 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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I hereby declare that the dissertation report entitled “**Drying of Quaternary Coatings of Poly(styrene) and Poly(methyl methacrylate)**” submitted to Thapar Institute of Engineering and Technology, Patiala in partial fulfillment for the award of degree of M. Tech in Chemical Engineering is a record of genuine and independent project work done by me carried under the supervisions of **Dr. Raj Kumar Arya** and **Dr. Sanjeev Kumar Ahuja**, Associate Professors, Department of Chemical Engineering, Thapar Institute of Engineering and Technology, Patiala. The work contained in this report has not been previously submitted to meet the requirements for a degree at this or any other higher education institution.

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Abstract

Gravimetric study of quaternary polymeric coatings has been investigated. The effect of various coating parameters, i.e., initial thickness and coating composition has been studied. Two quaternary systems: poly(styrene) – ethylbenzene – toluene – *p*-xylene and poly(methyl methacrylate) – ethylbenzene – toluene – acetone, have been studied. Their residual solvent, average concentrations of polymer, solvent and coating thickness have been compared with binary and ternary coatings. The results indicate that the amount of any costly solvent can be decreased to significant value in quaternary coating by using other cheaper solvents, which give nearly same drying rate and, hence, lowers the energy requirement for the drying.

Binary coatings of poly(styrene) – toluene, poly(styrene) – ethylbenzene, poly(styrene) – *p*-xylene, poly(methyl methacrylate) – toluene, poly(methyl methacrylate) – ethylbenzene, and poly(methyl methacrylate) – acetone has been compared with corresponding quaternary systems.

Ternary coatings of poly(styrene) – toluene – ethylbenzene, poly(styrene) – toluene – *p*-xylene, poly(styrene) – ethylbenzene – *p*-xylene, poly(methyl methacrylate) – toluene – acetone, poly(methyl methacrylate) – toluene – ethylbenzene, and poly(methyl methacrylate) – ethylbenzene – acetone has been compared with corresponding quaternary systems.

Key words: Drying of Quaternary coatings; Residual solvent; Thin films; Use of solvents blends

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Chapter 1

Introduction

1.1 Importance of polymeric coatings

Extensive amount of research activities are going in the field of polymeric materials and to make them applicable in each and every sector of life be it domestic or industrial. There is a large scale production of polymer coatings that are applied in individual area of engineering [1]. Polymer-based coatings have plentiful applications, for example, in manufacturing storage devices and magnetic tapes, fiber and an optical film, filters, and membrane, functional films for household, food packaging, controlled drug delivery, biomedical, protective films, pharmaceutical products, and decorative films [2].

Polymer coatings are applied using thinner. Thinners are used in order to get regular and consistent surface morphology. These solvents used in the coating solution should be cheaper, environmentally friendly and susceptible for simple recovery from the coating without causing any sort of manufacturing flaws like blisters, wrinkles, and cracks. By decreasing the residual solvent(s), these manufacturing defects can be controlled. The proportion of solvent in the polymer-based coating can be numerically decreased by using proper diffusion model, and we get the real product without defects by using the modeled variables.

Polymeric coatings are used for protection and decorative purposes and hence to increase their service life [3]. The coating smears the material in a uniform manner. Depending on the requirement, the material can be partially or fully glazed or coated. Polymer-based coatings can be developed by various means with solvent or without solvent. In the beginning of coating preparation, polymers can be cross-linked, elastic, or glassy in nature [1].

The solvents consisting of blends or mixtures are frequently engaged in coating expressions. The reason for using one or more solvents in polymeric coatings constitutes are: the rate of drying has to be controlled when the solvents departs. The cost of solvent can be minimized by replacing the expensive, useful solvent by a cheaper non-useful solvent [4]. Selection of solvents for mixing the polymer is an essential feature to get homogeneous solution. These aspects or conditions are arranged in relationships of the solubility parameters, which are

related to the phase behavior. The primary goal of drying operation is to get the defect free homogenous coating.

Reactive coatings are the coatings which can be applied on the concrete substrate or masonry substrates. It offers protection from water and its contaminants. The contaminants maybe salts, alkalis and acids. Thus, this type of coatings reacts with these contaminants present in the substrates to form covalent bonds. Epoxy, acrylic are the examples of reactive coatings. In case of some reactive coating solution, the drying of blend of solvents can be done to retain reactants and products in the solution till the coatings become gel. Then it allows the solvent retained in the coating to be removed with the help of drying [4].

1.2 Methods for preparation of coatings

There are several methods to prepare the polymeric coatings. Coatings can be prepared with and without solvent(s). A few commonly used coatings preparation methods are as follows:

1.2.1 Solution casting process: The solvent casting process is an easy and very old technique used for preparation of the polymeric coatings. The polymer(s) are dissolved in solvent(s) in order to get homogenous solution. The solution formed is either poured into the cavity or applied directly on the substrate with the help of a brush. This method is used for the manufacturing of the medical films, engineering plastics, sheets for electrical or electronic applications and optical films. For the manufacture of films with high class requirements, the solvent casting process is becoming more attractive in the present world [12]. In this technique, the main advantage is that the coating is having uniform thickness distribution, immensely low-haze and maximum optical purity. The films produced using this method are having excellent flatness and dimensional stability.

1.2.2 Spin coating technique: The spin coating approach is useful in producing high quality and very thin polymer films [5]. The polymeric solution is poured on the rotating substrate. Rotation is provided to the substrate at fixed rpm depending on the requirement. Centrifugal force helps to reduce the thickness of the solution by spreading it out equally. Coating thickness can be controlled by regulating the rotation speed of the substrate. It dries faster due to forced convective mass transfer

[6]. This technique is used to prepare gas separation membranes, photovoltaic cells, and field effect transistors.

1.2.3 Drop casting method: This method is useful in producing accurate and very small coatings of polymer. In this method, the polymeric is poured as droplet and left for drying. Thus, in this technique small quantity of solution is used. The films produced by this technique are very irregular due to poor spreading of solution. The thickness of the films produced by this technique is irregular. Films are thinner at the edges and thicker at the center and these issues can be overcome by using pin drop casting method [7]. This new technique offers an auxiliary approach for semiconductors made from polymers, which are very costly and have poor self-control.

1.2.4 Dip casting method: The dip casting technique is useful in protecting objects from corrosion. An object is immersed into the solution of polymer and is dragged out at certain speed. The thickness will be more at the bottom of the object as compared to the upper part of the object, which is due to the generation of extra drops of blend at the bottom.

1.2.5 Film casting method: This method is used to manufacture thin polymeric films. In this method, the polymer melt is extruded through the narrow opening and at the same time, stretched in the direction of machine by the movement of a chill roll. The chill roll provides faster cooling to the polymer melt at the time of stretching. Some examples of film casting are, optical films for flat panel displays, separators for Li-ion batteries. The films formed by this method are of regular thickness, optical quality, and higher quality. This type of film is useful to make separators for Li-ion batteries and optical films for flat panel displays[8, 9].

1.3 Classification of polymer coatings

Coatings can be classified into several types. Based on solvents, these can be classified as organic and inorganic coatings. Now, these coating can be further classified based on the number constituents involved in them. Figure 1.3 shows the classification of polymer coatings which are classified in two categories, i.e., binary coatings and multicomponent coatings. In binary coatings: there is one polymer-one solvent present in the coating. However, in multicomponent coatings more than two components are present. These can be

either solvents or polymers. In ternary coatings consists of either one polymer and two solvents or two polymers and one solvent. Another category is the quaternary coatings. In these coatings, four components are involved and these can be arranged in several ways. It may either be one polymer - three solvents systems, or two polymers - two solvents systems, or three polymers – one solvent systems.

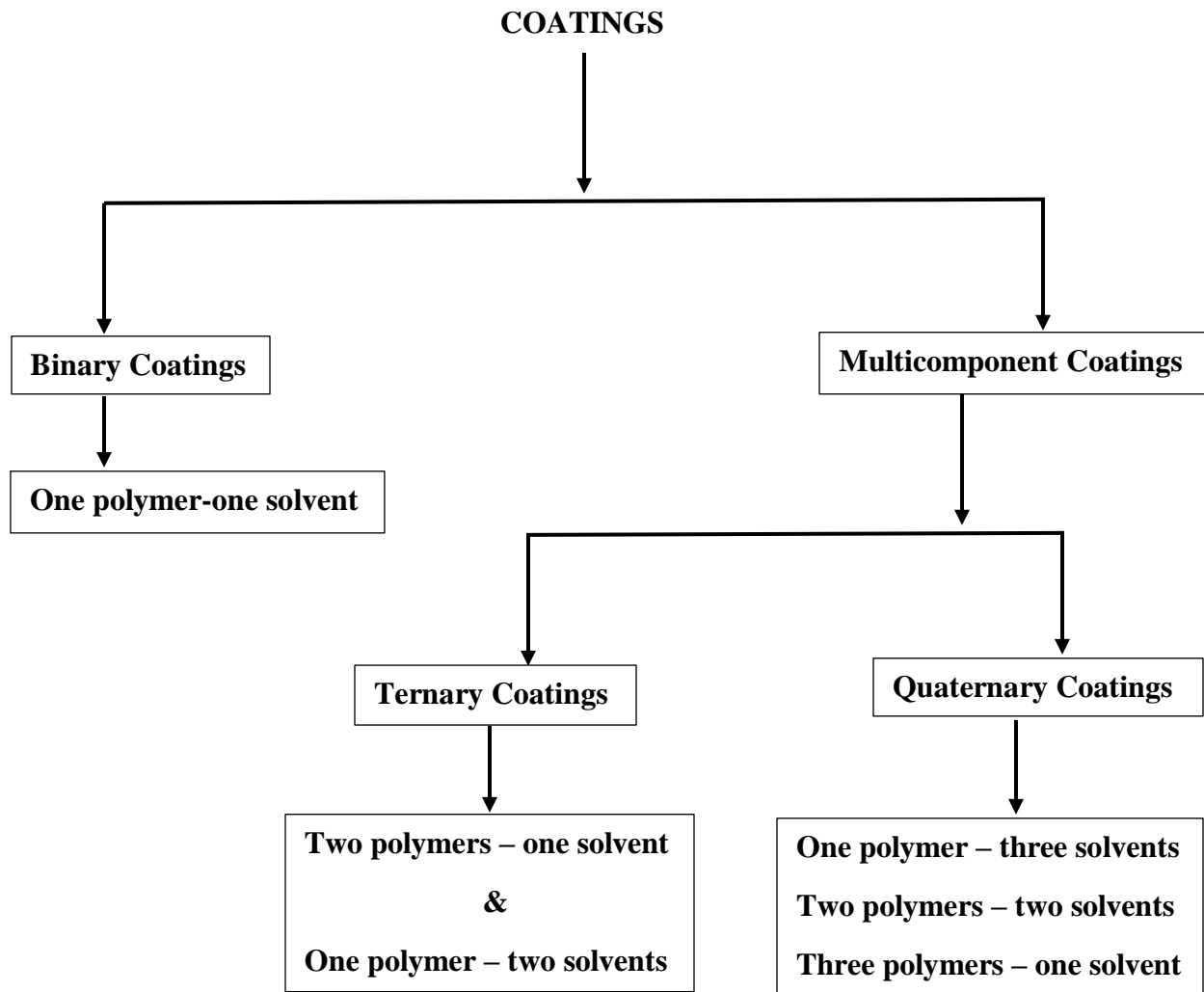


Figure 1.1: Schematic showing classification of polymer coatings.

1.4 Drying of polymeric coatings

In polymeric coatings, drying is final step and also a quality control step. The properties and final structure of coatings are extremely affected during the course of drying [10]. Due to irregular drying of the polymer coatings various defects may take place such as bending, cracks, blisters and inadequate residual solvent extraction. Proper controlled drying is required to avoid these types of defects. During the drying operation, solvent(s) diffuses within the polymeric film and depart from the coating – air interface into to atmosphere by evaporation process. The solvent evaporation from the surface is controlled by convection mass transfer and within the film by diffusion process. During the drying process, coating may either loose the temperature or gain the temperature depending on the surrounding atmosphere. So, drying is the complex process involving simultaneous heat and mass transfer processes.

Drying rate is mainly depending on the diffusion of solvent(s) within the polymeric films. Diffusion in dilute polymeric system is governed by Fick's law of diffusion which says rate of change if concentration is equal to the gradient of diffusion coefficient times the concentration gradient there. The diffusion coefficient in polymeric system is governed by the Vrentas and Duda free volume theory[11, 12] in conjunction with Flory-Huggins theory of polymer thermodynamics. These diffusion coefficients are related to self-diffusion coefficients and activity coefficients. There are several models to express these coefficients in polymer – solvent – solvent systems [13-16].

1.5 Dissertation outlines

Chapter 1: Introduction: importance of polymeric coatings, methods for preparation of coating, application of coatings, classification of polymeric coatings, drying in polymer-solvent coatings.

Chapter 2: Literature review: drying in quaternary coating, limitations and future scope of study, objectives

Chapter 3: Materials and methods: experimentation and calculations have been explained in this chapter.

Chapter 4: Results and discussion have been discussed.

Chapter 5: Conclusions based on the present study have been reported.

Chapter 2

Literature Survey

In this chapter, literature survey on quaternary coatings has been provided. The chapter is divided in several sections: drying in quaternary coatings, limitations and future scope of study, and objectives.

2.1 Drying in quaternary coatings

Siebel et al. [17] studied drying of quaternary coatings of poly(vinyl acetate) – toluene – methanol – dichloromethane. They studied the effect of coating composition on drying behavior. Their results showed that the thickness of the film in case of equal solvent loading was more as compared to the varying solvent loading case. Also, the drying rate was higher in case of varying solvent loading. The additional solvent increases the diffusional of the solvent mixture. They developed a diffusion model to predict the drying behavior in this system and validated using depth profiling data.

The following expressions are for components 1, 2, and 3:

$$\frac{\partial \rho_1^V}{\partial \zeta} = \rho_P^V \cdot \left[\frac{\partial X_1}{\partial \zeta} (1 - \varphi_1) - \frac{\partial X_2}{\partial \zeta} \frac{\bar{v}_2}{\bar{v}_1} \varphi_1 - \frac{\partial X_3}{\partial \zeta} \frac{\bar{v}_3}{\bar{v}_1} \varphi_1 \right] \quad (1)$$

$$\frac{\partial \rho_2^V}{\partial \zeta} = \rho_P^V \cdot \left[\frac{\partial X_2}{\partial \zeta} (1 - \varphi_2) - \frac{\partial X_1}{\partial \zeta} \frac{\bar{v}_1}{\bar{v}_2} \varphi_2 - \frac{\partial X_3}{\partial \zeta} \frac{\bar{v}_3}{\bar{v}_2} \varphi_2 \right] \quad (2)$$

$$\frac{\partial \rho_3^V}{\partial \zeta} = \rho_P^V \cdot \left[\frac{\partial X_3}{\partial \zeta} (1 - \varphi_3) - \frac{\partial X_1}{\partial \zeta} \frac{\bar{v}_1}{\bar{v}_3} \varphi_1 - \frac{\partial X_2}{\partial \zeta} \frac{\bar{v}_2}{\bar{v}_3} \varphi_3 \right] \quad (3)$$

where, ρ_i^V is mass concentration of component i, units: mass per unit volume

ζ is spacial coordinate and φ_P is volume faction of the polymer.

Equations (1), (2), (3) can be rewritten for obtaining flux equation:

$$D_{11}^P \frac{\partial X_1}{\partial \zeta} = \varphi_P \cdot \left[\frac{\partial X_1}{\partial \zeta} \cdot C_{1,1} + \frac{\partial X_2}{\partial \zeta} \cdot C_{1,2} + \frac{\partial X_3}{\partial \zeta} \cdot C_{1,3} \right] \quad (4)$$

Here, $C_{1,1} = D_{11}^V(1 - \varphi_2 - \varphi_3)(1 - \varphi_1) - D_{22}^V\varphi_1\varphi_2 - D_{33}^V\varphi_1\varphi_3$

$$C_{1,2} = D_{22}^V\varphi_1(1 - \varphi_2)\frac{\bar{V}_2}{\bar{V}_1} - D_{11}^V\varphi_1(1 - \varphi_2 - \varphi_3)\frac{\bar{V}_2}{\bar{V}_1} - D_{33}^V\varphi_1\varphi_3\frac{\bar{V}_2}{\bar{V}_1}$$

$$C_{1,3} = D_{33}^V\varphi_1(1 - \varphi_3)\frac{\bar{V}_3}{\bar{V}_1} - D_{11}^V\varphi_1(1 - \varphi_2 - \varphi_3)\frac{\bar{V}_3}{\bar{V}_1} - D_{33}^V\varphi_1\varphi_3\frac{\bar{V}_3}{\bar{V}_1}$$

The diffusion coefficients were calculated by the following expression:

$$\frac{D_{ii}^v}{m^2/s} = \exp\left(-\frac{A_i + B_i \times (X_i + X_j + X_k)}{1 + C_i \times (X_i + X_j + X_k)}\right) \quad (5)$$

where, A_i, B_i, C_i are empirical parameters.

D_{ii}^v is the diffusion coefficient, units: m^2/s

$X_i, X_j,$ and X_k are solvent loadings.

Luna *at el.* [18] presented convective drying of a multicomponent polymeric coating film using the solvents acetone, ethanol, ethylene glycol and cellulose acetate hydrogen phthalate polymer. The investigations showed that the drying rate possesses two different falling periods. They compared drying of ternary mixture of acetone, ethanol and polymer with quaternary mixture of acetone, ethanol, ethylene glycol and polymer. acted as a softener in the second set. Results showed that in quaternary coating, ethylene glycol acted as the softener and helped to increase the evaporation rates. The author presented the mathematical model to predict the composition profile in the film as a function of time.

Equation for diffusion in one dimension is as follows:

$$\frac{\partial(C_l X)}{\partial t} = \frac{\partial}{\partial z} \left(C_l D \frac{\partial X}{\partial z} \right) - \frac{\partial(G_l X)}{\partial z} \quad (6)$$

where, C_l is the total concentration, G_l is total flux and D is diffusion coefficient.

Energy balance for non - isothermal evaporation in liquid thin film:

$$\frac{\partial(C_l C_{pl} T_l)}{\partial t} = \frac{\partial}{\partial z} \left\{ k_l \frac{\partial T_l}{\partial z} \right\} - \frac{\partial(G_l C_{pl} T_l)}{\partial z} \quad (7)$$

where, T_l is temperature of liquid.

C_{pl} is molar heat capacity

k_l is thermal conductivity.

There is very limited amount of work has been done in the field of quaternary coatings till date, due to very complex nature of drying and suitability of multiple solvents in polymer due to phase separation. Extensive amount of work has been reported in the literature related to binary coatings be it modeling[11, 12, 14, 19, 20], experiments[13, 21, 22], and validation of models [23-25]. Several models have also been developed for polymer-solvent-solvent systems [13-16]. These models have also been tested for gravimetric data [4, 10, 13, 26] and measured concentration profile using confocal Raman spectroscopy [23, 25, 27, 28].

2.2 Limitations and future scope of study

- The literature regarding the quaternary coatings is limited and mainly focused on diffusion in binary and ternary coatings.
- Very limited studies and data are available regarding the diffusion of solvent in the quaternary coatings.
- Developed models are tested for a few systems only.
- There is limited study regarding the minimization of residual solvent which plays very important role in stability of coatings and defects of coatings like cracking, blistering and phase separation.
- Residual solvent study in the quaternary coatings is not yet reported.
- There is no literature given regarding the cost effectiveness of the coatings and to use the cheaper solvent.

For the present study, quaternary coatings containing one polymer - three solvents system have been selected. Two set of quaternary coatings has been prepared containing one polymer – three solvents. Choosing quaternary system will be cost effective instead of binary and ternary systems. The quantity of solvents used in quaternary system will be less as compared to others. Quantity of each solvent can be manipulated either to minimize the quantity of costlier solvent or

to minimize the drying time to cut energy demand for drying or both. Hence, quaternary system will be effective for making polymer and solvent coatings. For the present study, poly(styrene)-ethylbenzene-toluene-*p*-xylene system and poly(methyl methacrylate) – toluene – ethylbenzene – acetone systems are chosen. These two polymers are most commonly used commercial polymers with excellent mechanical, thermal, and optical properties. Solvent selection is being done based on solubility parameters and procedure develop by Hansen [29]. In this method, a spherical analysis was considered in which the center of sphere has values of δ_d , δ_p , δ_h of polymer. The interaction radius for the polymer is defined as R_o as the radius of sphere. For good solvents, the distance between solvent and polymer is defined as R_a and must be less than R_o . The value of R_a can be calculated using following expression:

$$R_a = \sqrt{4 \times (\delta_{dP} - \delta_{dS})^2 + (\delta_{pP} - \delta_{pS})^2 + (\delta_{hP} - \delta_{hS})^2} \quad (8)$$

where, the δ_{dP} , δ_{pP} , and δ_{hP} : are the values of dispersion, polar, and hydrogen bonding solubility parameters for polymer, and δ_{dS} , δ_{pS} , and δ_{hS} : are the values of dispersion, polar, and hydrogen bonding solubility parameters for solvent.

The values of solubility parameters for selected polymers and solvents are given in Table 2.1. The values of R_o for poly(styrene) and poly(methyl methacrylate) are $12.7 \text{ MPa}^{1/2}$ and $8.96 \text{ MPa}^{1/2}$ respectively [30]. The calculated values of R_a are given in Table 2.2. The solubility of polymer and solvents are also checked using Flory-Huggins interaction parameter(χ) and being calculated using Bristow and Watson correlation [31] as given below. The polymer will be miscible if calculated value of χ comes out to be less than 0.5 [32].

$$\chi_{ij} = 0.35 + \frac{\bar{V}_l}{RT} (\delta_i - \delta_j)^2 \quad (9)$$

where, χ_{ij} is interaction parameter, \bar{V}_l is partial molar volume of solvent (cm^3/mol), δ_i and δ_j are solubility parameters of the solvent and polymer, respectively, and T is temperature in K.

All the selected polymer – solvent combinations come out to be miscible because ratio of R_a/R_o is less than 1 as per Hansen criteria. The selected systems are also miscible as per Flory-Huggins theory because χ came out to be less than 0.5 as can be seen in Table 2.2.

Table 2.1: Solubility parameters of different solvents and polymers used.

S. No.	Polymer/Solvent	Dispersion solubility, δ_d , MPa ^{1/2}	Polar solubility, δ_p , MPa ^{1/2}	Hydrogen bonding, δ_h , MPa ^{1/2}
1.	Poly(styrene)	21.3	5.7	4.3
2.	Poly(methyl methacrylate)	17.7	6.7	6.2
3.	Ethylbenzene	17.8	0.6	1.4
4.	Toluene	18	1.4	2
5.	<i>p</i> -xylene	17.6	1.0	3.1
6.	Acetone	15.5	10.4	7

Table 2.2: The calculated values of interaction parameters and interaction radius for various polymer – solvent systems.

S. No.	Polymer – Solvent	χ_{ij}	R_a , MPa ^{1/2}	R_a/R_0
1.	poly(styrene) – toluene	0.351	8.20	0.64
2.	poly(styrene) – ethylbenzene	0.351	9.13	0.72
3.	poly(styrene) – <i>p</i> -xylene	0.351	8.85	0.69
4.	poly(methyl methacrylate) – toluene	0.35	6.78	0.75
5.	poly(methyl methacrylate) – ethylbenzene	0.35	5.80	0.86
6.	poly(methyl methacrylate) – acetone	0.35	7.76	0.64

2.3 Objectives

The objectives of the present work are:

- To study residual solvent content, coating thickness, average concentration of polymer and solvent in quaternary coatings.
- To study the effect of coating thickness on residual solvent, average concentration of polymer and solvent in quaternary coatings.
- To study effect of coating composition on residual solvent, coating thickness, average concentration of polymer and solvent in quaternary coatings.

Chapter 3

Materials and Methods

3.1 Experimentation

Poly(styrene)(PS) was purchased from Sigma Aldrich, Germany (molecular weight: 192000, density: 1.05 g cm^{-3}), poly(methyl methacrylate)(PMMA) was purchased from Sigma Aldrich, Germany (molecular weight: 120000, density: 1.181 g cm^{-3}), ethylbenzene(EB) was purchased from Spectrochem, India (molecular weight: 106.17, density: 0.866 g cm^{-3}), toluene(TOL) was purchased from Spectrochem, India (molecular weight: 92.14, density: 0.867 g cm^{-3}), *p*-xylene(PX) was purchased from Spectrochem, India (molecular weight: 106.16, density: 0.861 g cm^{-3}), acetone(ACE) was purchased from Spectrochem, India (molecular weight: 58.08, density: 0.785 g cm^{-3}).

Polymeric solutions of polymer-solvent-solvent-solvent were prepared in leach proof reagent bottles. The reagent bottles were shaken in mechanical shaker for 24 hrs. to get the homogenized solution. Solution casting technique was used to prepare the coating. A known amount of solution was poured into the circular sample holder with the help of micropipette to get the uniform coating. Coatings were prepared by pouring the known amount of polymeric solution in circular stainless-steel holder having 12.24 mm diameter and 2000 μm deep. The mass of the sample was recorded at a fix time interval using Precisa analytical weighing balance (ES 225SM-DR) having least count of $\pm 0.0001\text{g}$. All experiments were carried out without any air flow and at room temperature of $25 \text{ }^{\circ}\text{C}$. Figure 3.1 shows the steps involved in the coating preparation. The diffusion coefficients and cost of the solvents used are given in Table 3.1.

Table 3.1: Diffusion coefficients of solvents and their costs

Sr. No.	Solvent(s)	Diffusion coefficients, cm ² /s	Cost, Rs/Litre
1.	Acetone	1.06×10^{-4} [33]	593[34]
2.	Toluene	7×10^{-5} [35]	637[36]
3.	<i>p</i> -xylene	2.74×10^{-6} [37]	640[38]
4.	Ethylbenzene	4×10^{-5} [35]	1057[39]

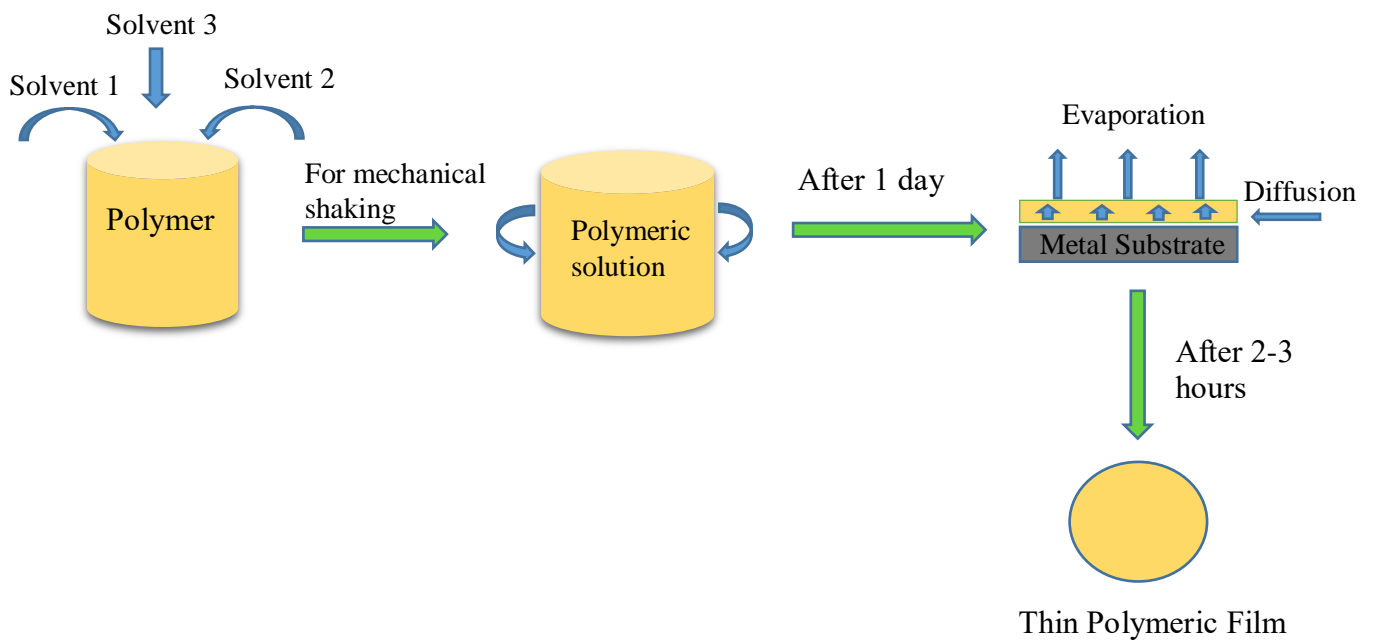


Figure 3.1: Schematic of coating preparation and its drying process

Several solutions of each polymeric systems were prepared as given below:

Poly(styrene) systems: Solutions of quaternary system of poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) system was prepared using the above procedure. The ternary combination of this system i.e., poly(styrene)(4.99%) – ethylbenzene(48.17%) – *p*-xylene(46.83%), poly(styrene)(5.1%) – toluene(46.43%) – ethylbenzene(48.47%), poly(styrene)(4.89%) – toluene(48.33%) – *p*-xylene(46.78%) and binary combination of the same system i.e., poly(styrene)(5.1%)–toluene(94.94%), poly(styrene)(4.95%) – *p*-xylene(95.04%), poly(styrene)(5.29%) – ethylbenzene(94.71%) were prepared as mentioned in Figure 3.2.

Poly(methyl methacrylate) systems: Quaternary solution of poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) was prepared. The ternary and binary combinations were poly(methyl methacrylate)(4.97%)–ethylbenzene(47.35%)–acetone(47.65%), poly(methyl methacrylate)(5.22%)–toluene(46.08%)–ethylbenzene(48.69%), poly(methyl methacrylate)(4.99%) – toluene(47.12%) – acetone(47.88%) and poly(methyl methacrylate)(4.96%) – toluene(95.04%), poly(methyl methacrylate)(4.98%) – acetone(95.01%), poly(methyl methacrylate)(4.96%) – ethylbenzene(95.03%) as mentioned in Figure 3.2.

In this work, our purpose is to prepare the quaternary coatings having low percentages of residual solvent and to select the appropriate system which can minimize the cost of the solvents. Two solutions of each quaternary systems were also prepared by varying the composition of the various solvents used. In poly(styrene) system, the concentration of toluene was kept higher as compared to other solvents, i.e., ethylbenzene and *p*-xylene due to low cost. In poly(methyl methacrylate) system, the concentration of toluene was also kept higher than acetone and ethylbenzene. In both systems, the concentration of ethylbenzene was kept nearly 20% because of high cost than the others. Residual solvent, coating thickness, average concentration of polymer and solvents has been studied in all the case and has been discussed in Chapter 4.

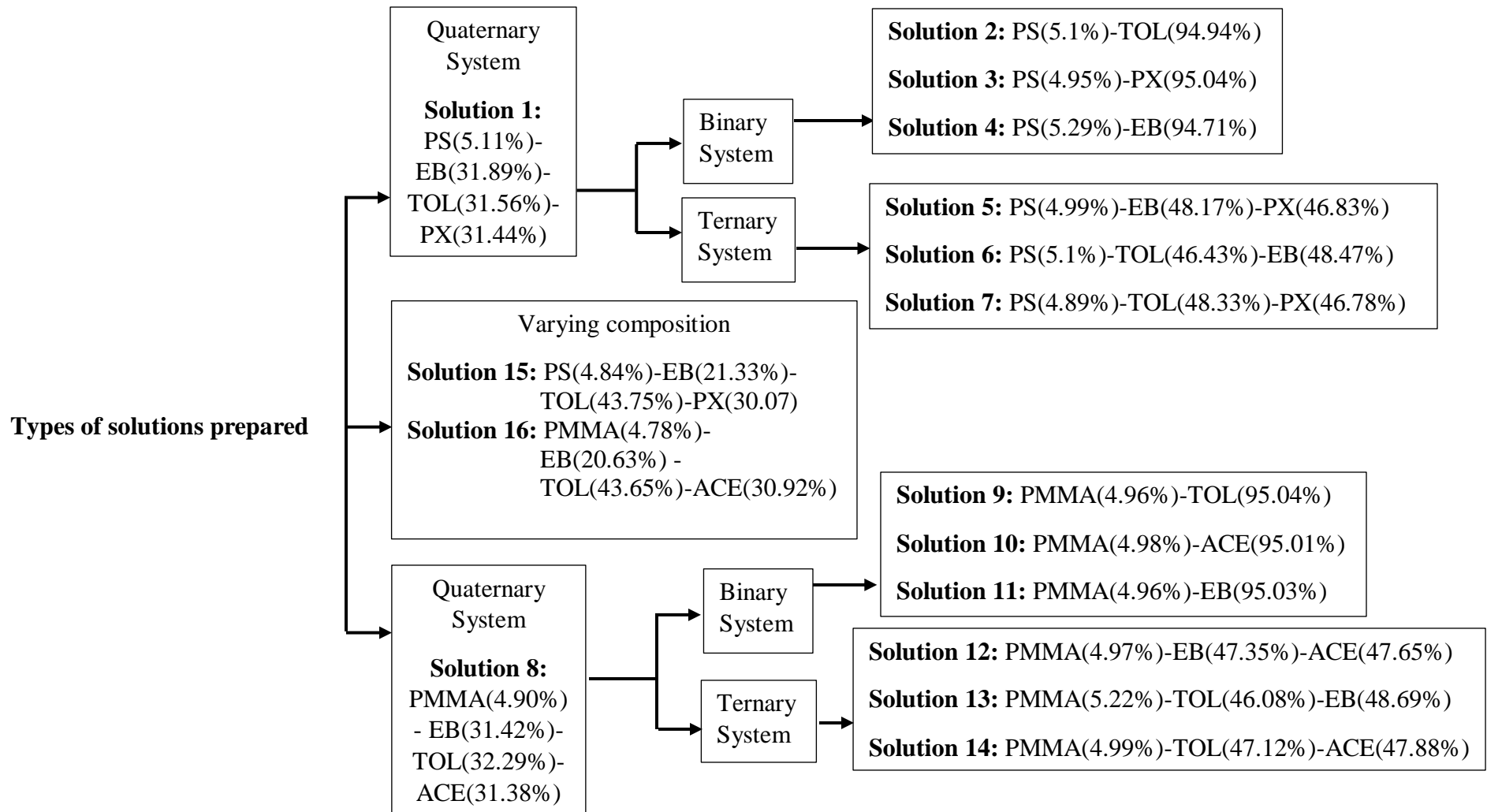


Figure 3.2 Details of coating solutions prepared.

3.2 Calculations

Let the initial mass of quaternary solution is “ m ”, in which 5% polymer and 95% of solvents.

$$\text{The cross-sectional area of the substrate} = \pi \left(\frac{d}{2}\right)^2 = \left(\frac{22}{7}\right) \times \left[\frac{\left(\frac{12.24}{10}\right)}{2}\right]^2 = 1.1771 \text{ cm}^2$$

$$\text{Mass of polymer, } M_p = m \times \frac{5}{100}$$

$$\text{Initial mass of all solvents, } M_s = m \times \frac{95}{100}$$

$$\text{Average density of solvents mixture, } \rho_{avg} = \frac{M_{s1} \times \rho_{s1} + M_{s2} \times \rho_{s2} + M_{s3} \times \rho_{s3}}{M_{s1} + M_{s2} + M_{s3}}$$

It was assumed that there was no change in average density of solvents mixture because the densities of all the organic solvents are nearly equal. The effect of composition of various solvents at later stage of drying was not considered.

$$\text{Volume of the polymer, } V_p = \frac{M_p}{\text{Density of polymer}}$$

$$\text{Volume of the solvent, } V_s = \frac{M_s}{\rho_{avg}}$$

$$\text{Total volume, } V_T = V_p + V_s$$

$$\text{Percentage of residual solvent} = \frac{\text{Mass of the coating} - M_p}{M_s} \times 100$$

$$\text{Coating thickness, } L = \frac{\text{Total Volume}}{\text{cross-sectional area of the coating}}$$

$$\text{Concentration of the polymer} = \frac{M_p}{\text{Total Volume}} \times \frac{5}{100}$$

$$\text{Average concentration of the solvents} = \frac{\text{Mass of the coating} - M_p}{\text{Volume}}$$

Chapter 4

Results and Discussion

The drying behavior of polymer – solvent – solvent – solvent coatings has been discussed in this chapter. Different type of quaternary, binary, and ternary solutions were prepared as shown in Figure 3.2.

4.1 Drying of poly(styrene) – ethylbenzene – toluene - *p*-xylene coatings of nearly 1150 microns thickness

4.1.1 Residual solvent with time

Figure 4.1 shows the residual solvent as a function of time in various coatings of poly(styrene), i.e., binary and quaternary systems. The percentage of polymer in each coating was nearly 5%. The initial coating thicknesses in case of poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%), poly(styrene)(5.1%) – toluene(94.94%), poly(styrene)(4.95%) – *p*-xylene(95.04%), poly(styrene)(5.29%) – ethylbenzene(94.71%) were 1145 microns, 1166 microns, 1171 microns, and 1141 microns, respectively. The solvent removal rate was highest in poly(styrene) – toluene and slowest in poly(styrene) – *p*-xylene. The residual solvent left in poly(styrene) – ethylbenzene – toluene – *p*-xylene, poly(styrene) – toluene, poly(styrene) – *p*-xylene, poly(styrene) – ethylbenzene coatings are 2.39%, 0.82%, 1.78%, and 2.1% respectively after 7252 s, 3226 s, 10594 s, and 8813 s. The residual solvent removal trend is same in all the four coatings. However, poly(styrene) – toluene coating is drying much faster due to high diffusion coefficient of toluene as compared to *p*-xylene, and ethylbenzene as shown in Table 3.1. The drying rate of quaternary system is reasonably high as compared to poly(styrene) – *p*-xylene and poly(styrene) – ethylbenzene systems but slower than poly(styrene) – toluene system. In this quaternary system, the amount of toluene is nearly one third of binary system, therefore, these coatings would be less toxic due to lower percentage of toluene. Also, the cost of producing these quaternary films will be lower as compared to binary coating due to use of other cheaper solvents.

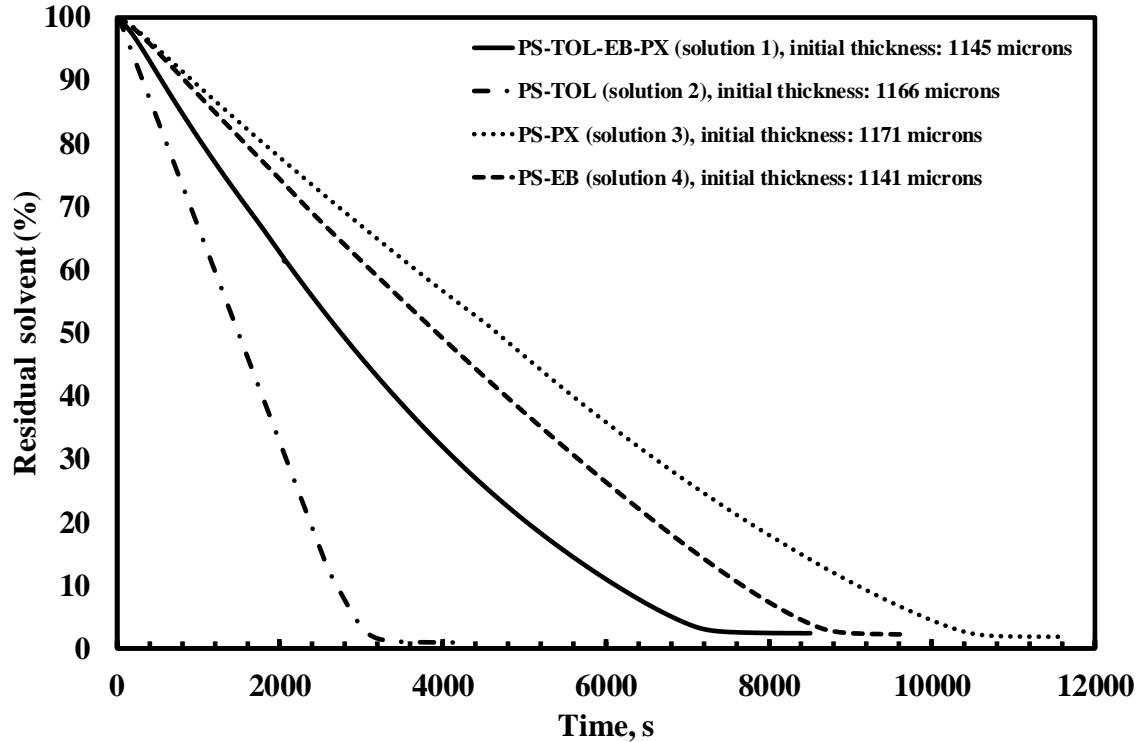


Figure 4.1: Residual solvent as a function of time in quaternary and binary coatings.

Figure 4.2 shows the residual solvent as a function of time in various coatings of poly(styrene), i.e., ternary and quaternary systems having the percentage of nearly 5% of polymer in each coating. The initial thickness of the coatings poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%), poly(styrene)(4.99%) – ethylbenzene(48.17%) – *p*-xylene(46.83%), poly(styrene)(5.29%) – ethylbenzene(94.71%) – toluene(46.43%), and poly(styrene)(4.89%) – toluene(48.33%) – *p*-xylene(46.78%) were 1145 microns, 1176 microns, 1107 microns, and 1145 microns, respectively, for each case. Percentage solvent removal was highest in poly(styrene) – ethylbenzene – toluene and slowest in poly(styrene) – ethylbenzene – *p*-xylene. The residual solvent left in poly(styrene) – ethylbenzene – toluene – *p*-xylene, poly(styrene) – ethylbenzene – *p*-xylene, poly(styrene) – ethylbenzene – toluene, and poly(styrene) – toluene – *p*-xylene coatings are 2.39%, 1.9%, 0.83%, and 2.24% respectively after 7252 s, 9578 s, 6532 s, and 6833 s. The residual solvent removal trend is same in all the four coatings. However, poly(styrene) – ethylbenzene – toluene and poly(styrene) – toluene – *p*-xylene coatings are drying much faster due to high diffusion coefficient of toluene as compared to *p*-xylene, and ethylbenzene as shown Table 3.1. The drying

of quaternary system is reasonably high as compared to poly(styrene) – ethylbenzene – *p*-xylene system but slower than poly(styrene) – ethylbenzene – toluene and poly(styrene) – toluene – *p*-xylene systems. In this quaternary system, the amount of toluene is nearly 2/3 of ternary system, therefore, these coatings would be less toxic due to lower percentage of toluene. The cost of quaternary coatings will be less as compared to other coatings.

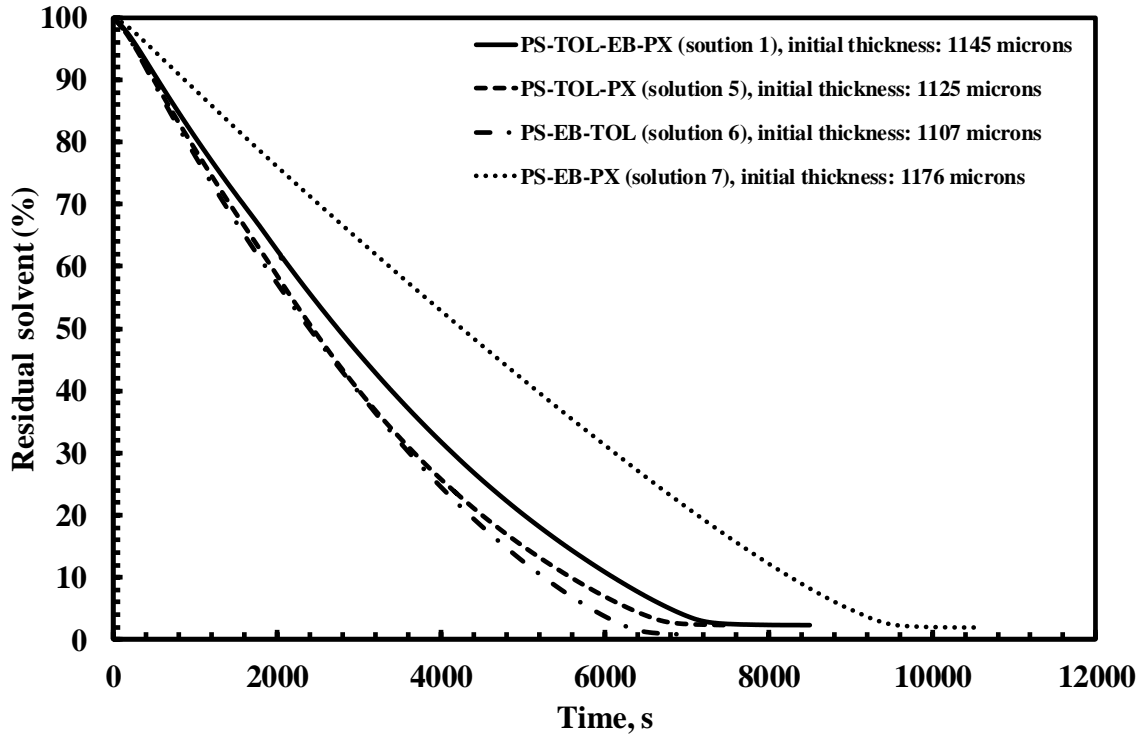


Figure 4.2: Residual solvent as a function of time in quaternary and ternary coatings.

4.1.2 Coating thickness with time

Figure 4.3 shows the coating thickness as a function of time in various coatings of poly(styrene), i.e., binary and quaternary systems. Each coating has the percentage of polymer nearly 5%. The initial coating thicknesses in case of poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%), poly(styrene)(5.1%) – toluene(94.94%), poly(styrene)(4.95%) – *p*-xylene(95.04%), poly(styrene)(5.29%) – ethylbenzene(94.71%) were 1145 microns, 1166 microns, 1171 microns, and 1141 microns, respectively. The decrease in coating thickness was faster in poly(styrene)-toluene and slowest in poly(styrene) – *p*-xylene. The final coating thickness in poly(styrene) – ethylbenzene – toluene –

p-xylene, poly(styrene) – toluene, poly(styrene) – *p*-xylene, and poly(styrene) – ethylbenzene coatings are 75 microns, 59 microns, 68 microns, and 74 microns respectively after 7252 s, 3226 s, 10594 s, and 8813 s. The decrease in coating thickness is following the same trend in all the four coatings. The decrease in coating thickness of quaternary system is reasonably high as compared to poly(styrene) – *p*-xylene and poly(styrene) – ethylbenzene system but slower than poly(styrene) – toluene system. All these coatings have nearly same thickness when drying is completed.

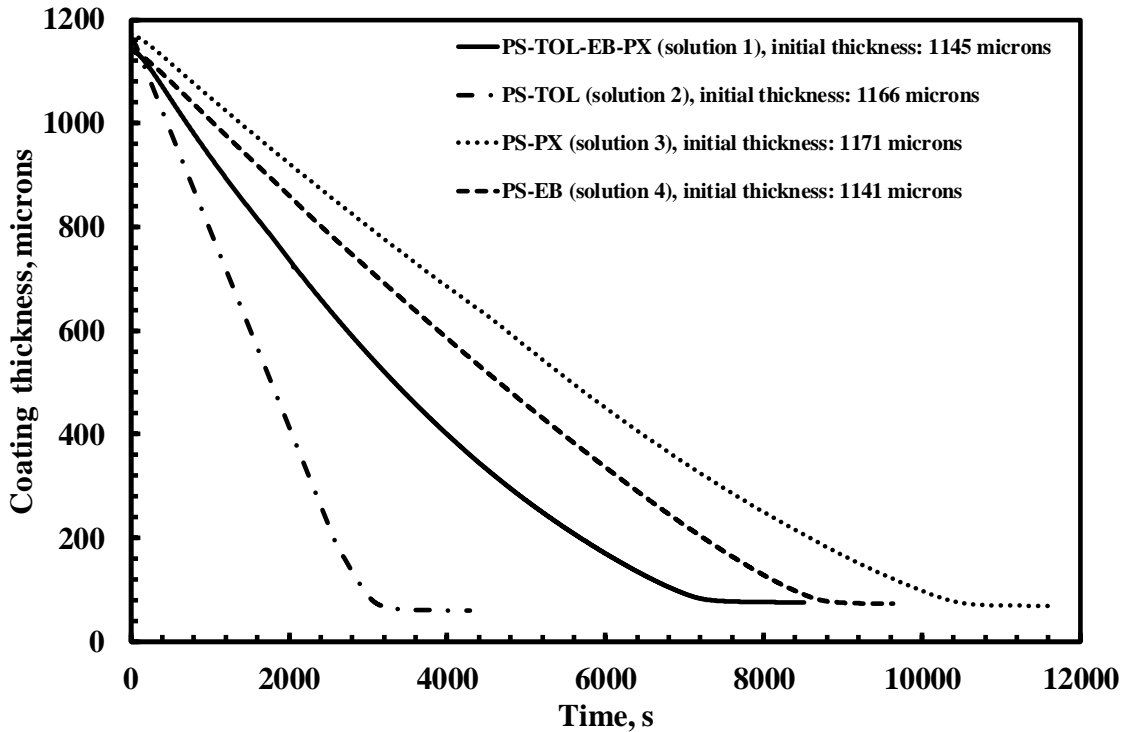


Figure 4.3: Coating thickness as a function of time in quaternary coating and binary coatings.

Figure 4.4 shows the coating thickness as a function of time in various coatings of poly(styrene), i.e., ternary and quaternary systems. The polymer in each coating has percentage of nearly 5%. The initial thickness of the coatings poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%), poly(styrene)(4.99%) – ethylbenzene(48.17%) – *p*-xylene(46.83%), poly(styrene)(5.29%) – ethylbenzene(94.71%) – toluene(46.43%), and poly(styrene)(4.89%) – toluene(48.33%) – *p*-xylene(46.78%) were 1145 microns, 1176 microns, 1107 microns, and 1145 microns, respectively. The decrease in coating thickness was highest in poly(styrene) – ethylbenzene – toluene and slowest in poly(styrene) – ethylbenzene – *p*-xylene.

The final coating thickness in poly(styrene) – ethylbenzene – toluene – *p*-xylene, poly(styrene) – ethylbenzene – *p*-xylene, poly(styrene) – ethylbenzene – toluene, and poly(styrene) – toluene – *p*-xylene coatings are 75 microns, 71 microns, 56 microns, and 70 microns respectively after 7252 s, 9578 s, 6532 s, and 6833 s. The decrease in coating thickness is following same trend in all the four coatings. The decrease in coating thickness of quaternary system is reasonably high as compared to poly(styrene) – ethylbenzene – *p*-xylene system but slower than poly(styrene) – toluene – ethylbenzene and poly(styrene) – toluene – *p*-xylene systems. All these coatings have nearly same thickness at the end of drying process. The poly(styrene) – toluene – ethylbenzene coating has less final thickness in the end because of less initial thickness.

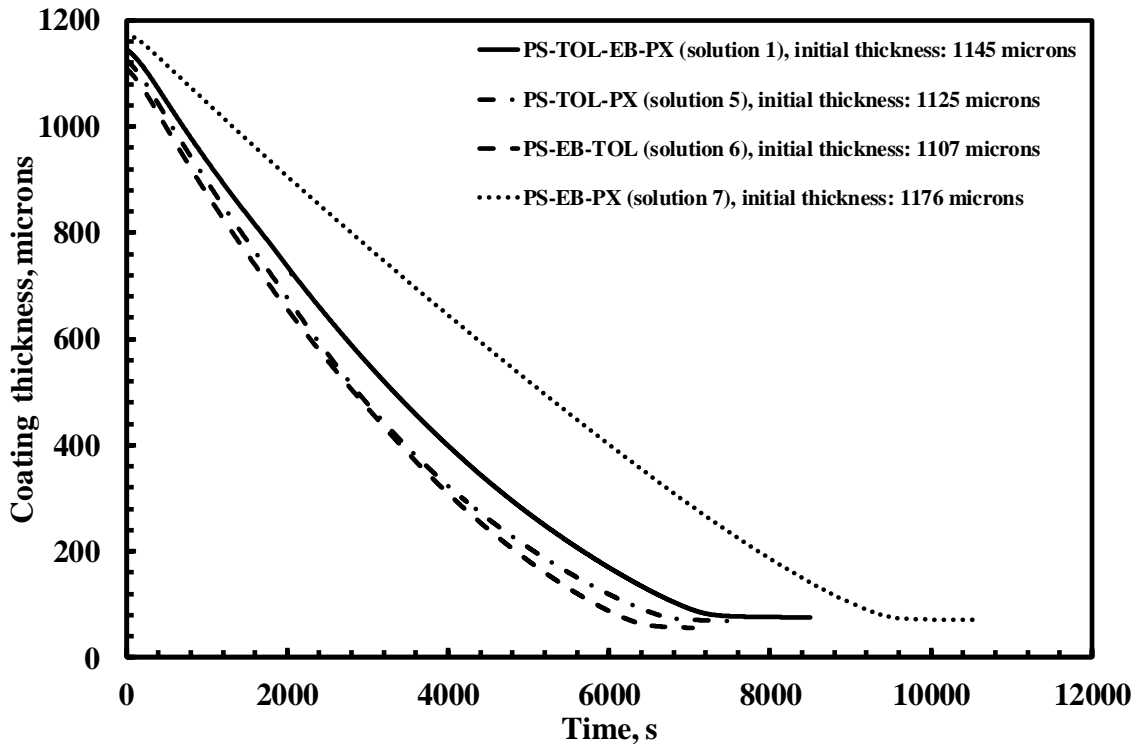


Figure 4.4: Coating thickness as a function of time in quaternary coating and ternary coatings.

4.1.3 Average concentration of solvent with time

Figure 4.5 shows the average concentration of solvent as a function of time in various coatings of poly(styrene), i.e., binary and quaternary systems having polymer of nearly 5% in each coating. The initial coating thicknesses in case of poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%), poly(styrene)(5.1%) – toluene(94.94%), poly(styrene)(4.95%) – *p*-xylene(95.04%), poly(styrene)(5.29%) –

ethylbenzene(94.71%) were 1145 microns, 1166 microns, 1171 microns, and 1141 microns, respectively. Write values of initial concentrations of solvents of poly(styrene) – ethylbenzene – toluene – *p*-xylene, poly(styrene) – toluene, poly(styrene) – *p*-xylene, and poly(styrene) – ethylbenzene coatings are 0.828 g.cm⁻³, 0.832 g.cm⁻³, 0.824 g.cm⁻³, 0.827 g.cm⁻³, respectively. The concentration of solvent left in poly(styrene) – ethylbenzene – toluene – *p*-xylene, poly(styrene) – toluene, poly(styrene) – *p*-xylene, and poly(styrene) – ethylbenzene coatings are 0.30 g cm⁻³, 0.13 g cm⁻³, 0.25 g cm⁻³, and 0.26 g cm⁻³, respectively after 7252 s, 3226 s, 10594 s, and 8813 s. The average concentration trend is in the form of Fickian diffusion for all the four coatings for almost entire drying period. Therefore, these coatings might be in rubbery state for that much time period. The concentration of poly(styrene) – toluene coating is decreasing faster than poly(styrene) – *p*-xylene coating. The concentration in poly(styrene) – toluene coating is less as compare to other coatings. The quaternary coatings have more concentration of solvent left in the coating but nearly same as other binary poly(styrene) – ethylbenzene and poly(styrene) – *p*-xylene coatings.

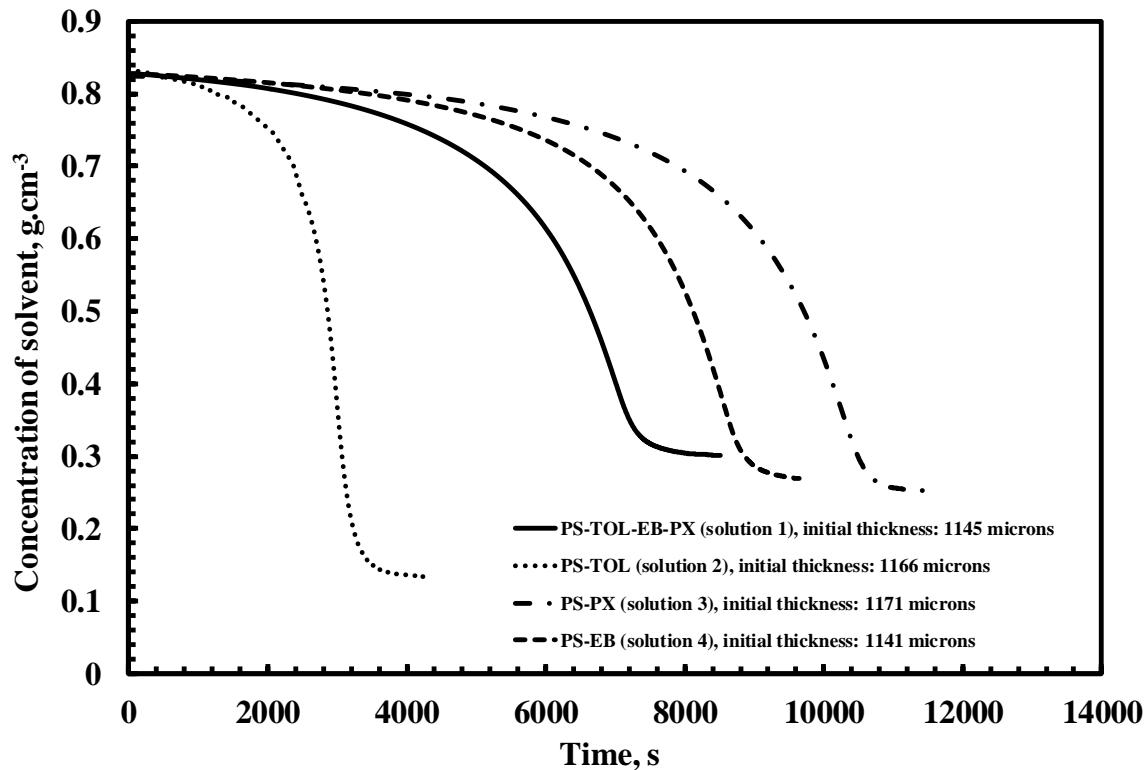


Figure 4.5: Concentration of solvent as a function of time in quaternary coating and binary.

Figure 4.6 shows the average concentration of solvent as a function of time in various coatings of poly(styrene), i.e., ternary and quaternary systems. The initial thickness of the coatings poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%), poly(styrene)(4.99%) – ethylbenzene(48.17%) – *p*-xylene(46.83%), poly(styrene)(5.29%) – ethylbenzene(94.71%) – toluene(46.43%), and poly(styrene)(4.89%) – toluene(48.33%) – *p*-xylene(46.78%) were 1145 microns, 1176 microns, 1107 microns, and 1145 microns, respectively. The initial concentrations of solvents of poly(styrene) – ethylbenzene – toluene – *p*-xylene, poly(styrene) – ethylbenzene – *p*-xylene, poly(styrene) – toluene – ethylbenzene, and poly(styrene) – toluene – *p*-xylene coatings are 0.828 g.cm⁻³, 0.827 g.cm⁻³, 0.830 g.cm⁻³, 0.830 g.cm⁻³, respectively. The concentration of solvent left in poly(styrene) – ethylbenzene – toluene – *p*-xylene, poly(styrene) – ethylbenzene – *p*-xylene, poly(styrene) – toluene – ethylbenzene, and poly(styrene) – toluene – *p*-xylene coatings are 0.30 g.cm⁻³, 0.26 g.cm⁻³, 0.14 g.cm⁻³, and 0.29 g.cm⁻³, respectively which are consuming 7252 s, 9578 s, 6532 s, and 6833 s. The average concentration trend is in form of Fickian diffusion in all the four coatings. The concentration of poly(styrene) – toluene – ethylbenzene and poly(styrene) – toluene – *p*-xylene coatings is decreasing faster than poly(styrene) – ethylbenzene – *p*-xylene coating. The concentration in poly(styrene) – toluene – ethylbenzene and poly(styrene) – toluene – *p*-xylene coatings is less as compare to other coatings. The quaternary coatings have more concentration of solvent left in the coating but nearly same as other ternary poly(styrene) – ethylbenzene – *p*-xylene and poly(styrene) – toluene – *p*-xylene coatings.

4.1.4 Average concentration of polymer with time

Figure 4.7 shows the average concentration of polymer as a function of time in various coatings of poly(styrene), i.e., binary and quaternary systems having nearly 5% of polymer in each coating. The initial coating thicknesses in case of poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%), poly(styrene)(5.1%) – toluene(94.94%), poly(styrene)(4.95%) – *p*-xylene(95.04%), poly(styrene)(5.29%) – ethylbenzene(94.71%) were 1145 microns, 1166 microns, 1171 microns, and 1141 microns, respectively. The initial concentration of poly(styrene) in poly(styrene) – ethylbenzene – toluene – *p*-xylene, poly(styrene) – toluene, poly(styrene) – *p*-xylene, and poly(styrene) – ethylbenzene coatings were 0.0446 g.cm⁻³, 0.0447 g.cm⁻³, 0.0429 g.cm⁻³, and 0.0462 g.cm⁻³, respectively. The

concentration of poly(styrene) left in poly(styrene) – ethylbenzene – toluene – *p*-xylene, poly(styrene) – toluene, poly(styrene) – *p*-xylene, and poly(styrene) – ethylbenzene coatings are 0.67 g cm^{-3} , 0.87 g cm^{-3} , 0.74 g cm^{-3} , and 0.71 g cm^{-3} , respectively after 7252 s, 3226 s, 10594 s, and 8813 s. There is exponentially increase in average concentration of polymer in all the four coatings. The concentration of poly(styrene) in poly(styrene) – toluene coating is increasing faster than poly(styrene) – *p*-xylene coating. The concentration of polymer in poly(styrene) – toluene coating is more as compare to other coatings. The ultimate concentration of poly(styrene) in quaternary coating is lower than poly(styrene) – toluene coating but nearly equal to other binary coatings of poly(styrene) – ethylbenzene and poly(styrene) – *p*-xylene.

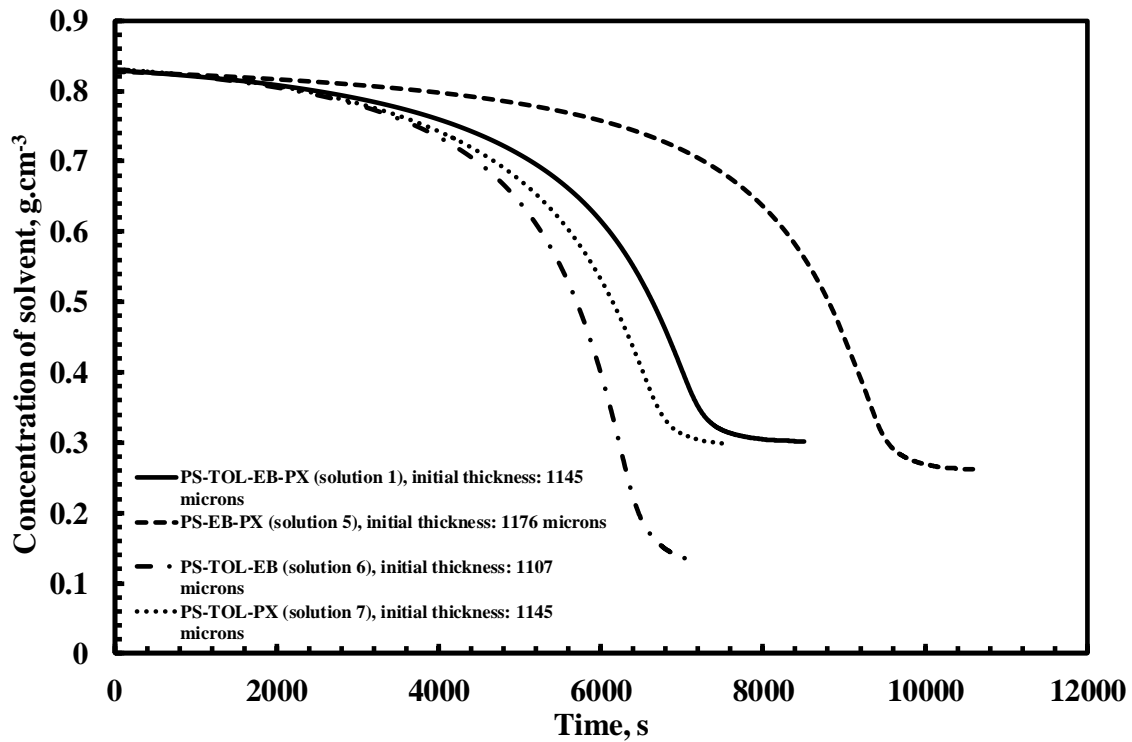


Figure 4.6: Concentration of solvent as a function of time in quaternary coating and ternary coatings.

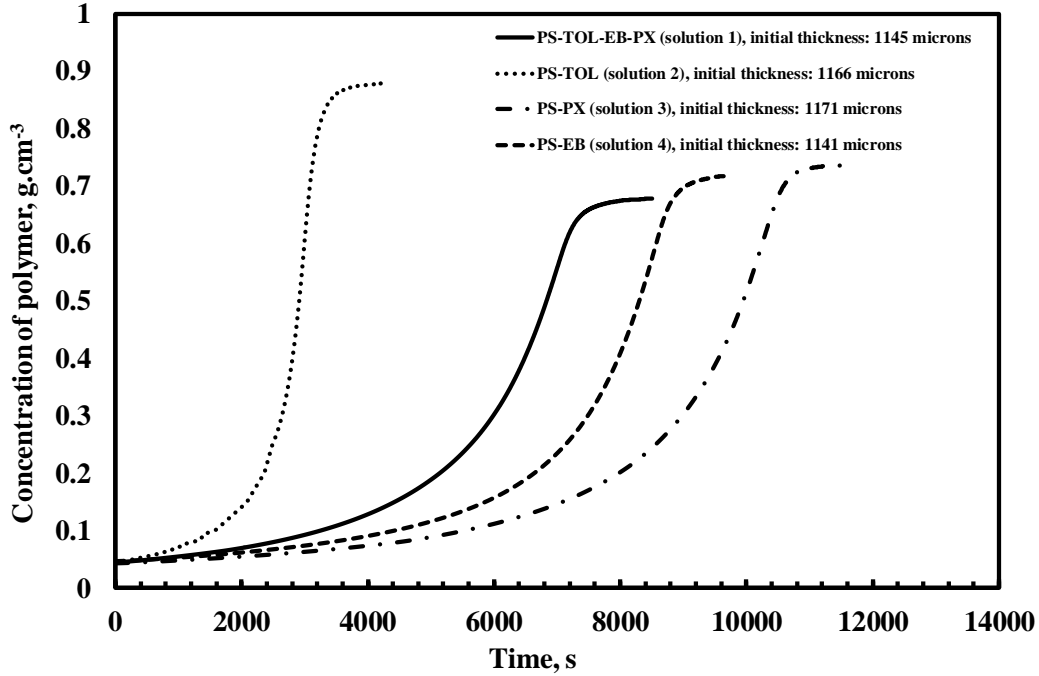


Figure 4.7: Concentration of polymer a function of time in quaternary coating and binary coatings.

Figure 4.8 shows the average concentration of polymer as a function of time in various coatings of poly(styrene), i.e., ternary and quaternary systems. The percentage of polymer was nearly 5% for all the coatings. The initial thickness of the coatings poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%), poly(styrene)(4.99%) – ethylbenzene(48.17%) – *p*-xylene(46.83%), poly(styrene)(5.29%) – ethylbenzene(94.71%) – toluene(46.43%), and poly(styrene)(4.89%) – toluene(48.33%) – *p*-xylene(46.78%) were 1145 microns, 1176 microns, 1107 microns, and 1145 microns, respectively. The initial concentration of poly(styrene) in poly(styrene) – ethylbenzene – toluene – *p*-xylene, poly(styrene) – ethylbenzene – *p*-xylene, poly(styrene) – toluene – ethylbenzene, and poly(styrene) – toluene – *p*-xylene were 0.0446 g.cm^{-3} , 0.0434 g.cm^{-3} , 0.044 g.cm^{-3} , and 0.0427 g.cm^{-3} , respectively. The concentration of polymer left in poly(styrene) – ethylbenzene – toluene – *p*-xylene, poly(styrene) – ethylbenzene – *p*-xylene, poly(styrene) – toluene – ethylbenzene, and poly(styrene) – toluene – *p*-xylene coatings are 0.67 g.cm^{-3} , 0.72 g.cm^{-3} , 0.87 g.cm^{-3} , and 0.68 g.cm^{-3} , respectively which are consuming 7252 s, 9578 s, 6532 s, and 6833 s. The average concentration trend is exponentially increasing in all the four types of coatings. The concentration of polymer in

poly(styrene) – toluene – ethylbenzene coating is increasing faster than poly(styrene) – ethylbenzene – *p*-xylene coating. The concentration of polymer in poly(styrene) – toluene – ethylbenzene coating is more as compare to other coatings. The quaternary coatings have less concentration of polymer left in the coating but nearly same as other ternary poly(styrene) – ethylbenzene – *p*-xylene and poly(styrene) – toluene – *p*-xylene coatings.

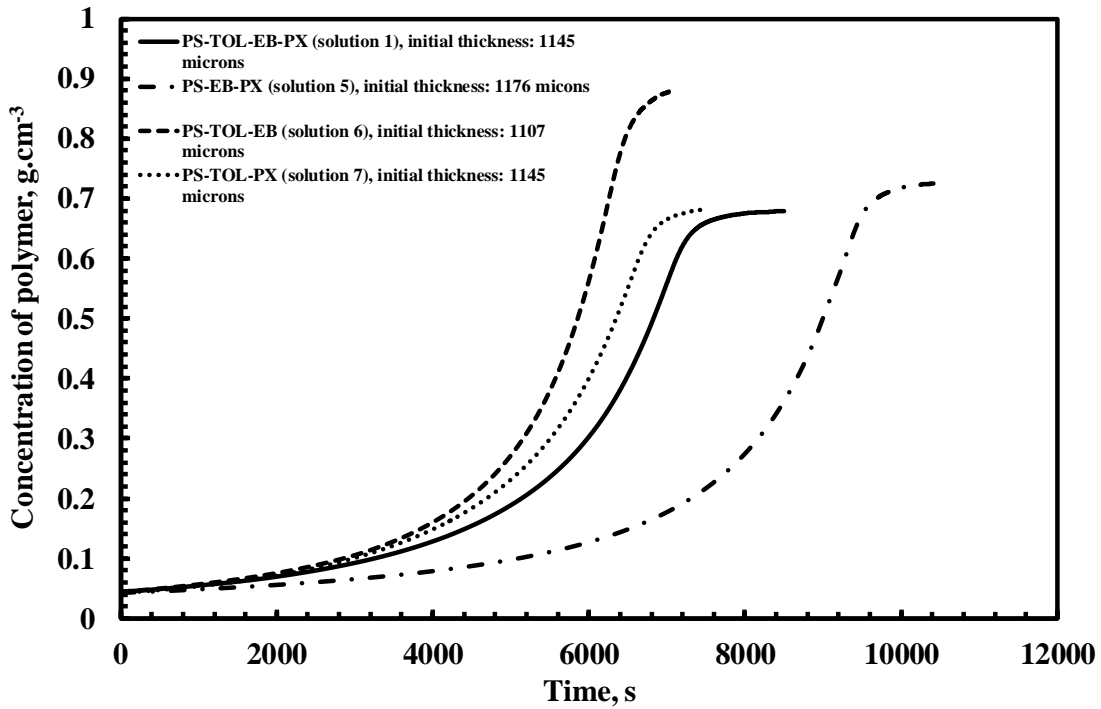


Figure 4.8: Concentration of polymer a function of time in quaternary coating and ternary coatings.

4.2 Drying of poly(styrene) – ethylbenzene – toluene – *p*-xylene system of nearly 1970 microns thickness

In this case, initial coating is increased to study its effect on the residual solvent, coating thickness, average concentration of poly(styrene) and solvents.

4.2.1 Residual solvent with time

Figure 4.9 shows the residual solvent as a function of time in various coatings of poly(styrene), i.e., binary and quaternary systems. The percentage of polymer in each coating was nearly 5%. The initial coating thicknesses in case of poly(styrene)(5.11%)-

ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%), poly(styrene)(5.1%) – toluene(94.94%), poly(styrene)(4.95%) – *p*-xylene(95.04%), poly(styrene)(5.29%) – ethylbenzene(94.71%) were 1963 microns, 1959 microns, 1975 microns, and 1958 microns, respectively. The removal of solvent rate was highest in poly(styrene) – toluene and slowest in poly(styrene) – *p*-xylene. The residual solvent left in poly(styrene) – ethylbenzene – toluene – *p*-xylene, poly(styrene) – toluene, poly(styrene) – *p*-xylene, and poly(styrene) – ethylbenzene coatings are 2.94%, 1.21%, 2.92%, and 2.47% respectively which are consuming 10603 s, 5067 s, 13994 s, and 12985 s. The residual solvent removal trend is same in all the four coatings. However, poly(styrene) – toluene coating is drying much faster due to high diffusion coefficient of toluene as compared to *p*-xylene, and ethylbenzene (in Table 3.1). The drying of quaternary system is reasonably high as compared to poly(styrene) – *p*-xylene and poly(styrene) – ethylbenzene system but slower than poly(styrene) – toluene system. In this quaternary system the amount of toluene is nearly one third of binary system, therefore, these coatings would be less toxic due to lower percentage of toluene.

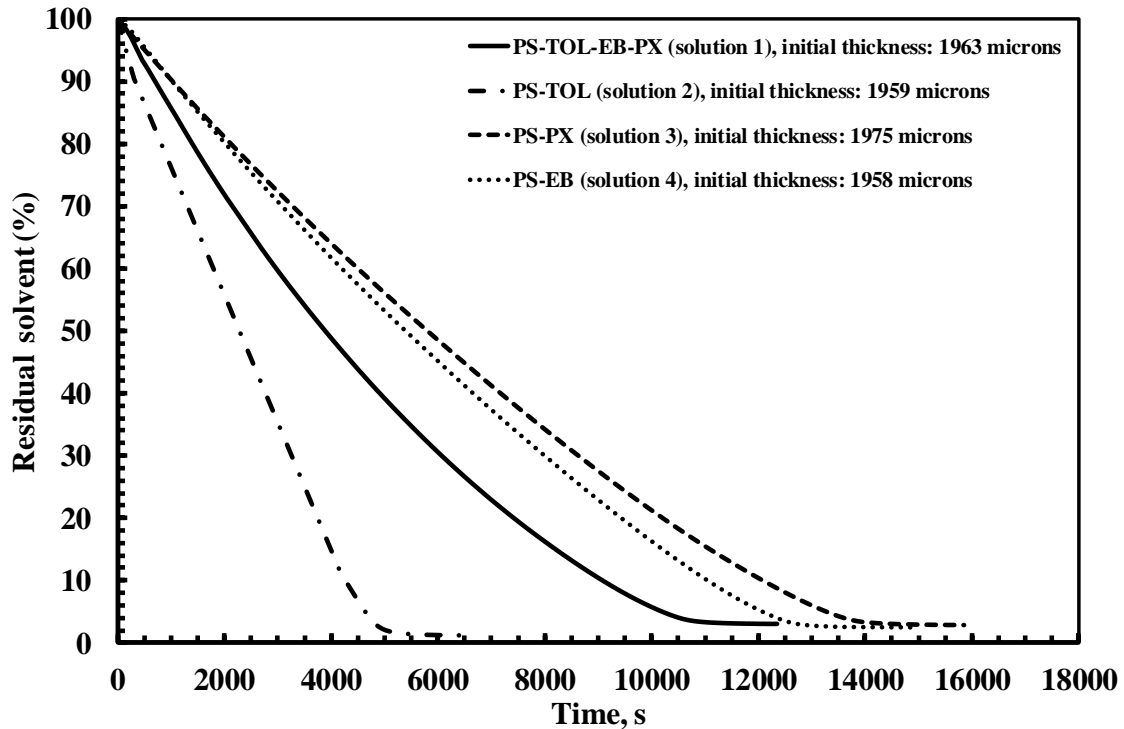


Figure 4.9: Residual solvent as a function of time in quaternary coating and binary coatings.

Figure 4.10 shows the residual solvent as a function of time in various coatings of poly(styrene), i.e., ternary and quaternary systems. The percentage of polymer in each coating was nearly 5%. The initial thickness of the coatings poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%), poly(styrene)(4.99%) – ethylbenzene(48.17%) – *p*-xylene(46.83%), poly(styrene)(5.29%) – ethylbenzene(94.71%) – toluene(46.43%), and poly(styrene)(4.89%) – toluene(48.33%) – *p*-xylene(46.78%) were 1963 microns, 1964 microns, 1998 microns, and 1988 microns, respectively. The removal of solvent rate was highest in poly(styrene) – ethylbenzene – toluene and slowest in poly(styrene) – ethylbenzene – *p*-xylene. The residual solvent left in poly(styrene) – ethylbenzene – toluene – *p*-xylene, poly(styrene) – ethylbenzene – *p*-xylene, poly(styrene) – toluene – ethylbenzene, and poly(styrene) – toluene – *p*-xylene coatings are 2.94%, 1.94%, 1.63%, and 2.85% respectively which are consuming 10603 s, 14200 s, 9313 s, and 9358 s. The residual solvent removal trend is same in all the four coatings. However, poly(styrene) – toluene – ethylbenzene and poly(styrene) – toluene – *p*-xylene coatings are drying much faster due to high diffusion coefficient of toluene as compared to *p*-xylene, and ethylbenzene (in Table 3.1). The drying of quaternary system is reasonably high as compared to poly(styrene) – ethylbenzene – *p*-xylene system but slower than poly(styrene) – toluene – ethylbenzene and poly(styrene) – toluene – *p*-xylene systems. In this quaternary system the amount of toluene is 2/3 of ternary system, therefore, these coatings would be less toxic due to lower percentage of toluene.

4.2.2 Coating thickness with time

Figure 4.11 shows the coating thickness as a function of time in various coatings of poly(styrene), i.e., binary and quaternary systems. The percentage of polymer in each coating was nearly 5%. The initial coating thicknesses in case of poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%), poly(styrene)(5.1%) – toluene(94.94%), poly(styrene)(4.95%) – *p*-xylene(95.04%), poly(styrene)(5.29%) – ethylbenzene(94.71%) were 1963 microns, 1959 microns, 1975 microns, and 1958 microns, respectively. The decrease in coating thickness was highest in poly(styrene) – toluene and slowest in poly(styrene) – *p*-xylene. The final coating thickness in poly(styrene) – ethylbenzene – toluene – *p*-xylene, poly(styrene) – toluene, poly(styrene) – *p*-xylene, and poly(styrene) – ethylbenzene coatings are 139 microns, 107 microns, 137 microns, and 133 microns respectively

which are consuming 10603 s, 5067 s, 13994 s, and 12659 s. The coating thickness trend is same in all the four coatings. The decrease in coating thickness of quaternary system is reasonably high as compared to poly(styrene) – *p*-xylene and poly(styrene) – ethylbenzene system but slower than poly(styrene) – toluene system. In this quaternary system the amount of toluene is nearly one third of binary system, therefore, these coatings have less thickness.

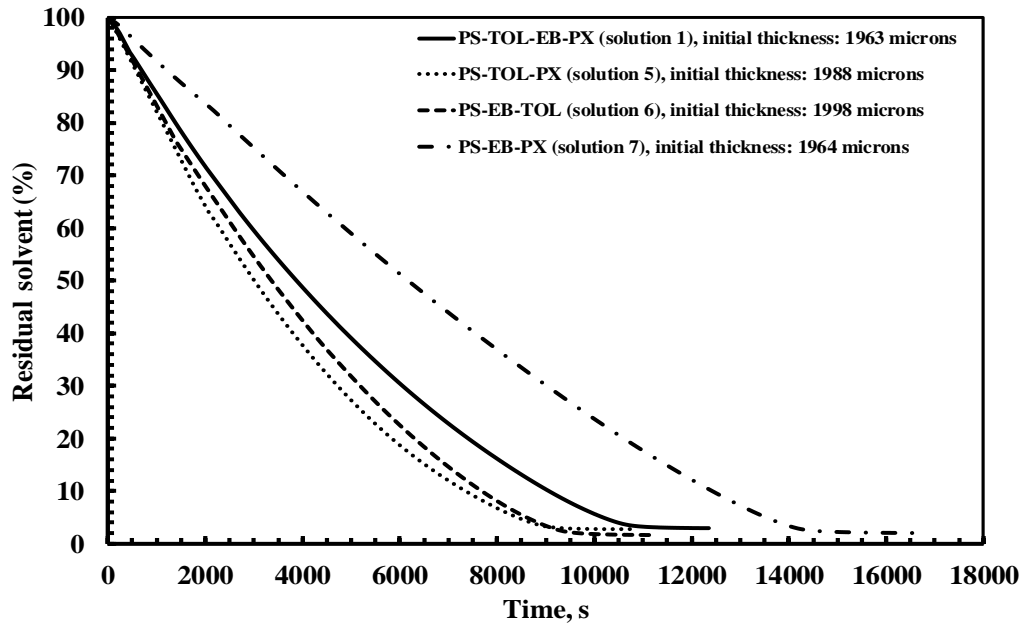


Figure 4.10: Residual solvent as a function of time in quaternary coating and ternary coating.

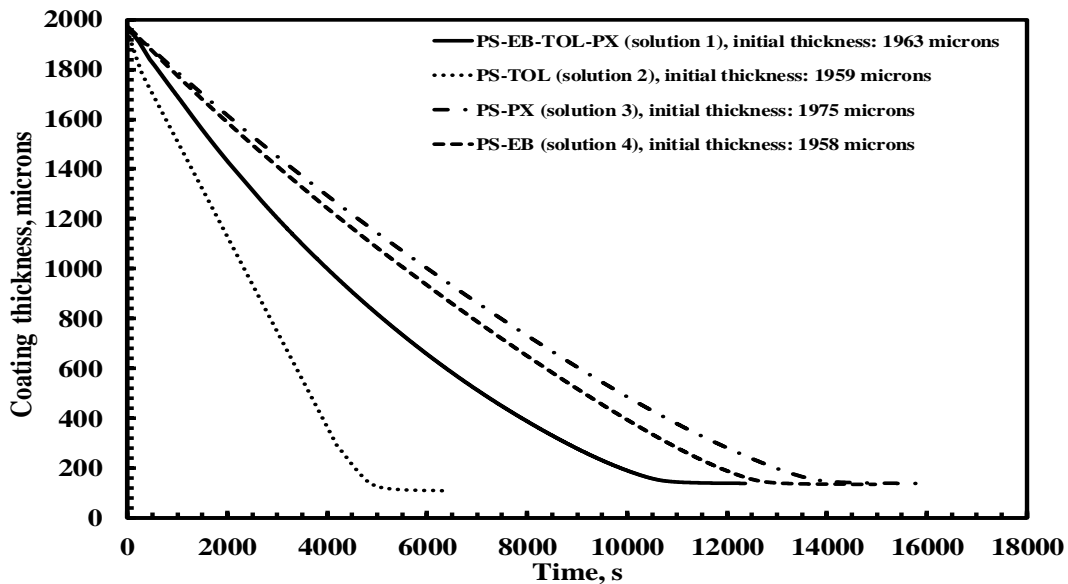


Figure 4.11: Coating thickness as a function of time in quaternary coating and binary coatings.

Figure 4.12 shows the coating thickness as a function of time in various coatings of poly(styrene), i.e., ternary and quaternary systems. The percentage of polymer in each coating was nearly 5%. The initial thickness of the coatings poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%), poly(styrene)(4.99%) – ethylbenzene(48.17%) – *p*-xylene(46.83%), poly(styrene)(5.29%) – ethylbenzene(94.71%) – toluene(46.43%), and poly(styrene)(4.89%) – toluene(48.33%) – *p*-xylene(46.78%) were 1963 microns, 1964 microns, 1998 microns, and 1988 microns, respectively. The decrease in coating thickness was highest in poly(styrene) – ethylbenzene – toluene and slowest in poly(styrene) – ethylbenzene – *p*-xylene. The final coating thickness in poly(styrene) – ethylbenzene – toluene – *p*-xylene, poly(styrene) – ethylbenzene – *p*-xylene, poly(styrene) – toluene – ethylbenzene, and poly(styrene) – toluene – *p*-xylene coatings are 139 microns, 119 microns, 117 microns, and 136 microns respectively which are consuming 10603 s, 14200 s, 9313 s, and 9358 s. The residual solvent removal trend is same in all the four coatings. The decrease in coating thickness of quaternary system is reasonably high as compared to poly(styrene) – ethylbenzene – *p*-xylene system but slower than poly(styrene) – toluene – ethylbenzene and poly(styrene) – toluene – *p*-xylene systems. In this quaternary system the amount of toluene is nearly 2/3 of ternary system, therefore, these coatings have less thickness.

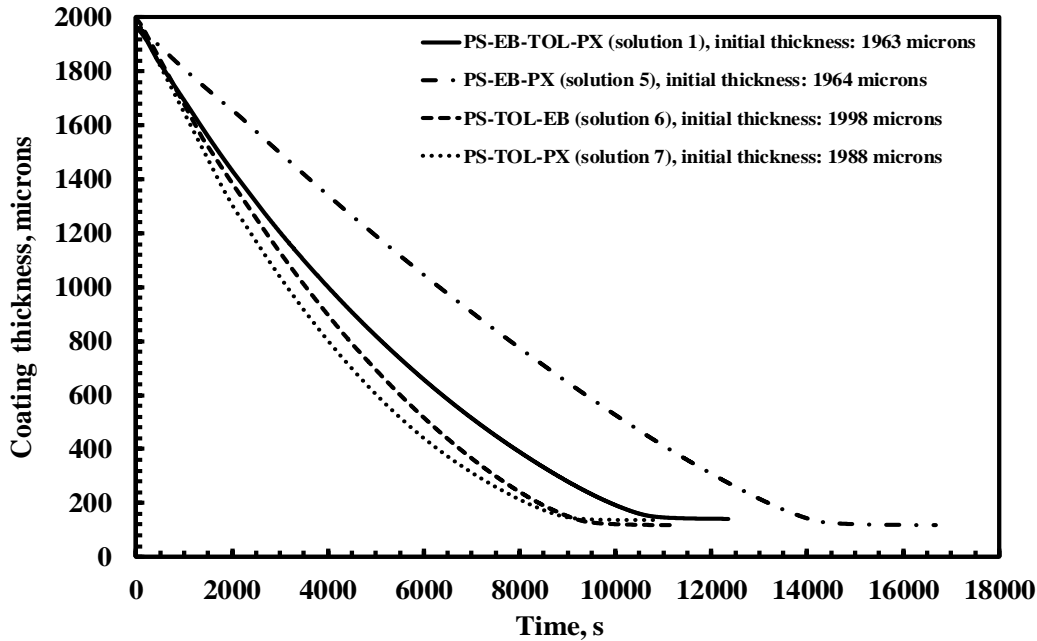


Figure 4.12: Coating thickness as a function of time in quaternary coating and ternary coatings.

4.2.3 Average concentration of solvent with time

Figure 4.13 shows the average concentration of solvent as a function of time in various coatings of poly(styrene), i.e., binary and quaternary systems. The percentage of polymer in each coating was nearly 5%. The initial coating thicknesses in case of poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%), poly(styrene)(5.1%) – toluene(94.94%), poly(styrene)(4.95%) – *p*-xylene(95.04%), poly(styrene)(5.29%) – ethylbenzene(94.71%) were 1963 microns, 1959 microns, 1975 microns, and 1958 microns, respectively. The initial concentration of solvent in poly(styrene) – ethylbenzene – toluene – *p*-xylene, poly(styrene) – toluene, poly(styrene) – *p*-xylene, and poly(styrene) – ethylbenzene coatings were 0.828 g.cm⁻³, 0.832 g.cm⁻³, 0.824 g.cm⁻³, and 0.827 g.cm⁻³, respectively. The concentration of solvent left in poly(styrene) – ethylbenzene – toluene – *p*-xylene, poly(styrene) – toluene, poly(styrene) – *p*-xylene, and poly(styrene) – ethylbenzene coatings are 0.34 g.cm⁻³, 0.18 g.cm⁻³, 0.34 g.cm⁻³, and 0.30 g.cm⁻³, respectively which are consuming 10603 s, 5067 s, 13994 s, and 12659 s. The average concentration trend is same in all the four coatings. The concentration of solvent in poly(styrene) – toluene coating is decreasing faster than poly(styrene) – *p*-xylene coating. The concentration in poly(styrene) – toluene coating is less as compare to other coatings. the quaternary coatings have more concentration of solvent left in the coating but nearly same as other binary poly(styrene) – ethylbenzene and poly(styrene) – *p*-xylene coatings.

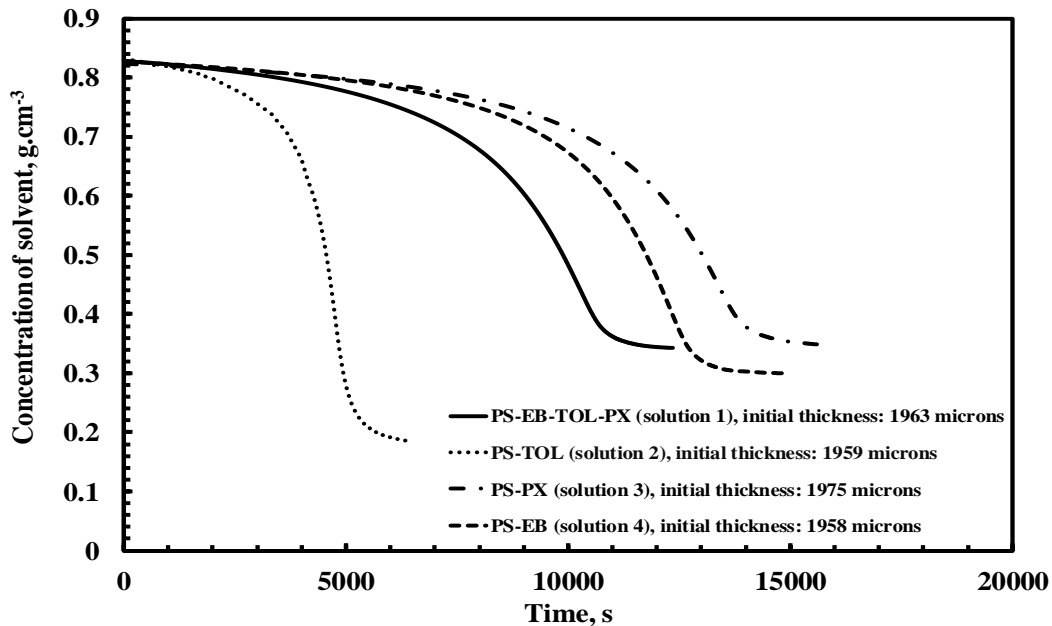


Figure 4.13: Concentration as a function of time in quaternary coating and binary coatings.

Figure 4.14 shows the average concentration of solvent as a function of time in various coatings of poly(styrene), i.e., ternary and quaternary systems. The percentage of polymer in each coating was nearly 5%. The initial thickness of the coatings poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%), poly(styrene)(4.99%) – ethylbenzene(48.17%) – *p*-xylene(46.83%), poly(styrene)(5.29%) – ethylbenzene(94.71%) – toluene(46.43%), and poly(styrene)(4.89%) – toluene(48.33%) – *p*-xylene(46.78%) were 1963 microns, 1964 microns, 1998 microns, and 1988 microns, respectively. The initial concentrations of solvents of poly(styrene) – ethylbenzene – toluene – *p*-xylene, poly(styrene) – ethylbenzene – *p*-xylene, poly(styrene) – toluene – ethylbenzene, and poly(styrene) – toluene – *p*-xylene coatings are 0.828 g.cm⁻³, 0.827 g.cm⁻³, 0.830 g.cm⁻³, 0.830 g.cm⁻³, respectively. The concentration of solvent left in poly(styrene) – ethylbenzene – toluene – *p*-xylene, poly(styrene) – ethylbenzene – *p*-xylene, poly(styrene) – toluene – ethylbenzene, and poly(styrene) – toluene – *p*-xylene coatings are 0.34 g.cm⁻³, 0.26 g.cm⁻³, 0.23 g.cm⁻³, and 0.34 g.cm⁻³, respectively which are consuming 10603 s, 14200 s, 9313 s, and 9358 s. The average concentration trend is same in all the four coatings. The concentration of solvent in poly(styrene) – toluene – ethylbenzene and poly(styrene) – toluene – *p*-xylene coatings is decreasing faster than poly(styrene) – ethylbenzene – *p*-xylene coating. The concentration in poly(styrene) – toluene – ethylbenzene and poly(styrene) – toluene – *p*-xylene coatings is less as compare to other coatings. The quaternary coatings have more concentration of solvent left in the coating but nearly same as other ternary poly(styrene) – ethylbenzene – *p*-xylene and poly(styrene) – toluene – *p*-xylene coatings.

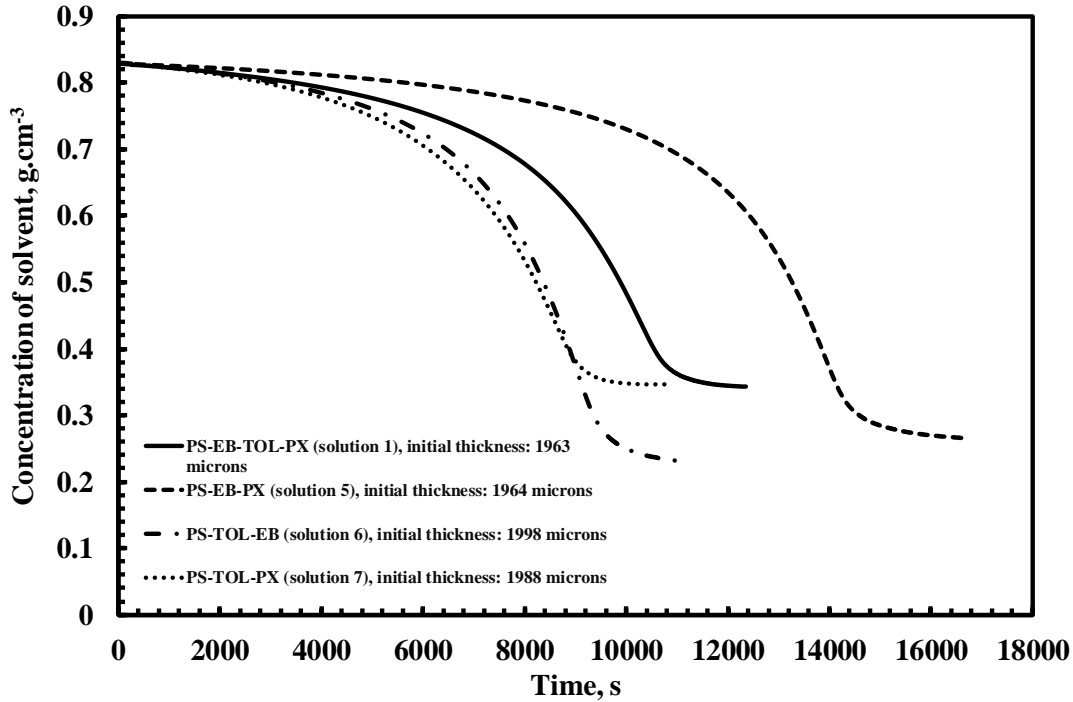


Figure 4.14: Concentration of solvent as a function of time in quaternary coating and ternary coatings.

4.2.4 Average concentration of polymer with time

Figure 4.15 shows the average concentration of polymer as a function of time in various coatings of poly(styrene), i.e., binary and quaternary systems. The percentage of polymer in each coating was nearly 5%. The initial coating thicknesses in case of poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%), poly(styrene)(5.1%) – toluene(94.94%), poly(styrene)(4.95%) – *p*-xylene(95.04%), poly(styrene)(5.29%) – ethylbenzene(94.71%) were 1963 microns, 1959 microns, 1975 microns, and 1958 microns, respectively. The initial concentration of poly(styrene) in poly(styrene) – ethylbenzene – toluene – *p*-xylene, poly(styrene) – toluene, poly(styrene) – *p*-xylene, and poly(styrene) – ethylbenzene coatings were 0.0446 g.cm⁻³, 0.0447 g.cm⁻³, 0.0429 g.cm⁻³, and 0.0462 g.cm⁻³, respectively. The concentration of poly(styrene) left in poly(styrene) – ethylbenzene – toluene – *p*-xylene, poly(styrene) – toluene, poly(styrene) – *p*-xylene, and poly(styrene) – ethylbenzene coatings are 0.63 g.cm⁻³, 0.82 g.cm⁻³, 0.62 g.cm⁻³, and 0.67 g.cm⁻³, respectively which are consuming 10603 s, 14200 s, 9313 s, and 9358 s. The average concentration trend is same in all the four coatings. The concentration of polymer in poly(styrene) – toluene coating is increasing faster than

poly(styrene) – *p*-xylene coating. The concentration of polymer in poly(styrene) – toluene coating is more as compare to other coatings. The quaternary coatings have less concentration of polymer left in the coating but nearly same as other binary poly(styrene) – ethylbenzene and poly(styrene) – *p*-xylene coatings.

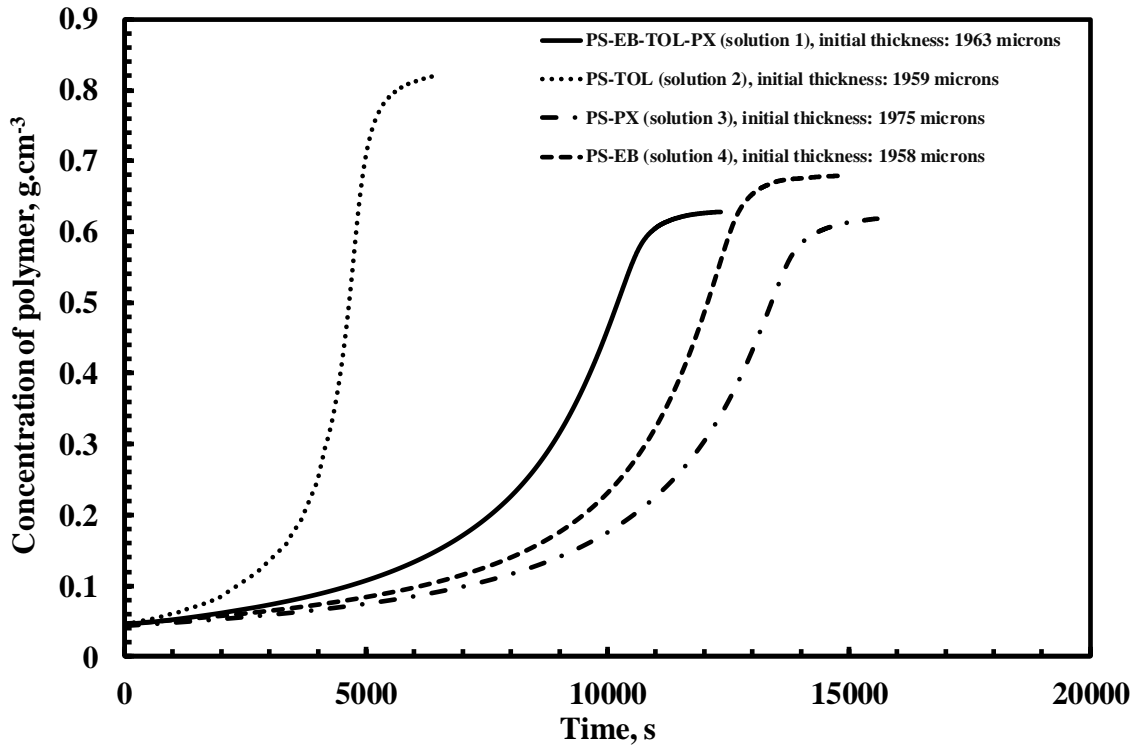


Figure 4.15: Concentration of polymer as a function of time in quaternary coating and binary coatings.

Figure 4.16 shows the average concentration of polymer as a function of time in various coatings of poly(styrene), i.e., ternary and quaternary systems. The percentage of polymer in each coating was nearly 5%. The initial thickness of the coatings poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%), poly(styrene)(4.99%) – ethylbenzene(48.17%) – *p*-xylene(46.83%), poly(styrene)(5.29%) – ethylbenzene(94.71%) – toluene(46.43%), and poly(styrene)(4.89%) – toluene(48.33%) – *p*-xylene(46.78%) were 1963 microns, 1964 microns, 1998 microns, and 1988 microns, respectively. The initial concentration of poly(styrene) in poly(styrene) – ethylbenzene – toluene – *p*-xylene, poly(styrene) – ethylbenzene – *p*-xylene, poly(styrene) – ethylbenzene – toluene, and poly(styrene) – toluene – *p*-xylene were 0.0446 g.cm⁻³, 0.0434 g.cm⁻³, 0.044 g.cm⁻³, and 0.0427 g.cm⁻³, respectively. The

concentration of polymer left in poly(styrene) – ethylbenzene – toluene – *p*-xylene, poly(styrene) – ethylbenzene – *p*-xylene, poly(styrene) – toluene – ethylbenzene, and poly(styrene) – toluene – *p*-xylene coatings are 0.63 g.cm⁻³, 0.72 g.cm⁻³, 0.76 g.cm⁻³, and 0.62 g.cm⁻³, respectively which are consuming 10603 s, 14200 s, 9313 s, and 9358 s. The average concentration trend is same in all the four coatings. The concentration of polymer in poly(styrene) – toluene – ethylbenzene coating is increasing faster than poly(styrene) – ethylbenzene – *p*-xylene coating. The concentration of polymer in poly(styrene) – toluene – ethylbenzene coating is more as compare to other coatings. The quaternary coatings have less concentration of polymer left in the coating but nearly same as other ternary poly(styrene) – ethylbenzene – *p*-xylene and poly(styrene) – toluene – *p*-xylene coatings.

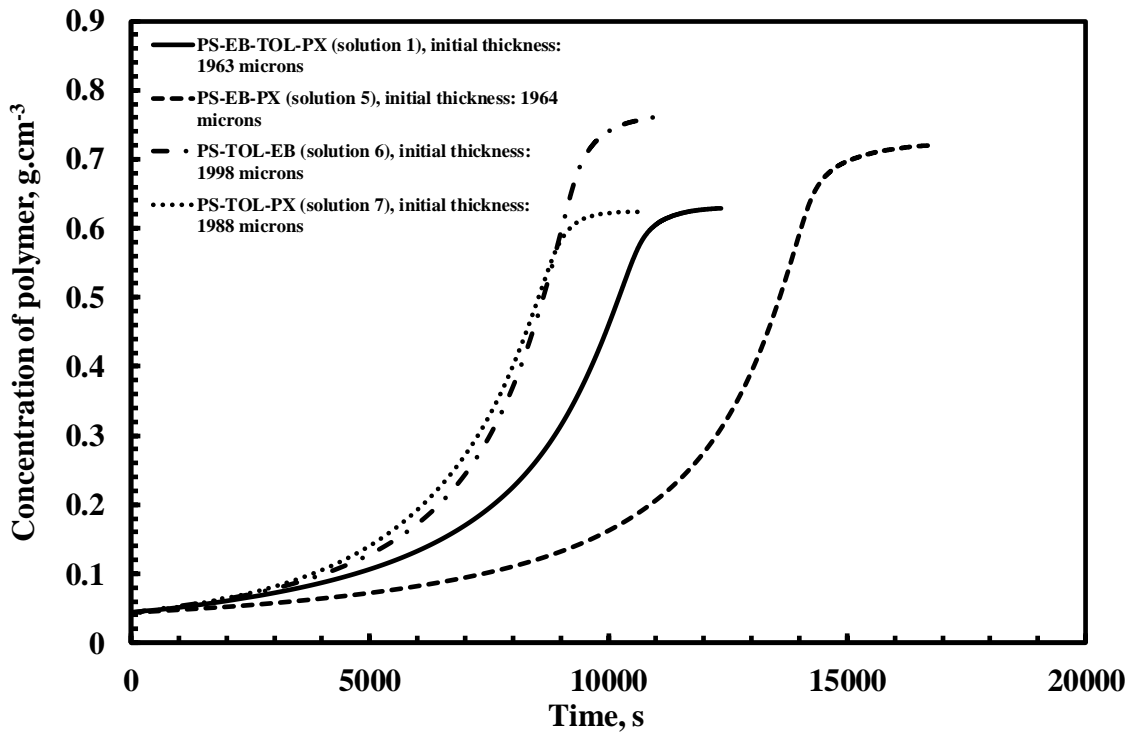


Figure 4.16: Concentration of polymer as a function of time in quaternary coating and ternary coatings.

4.3 Effect of coating composition on drying of poly(styrene) – ethylbenzene – toluene – *p*-xylene Coatings

Drying of two quaternary systems of poly(styrene) – toluene – ethylbenzene- *p*-xylene were prepared having composition, poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) and poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) The results of both the systems are compared for different coating thicknesses, 1150 microns and 1970 microns.

4.3.1 Effect of coating composition and thickness on residual solvent

Figure 4.17 shows the residual solvent as a function of time in various coatings of poly(styrene) in quaternary systems, i.e., poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) and poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%). For 1150 microns thickness: poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) and poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) having initial coating thickness of 1149 microns and 1145 microns respectively. For 1970 microns thickness: poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) and poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) having initial coating thickness of 1963 microns and 1963 microns respectively. The removal of solvent rate was highest in poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) and slowest in poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%). The residual solvent left in poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) and in poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) coatings are 1.04% and 2.39% respectively for 1150 microns thickness which are consuming 6677 s and 7252 s. Also, the residual solvent left in poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) and in poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) coatings are 2.9% and 2.94% respectively for 1970 microns thickness which are consuming 8483 s and 10603 s. The residual solvent removal trend is same in both the coatings. The quaternary poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) coating are drying faster than the other quaternary coating. This is because of the presence of high

loading of toluene in the coating. Toluene has high diffusion coefficient than *p*-xylene and ethylbenzene. Also, by changing the composition and increasing the thickness, the residual solvent is becoming less.

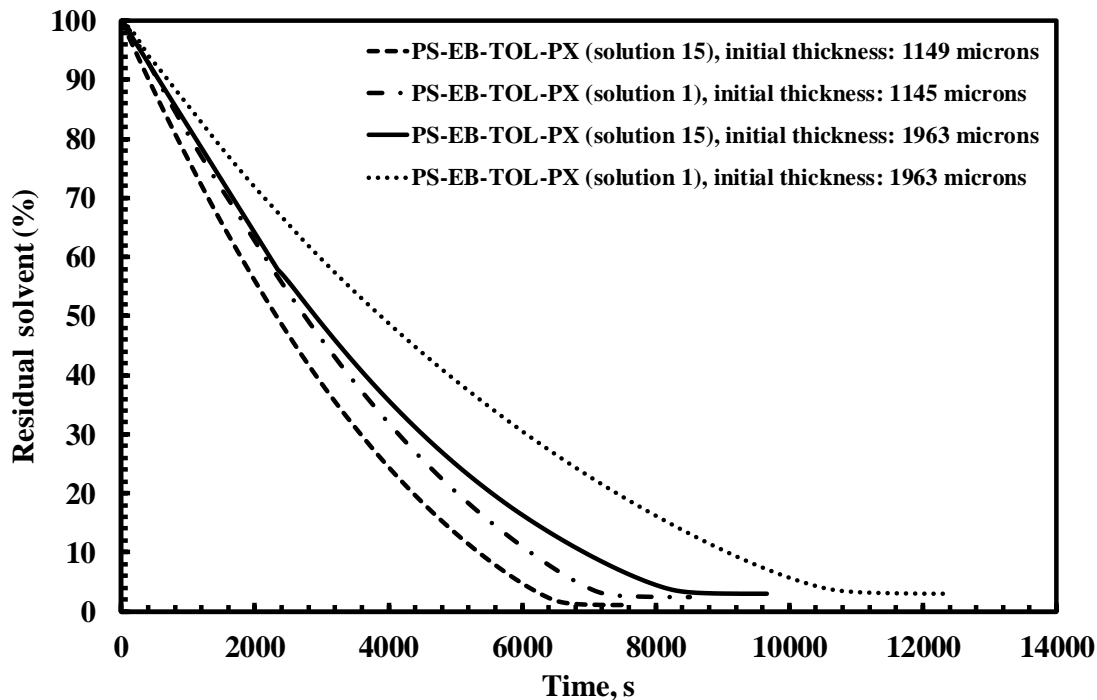


Figure 4.17: Residual solvent as a function of time in quaternary coatings of poly(styrene)-ethylbenzene-toluene-*p*-xylene having composition and initial thicknesses: poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) and poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%), and 1150 and 1970 microns, respectively.

4.3.2 Effect of coating composition and thickness on coating thickness

Figure 4.18 shows the coating thickness as a function of time in quaternary coatings of poly(styrene). For 1150 microns thickness: poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) and poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) having initial coating thickness of 1149 microns and 1145 microns respectively. For 1970 microns thickness: poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) and poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) having initial coating thickness of

1963 microns and 1963 microns respectively. The decrease in coating thickness was highest in poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) and slowest in poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%). The final coating thickness in poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) and poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) coatings are 58 microns and 75 microns respectively for 1150 microns thickness which are consuming 6677 s and 7252 s. Also, The final coating thickness in poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) and poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) coatings are 134 microns and 139 microns respectively for 1970 microns thickness which are consuming 8483 s and 10603 s. The coating thickness in quaternary poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) coating is less as compared to the other coating. Thus, this type of coating is more efficient.

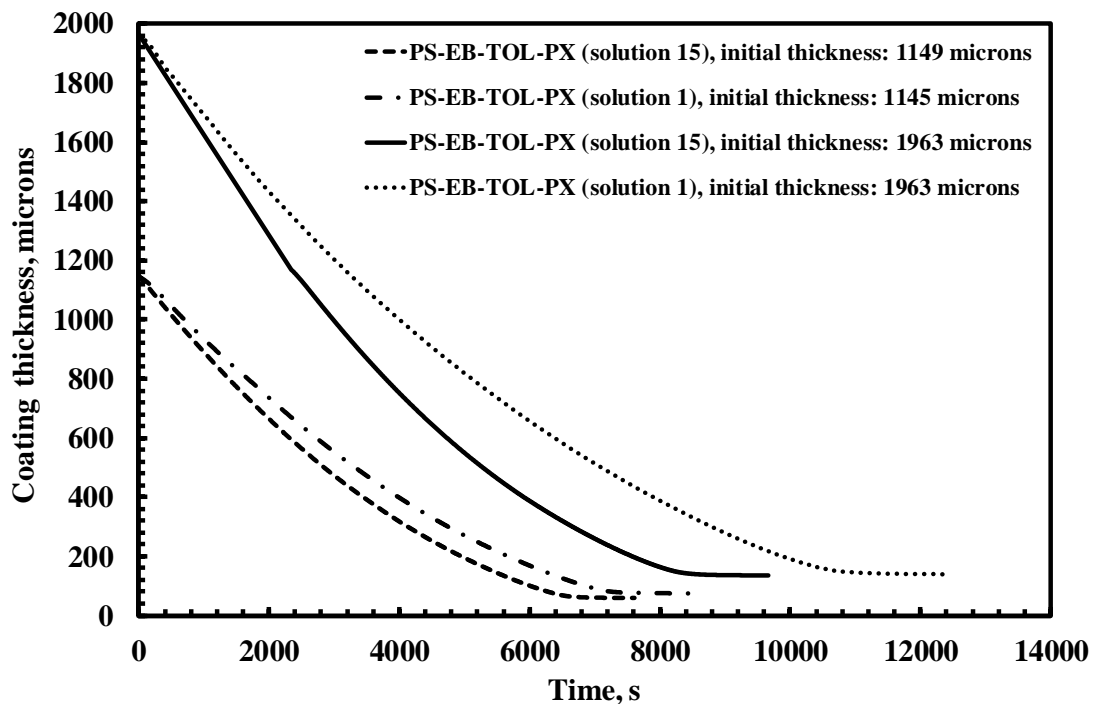


Figure 4.18: Coating thickness a function of time in quaternary coatings of poly(styrene)-ethylbenzene-toluene-*p*-xylene having composition and initial thicknesses: poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) and poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%), and 1150 and 1970 microns, respectively.

4.3.3 Effect of coating composition and thickness on average concentration of solvent

Figure 4.19 shows the average concentration of solvent as a function of time in various coatings of poly(styrene) in quaternary systems. For 1150 microns thickness: poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) and poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) having initial coating thickness of 1149 microns and 1145 microns respectively. The initial concentrations of solvent in poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) and poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) coatings were 0.831 g.cm⁻³ and 0.828 g.cm⁻³, respectively. The final concentrations of solvent in poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) and poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) coatings are 0.17 g.cm⁻³ and 0.30 g.cm⁻³ respectively which are consuming 6677 s and 7252 s. For 1970 microns thickness: poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) and poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) having initial coating thickness of 1963 microns and 1963 microns respectively. The exponential decrease in concentration of solvent was highest in poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) and slowest in poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%). The initial concentrations of solvent in poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) and poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) coatings were 0.831 g.cm⁻³ and 0.828 g.cm⁻³, respectively. The final concentrations of solvent in poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) and poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) coatings are 0.352 g.cm⁻³ and 0.342 g.cm⁻³ respectively which are consuming 8483 s and 10603 s. The concentration of solvent in quaternary poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) coating is less as compared to the other coating. Thus, this type of coating is more efficient.

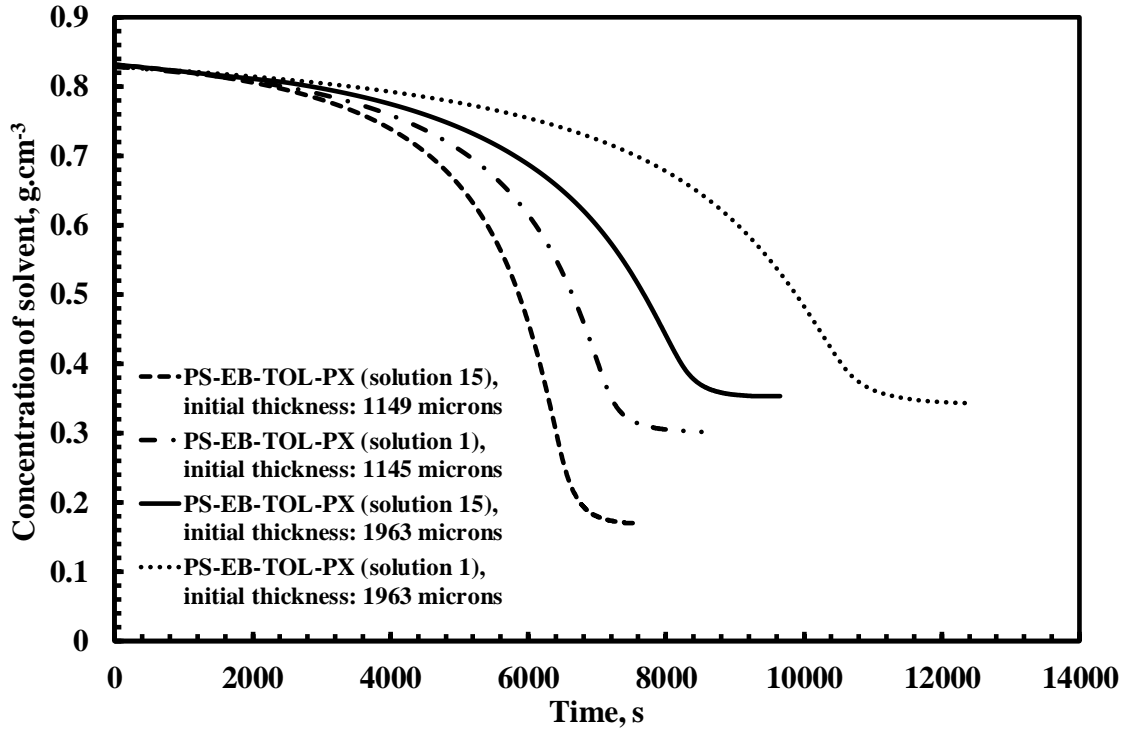


Figure 4.19: Concentration of solvent as a function of time in quaternary coatings of poly(styrene)-ethylbenzene-toluene-*p*-xylene having composition and initial thicknesses: poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) and poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%), and 1150 and 1970 microns, respectively.

4.3.4 Effect of coating composition and thickness on average concentration of polymer

Figure 4.20 shows the average concentration of poly(styrene) as a function of time in various coatings of poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) and poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%). For 1150 microns thickness: poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) and poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) having initial coating thickness of 1149 microns and 1145 microns respectively. The exponential increase in concentration of poly(styrene) was highest in poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) and slowest in poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-

xylene(31.44%). The final concentrations of solvent in poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) and poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) coatings are 0.84 g.cm⁻³ and 0.67 g.cm⁻³ respectively which are consuming 6677 s and 7252 s. For 1970 microns thickness: poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) and poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) having initial coating thickness of 1963 microns and 1963 microns, respectively. The final concentrations of solvent in poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) and poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) coatings are 0.62 g.cm⁻³ and 0.67 g.cm⁻³ respectively which are consuming 8483 s and 10603 s. The concentration of poly(styrene) in poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%) coating is more as compared to the other coating.

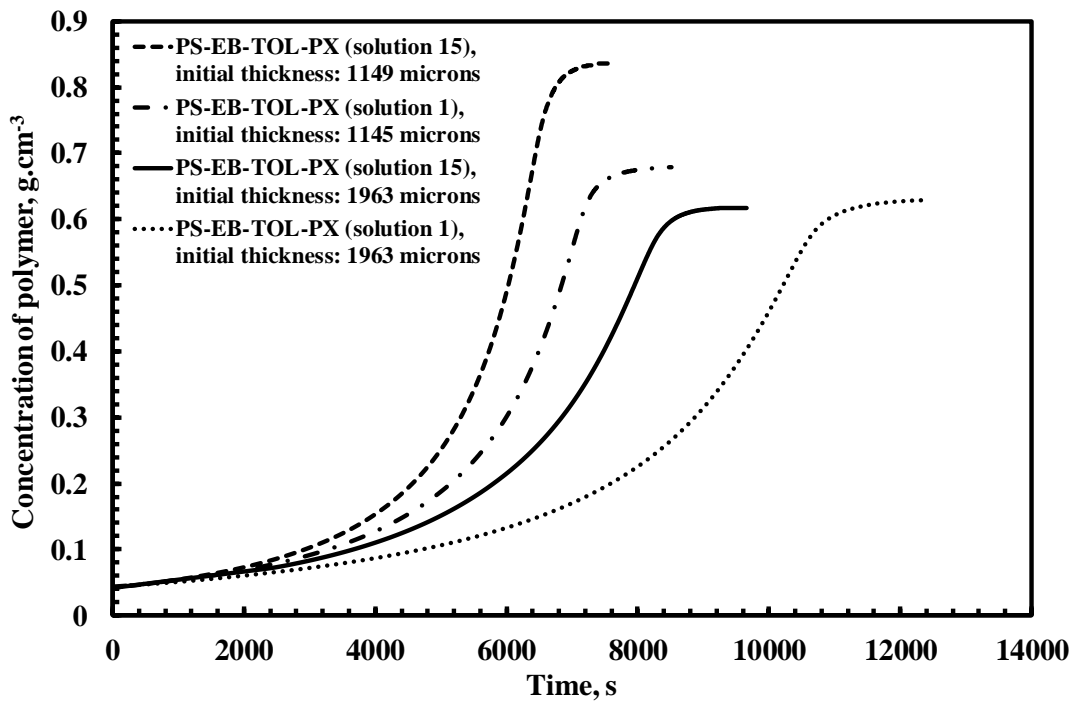


Figure 4.20: Concentration of polymer as a function of time in quaternary coatings of poly(styrene)-ethylbenzene-toluene-*p*-xylene having composition and initial thicknesses: poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%) and poly(styrene)(4.84%) – ethylbenzene(21.33%) – toluene(43.75%) – *p*-xylene(30.07%), and 1150 and 1970 microns, respectively.

4.4 Drying of poly(methyl methacrylate) – ethylbenzene – toluene – acetone system for 976 microns thickness

4.4.1 Residual solvent with time

Figure 4.21 shows the residual solvent as a function of time in various coatings of poly(methyl methacrylate), i.e., binary and quaternary systems. The percentage of polymer in each coating was nearly 5% and the initial coating thickness for poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%), poly(methyl methacrylate)(4.96%) – toluene(95.04%), poly(methyl methacrylate)(4.98%) – acetone(95.01%), and poly(methyl methacrylate)(4.96%) – ethylbenzene(95.03%) coatings was 976 microns, 976 microns, 970 microns, and 980 microns, respectively. The removal of solvent rate was highest in poly(methyl methacrylate) – acetone and slowest in poly(methyl methacrylate) – ethylbenzene. The residual solvent left in poly(methyl methacrylate) – ethylbenzene – toluene – acetone, poly(methyl methacrylate) – toluene, poly(methyl methacrylate) – acetone, and poly(methyl methacrylate) – ethylbenzene coatings are 1.66%, 2.23%, 1.26%, and 2.28% respectively which are consuming 4271 s, 3065 s, 420 s, and 7548 s. The residual solvent removal is following the same trend in all the four coatings. However, poly(methyl methacrylate) – acetone coating is drying much faster due to high diffusion coefficient of acetone as compared to toluene, and ethylbenzene (in Table 3.1). The drying rate of quaternary system is reasonably high as compared to poly(methyl methacrylate) – ethylbenzene system but slower than poly(methyl methacrylate) – acetone and poly(methyl methacrylate) – toluene system. In this quaternary system, the amount of acetone and toluene is nearly one third of binary system, therefore, these coatings would be less toxic due to lower percentage of acetone and toluene. Also, the cost of producing quaternary coating will be less as compared to others because of less composition of solvents used in it.

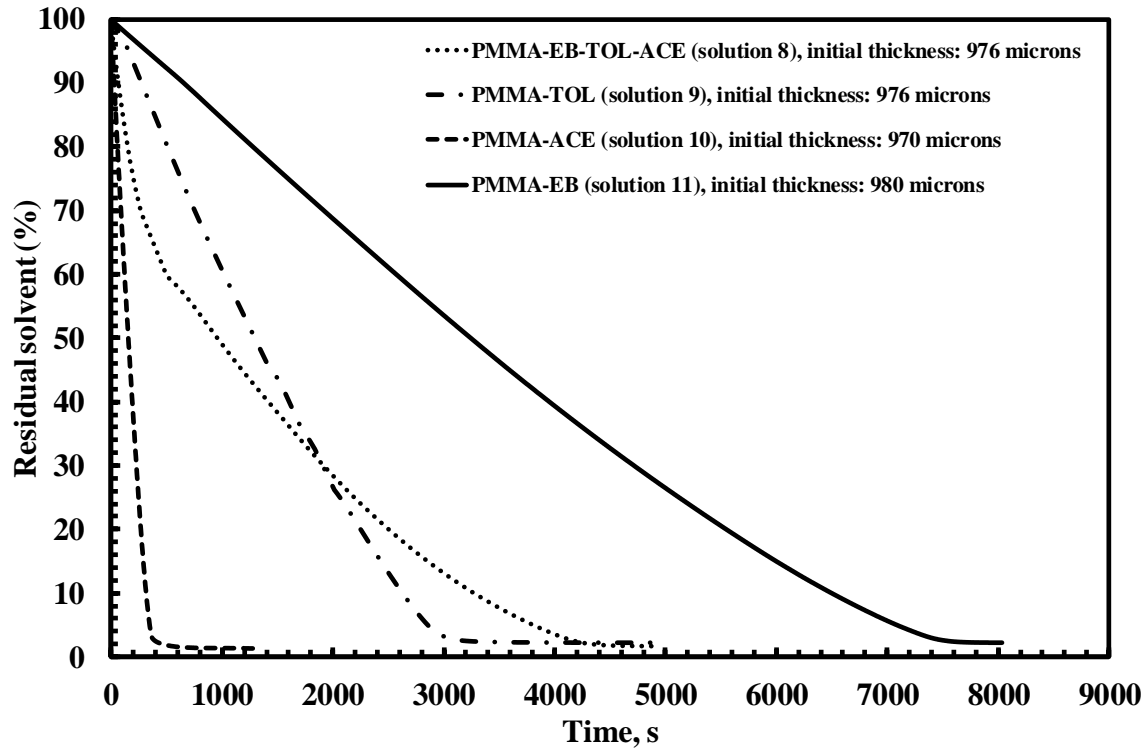


Figure 4.21: Residual solvent as a function of time in quaternary and binary coatings.

Figure 4.22 shows the residual solvent as a function of time in various coatings of poly(methyl methacrylate), i.e., ternary and quaternary systems having the percentage of nearly 5% of polymer in each coating and the initial thickness of coatings of poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%), poly(methyl methacrylate)(4.97%) – ethylbenzene(47.35%) – acetone(47.65%), poly(methyl methacrylate)(5.22%) – toluene(46.08%) – ethylbenzene(48.69%), and poly(methyl methacrylate)(4.99%) – toluene(47.12%) – acetone(47.88%) was 976 microns, 973 microns, 977 microns, and 972 microns, respectively. The removal of solvent rate was highest in poly(methyl methacrylate) – toluene – acetone and slowest in poly(methyl methacrylate) – toluene – ethylbenzene. The residual solvent left in poly(methyl methacrylate) – ethylbenzene – toluene – acetone, poly(methyl methacrylate) – ethylbenzene – acetone, poly(methyl methacrylate) – toluene – ethylbenzene, and poly(methyl methacrylate) – toluene – acetone coatings are 1.66%, 1.75%, 0.32%, and 1.43% respectively which are consuming 4271 s, 4917 s, 5966 s, and 1881 s. The residual solvent removal trend is same in all the four coatings. However, poly(methyl

methacrylate) – toluene – acetone coating is drying much faster due to high diffusion coefficient of acetone as compared to toluene, and ethylbenzene (in Table 3.1). The drying of quaternary system is reasonably high as compared to poly(methyl methacrylate) – ethylbenzene – acetone and poly(methyl methacrylate) – toluene – ethylbenzene systems but slower than poly(methyl methacrylate) – toluene – acetone system. In this quaternary system, the amount of acetone is nearly 2/3 of ternary system, therefore, these coatings would be less toxic due to lower percentage of acetone. The cost for producing this type of coating will be less as compared to other ternary coatings. This is because of less cost of acetone and toluene than ethylbenzene.

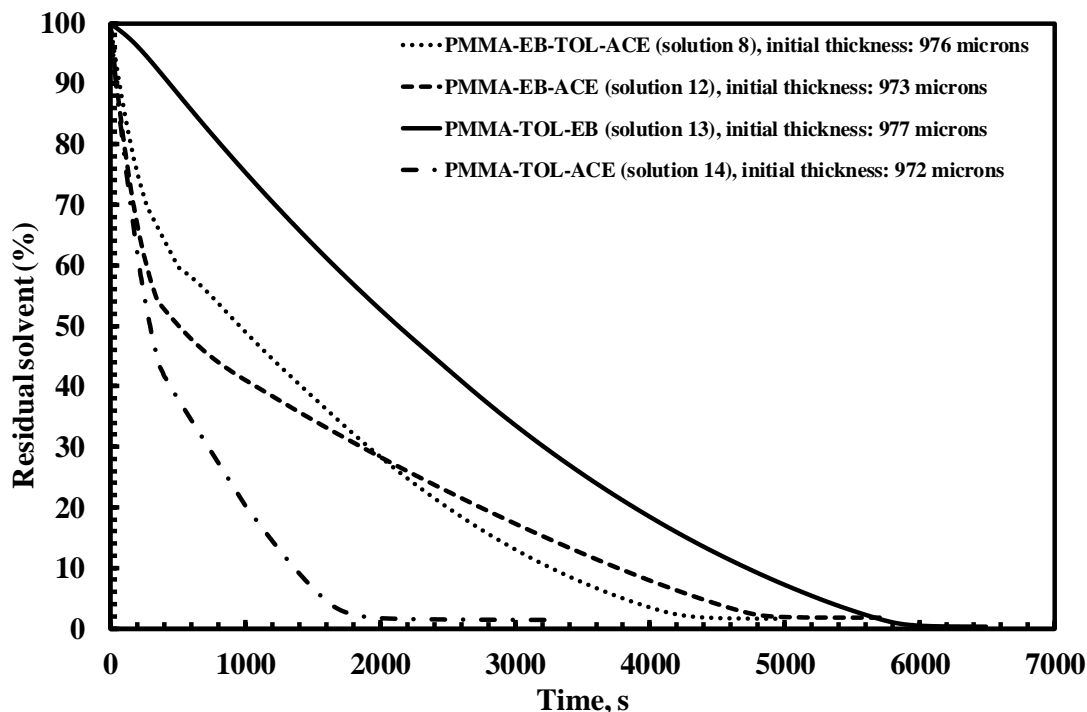


Figure 4.22: Residual solvent as a function of time in quaternary and ternary coatings.

4.4.2 Coating thickness with time

Figure 4.23 shows the coating thickness as a function of time in various coatings of binary and quaternary systems containing poly(methyl methacrylate). Each coating has the percentage of polymer nearly 5% and the initial thickness of the coating for poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%), poly(methyl methacrylate)(4.96%) – toluene(95.04%), poly(methyl methacrylate)(4.98%) – acetone(95.01%), and poly(methyl methacrylate)(4.96%) – ethylbenzene(95.03%) coatings was

976 microns, 976 microns, 970 microns, and 980 microns, respectively. The decrease in coating thickness was highest in poly(methyl methacrylate) – acetone and slowest in poly(methyl methacrylate) – ethylbenzene. The final coating thickness in poly(methyl methacrylate) – ethylbenzene – toluene – acetone, poly(methyl methacrylate) – toluene, poly(methyl methacrylate) – acetone, and poly(methyl methacrylate) – ethylbenzene coatings are 50 microns, 57 microns, 45 microns, and 58 microns respectively which are consuming 4271 s, 3065 s, 420 s, and 7548 s. The decrease in coating thickness of quaternary system is reasonably high as compared to poly(methyl methacrylate) – ethylbenzene system but slower than poly(methyl methacrylate) – toluene and poly(methyl methacrylate) – acetone systems. All these coatings have nearly same thickness when drying is completed.

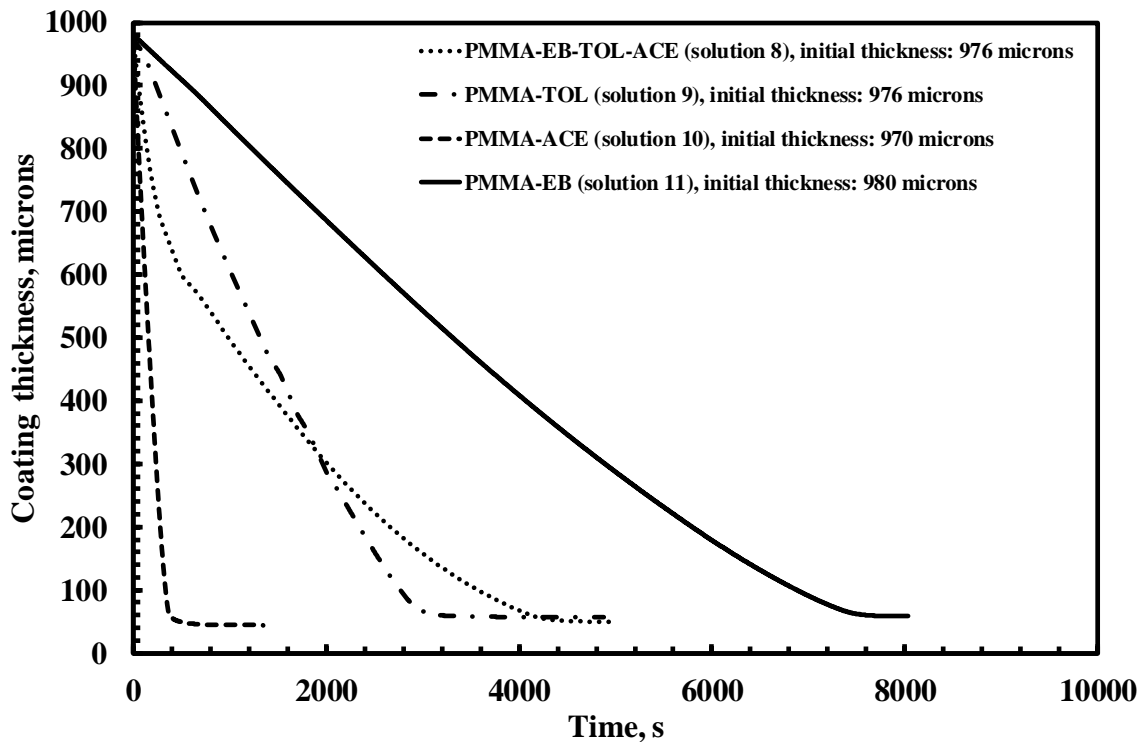


Figure 4.23: Coating thickness as a function of time in quaternary and binary coatings.

Figure 4.24 shows the coating thickness as a function of time in various coatings of ternary and quaternary systems containing poly(methyl methacrylate). Each coating has the percentage of polymer nearly 5% and the initial thickness of the coating for poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%), poly(methyl methacrylate)(4.97%) – ethylbenzene(47.35%) – acetone(47.65%), poly(methyl

methacrylate)(5.22%) – toluene(46.08%) – ethylbenzene(48.69%), and poly(methyl methacrylate)(4.99%) – toluene(47.12%) – acetone(47.88%) was 976 microns, 973 microns, 977 microns, and 972 microns, respectively. The decrease in coating thickness was highest in poly(methyl methacrylate) – toluene – acetone and slowest in poly(methyl methacrylate) – toluene – ethylbenzene. The final coating thickness in poly(methyl methacrylate) – ethylbenzene – toluene – acetone, poly(methyl methacrylate) – ethylbenzene – acetone, poly(methyl methacrylate) – toluene – ethylbenzene, and poly(methyl methacrylate) – toluene – acetone coatings are 50 microns, 51 microns, 41 microns, and 48 microns respectively which are consuming 4271 s, 4917 s, 5966 s, and 1881 s. The decrease in coating thickness of quaternary system is reasonably high as compared to poly(methyl methacrylate) – ethylbenzene – acetone and poly(methyl methacrylate) – toluene – ethylbenzene systems but slower than poly(methyl methacrylate) – toluene – acetone systems. All these coatings have nearly same thickness when drying is completed.

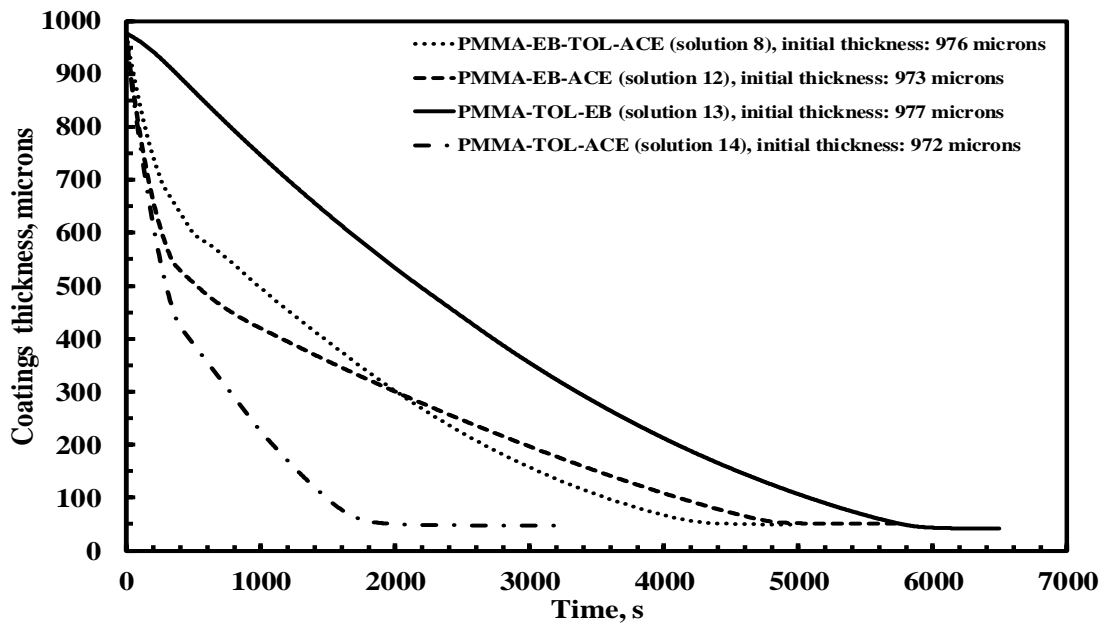


Figure 4.24: Coating thickness as a function of time in quaternary and ternary coatings.

4.4.3 Average concentration of solvent with time

Figure 4.25 shows the average concentration of solvent as a function of time in various coatings of poly(methyl methacrylate), i.e., binary and quaternary systems having polymer of nearly 5% in each coating. The initial coating thickness for poly(methyl methacrylate)(4.90%) –

ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%), poly(methyl methacrylate)(4.96%) – toluene(95.04%), poly(methyl methacrylate)(4.98%) – acetone(95.01%), and poly(methyl methacrylate)(4.96%) – ethylbenzene(95.03%) coatings was 976 microns, 976 microns, 970 microns, and 980 microns, respectively. The initial concentrations of solvent in poly(methyl methacrylate) – ethylbenzene – toluene – acetone, poly(methyl methacrylate) – toluene, poly(methyl methacrylate) – acetone, and poly(methyl methacrylate) – ethylbenzene coatings were 0.811 g.cm^{-3} , 0.837 g.cm^{-3} , 0.759 g.cm^{-3} , and 0.834 g.cm^{-3} , respectively. The concentration of solvent left in poly(methyl methacrylate) – ethylbenzene – toluene – acetone, poly(methyl methacrylate) – toluene, poly(methyl methacrylate) – acetone, and poly(methyl methacrylate) – ethylbenzene coatings are 0.26 g.cm^{-3} , 0.32 g.cm^{-3} , 0.21 g.cm^{-3} , and 0.32 g.cm^{-3} , respectively which are consuming 4271 s, 3065 s, 420 s, and 7548 s. The average concentration trend is in the form of Fickian diffusion for all the four coatings for almost all drying period. Therefore, these coatings might be in rubbery state for that much time period. The concentration of solvent in poly(methyl methacrylate) – acetone coating is decreasing faster than poly(methyl methacrylate) – ethylbenzene coating. The concentration of solvent is nearly same in all the coatings.

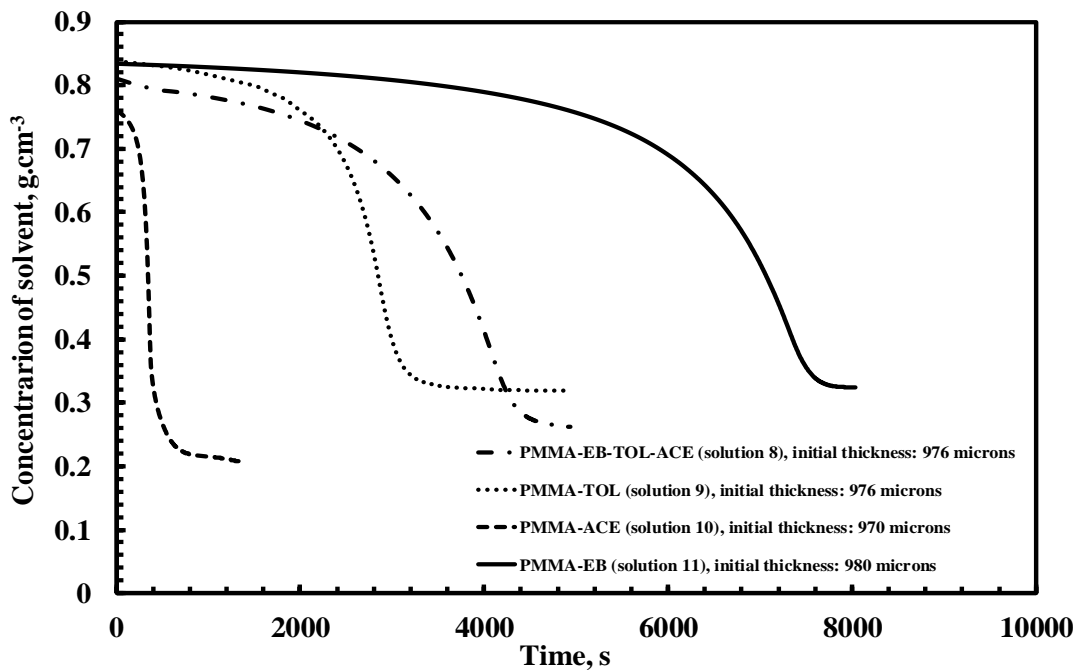


Figure 4.25: Concentration of solvent as a function of time in quaternary and binary coatings.

Figure 4.26 shows the average concentration of solvent as a function of time in various coatings of poly(methyl methacrylate), i.e., binary and quaternary systems having polymer of nearly 5% in each coating. The initial coating thickness for poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%), poly(methyl methacrylate)(4.97%) – ethylbenzene(47.35%) – acetone(47.65%), poly(methyl methacrylate)(5.22%) – toluene(46.08%) – ethylbenzene(48.69%), and poly(methyl methacrylate)(4.99%) – toluene(47.12%) – acetone(47.88%) was 976 microns, 973 microns, 977 microns, and 972 microns, respectively. The concentrations of solvent in poly(methyl methacrylate) – ethylbenzene – toluene – acetone, poly(methyl methacrylate) – ethylbenzene – acetone, poly(methyl methacrylate) – toluene – ethylbenzene, and poly(methyl methacrylate) – toluene – acetone coatings were 0.811 g.cm^{-3} , 0.796 g.cm^{-3} , 0.834 g.cm^{-3} , and 0.798 g.cm^{-3} , respectively. The concentration of solvent left in poly(methyl methacrylate) – ethylbenzene – toluene – acetone, poly(methyl methacrylate) – ethylbenzene – acetone, poly(methyl methacrylate) – toluene – ethylbenzene, and poly(methyl methacrylate) – toluene – acetone coatings are 0.26 g.cm^{-3} , 0.26 g.cm^{-3} , 0.06 g.cm^{-3} , and 0.23 g.cm^{-3} , respectively which are consuming 4271 s, 3065 s, 420 s, and 7548 s. The average concentration trend is in the form of Fickian diffusion for all the four coatings for almost all drying period. Therefore, these coatings might be in rubbery state for that much time period. The concentration of solvent in poly(methyl methacrylate) – toluene – acetone coating is decreasing faster than poly(methyl methacrylate) – toluene – ethylbenzene coating. The concentration of solvent is nearly same in all the coatings except poly(methyl methacrylate) – toluene – ethylbenzene coating because of less residual solvent left in the coating.

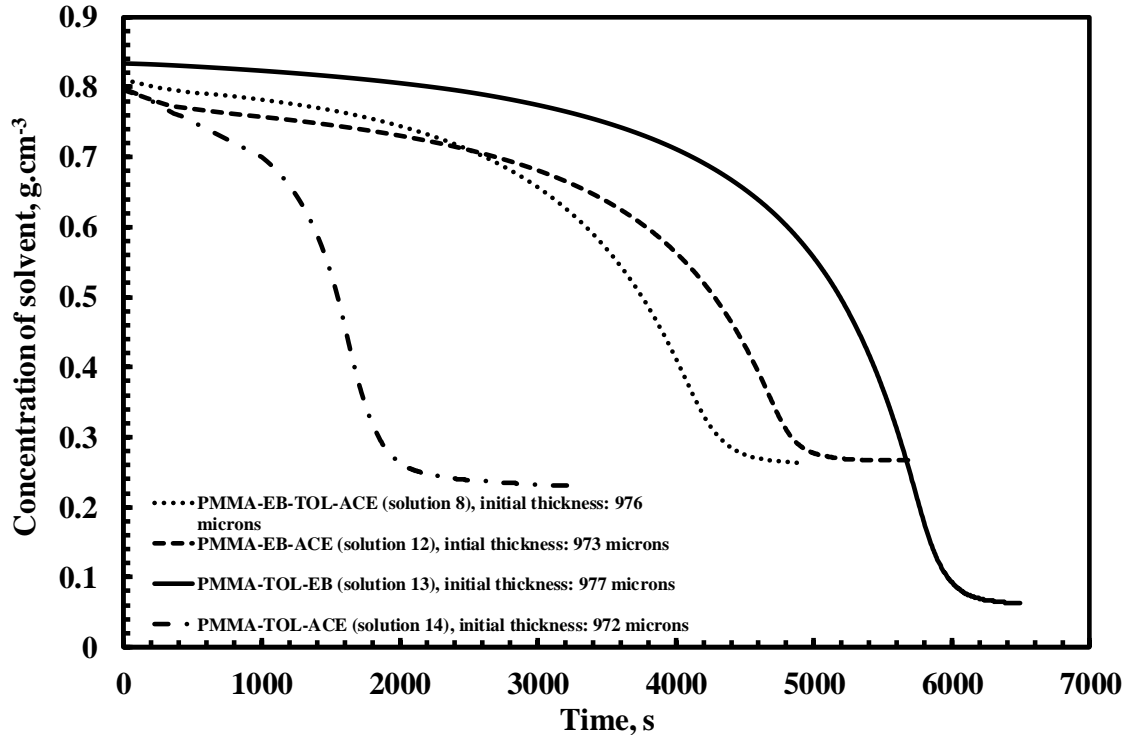


Figure 4.26: Concentration of solvent as a function of time in quaternary and ternary coatings.

4.4.4 Average concentration of polymer with time

Figure 4.27 shows the average concentration of polymer as a function of time in various coatings of poly(methyl methacrylate), i.e., binary and quaternary systems having nearly 5% of polymer in each coating. The initial coating thickness for poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%), poly(methyl methacrylate)(4.96%) – toluene(95.04%), poly(methyl methacrylate)(4.98%) – acetone(95.01%), and poly(methyl methacrylate)(4.96%) – ethylbenzene(95.03%) coatings was 976 microns, 976 microns, 970 microns, and 980 microns, respectively. The initial concentration of poly(methyl methacrylate) in poly(methyl methacrylate) – ethylbenzene – toluene – acetone, poly(methyl methacrylate) – toluene, poly(methyl methacrylate) – acetone, and poly(methyl methacrylate) – ethylbenzene coatings were 0.0418 g.cm^{-3} , 0.0437 g.cm^{-3} , 0.0398 g.cm^{-3} , and 0.0436 g.cm^{-3} , respectively. The concentration of polymer left in poly(methyl methacrylate) – ethylbenzene – toluene – acetone, poly(methyl methacrylate) – toluene, poly(methyl methacrylate) – acetone, and poly(methyl methacrylate) – ethylbenzene coatings are 0.81 g.cm^{-3} , 0.74 g.cm^{-3} , 0.86 g.cm^{-3} , and 0.74 g.cm^{-3} , respectively which are consuming 4271 s, 3065 s, 420 s, and 7548 s. The average concentration

trend is exponentially increasing in all the four coatings. The concentration of polymer in poly(methyl methacrylate) – acetone coating is increasing faster than poly(methyl methacrylate) – ethylbenzene coating. The quaternary coatings have nearly same concentration of polymer left in the coating as other binary coatings.

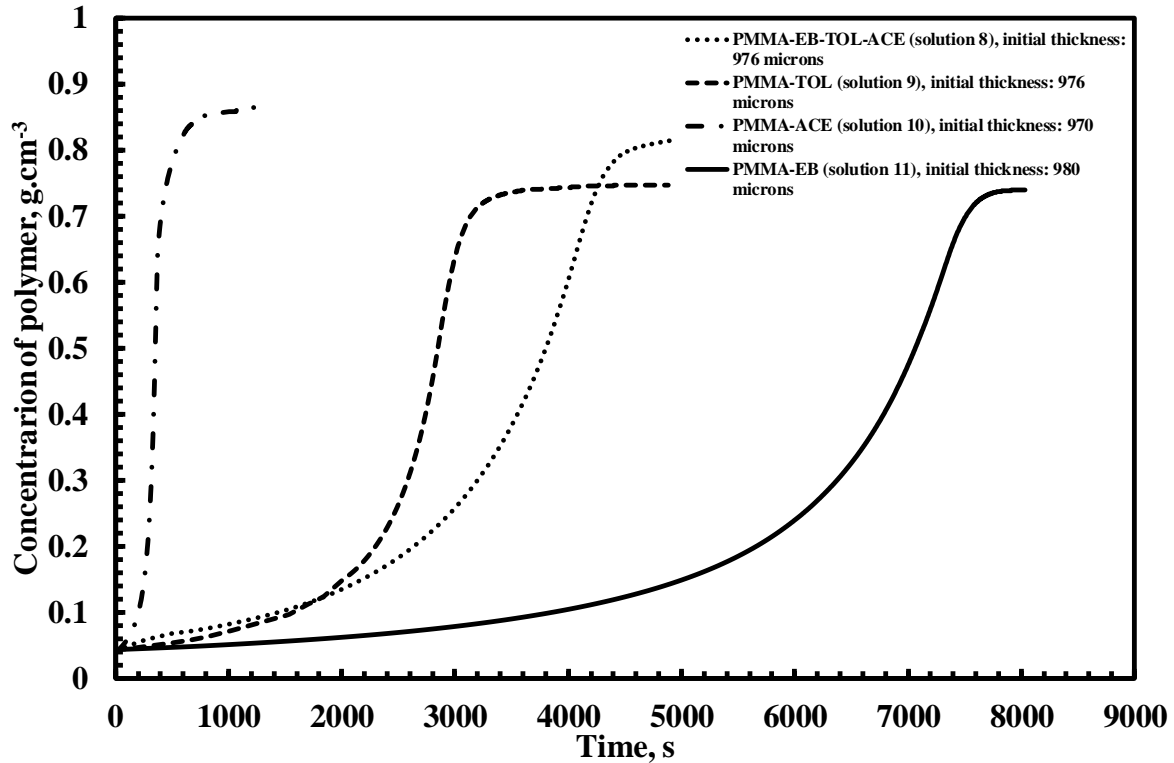


Figure 4.27: Concentration of polymer as a function of time in quaternary and binary coatings.

Figure 4.28 shows the average concentration of polymer as a function of time in various coatings of poly(methyl methacrylate), i.e., ternary and quaternary systems having nearly 5% of polymer in each coating. The initial coating thickness for poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%), poly(methyl methacrylate)(4.97%) – ethylbenzene(47.35%) – acetone(47.65%), poly(methyl methacrylate)(5.22%) – toluene(46.08%) – ethylbenzene(48.69%), and poly(methyl methacrylate)(4.99%) – toluene(47.12%) – acetone(47.88%) was 976 microns, 973 microns, 977 microns, and 972 microns, respectively. The concentrations of poly(methyl methacrylate) in poly(methyl methacrylate) – ethylbenzene – toluene – acetone, poly(methyl methacrylate) – ethylbenzene – acetone, poly(methyl methacrylate) – toluene – ethylbenzene, and poly(methyl methacrylate) –

toluene – acetone coatings were 0.0418 g.cm^{-3} , 0.0416 g.cm^{-3} , 0.0459 g.cm^{-3} , and 0.0419 g.cm^{-3} , respectively. The concentration of poly(methyl methacrylate) left in poly(methyl methacrylate) – ethylbenzene – toluene – acetone, poly(methyl methacrylate) – ethylbenzene – acetone, poly(methyl methacrylate) – toluene – ethylbenzene, and poly(methyl methacrylate) – toluene – acetone coatings are 0.81 g.cm^{-3} , 0.79 g.cm^{-3} , 1.09 g.cm^{-3} , and 0.85 g.cm^{-3} , respectively which are consuming 4271 s, 4917 s, 5966 s, and 1956 s. The average concentration trend is exponentially increasing in all the four coatings. The concentration of polymer in poly(methyl methacrylate) – toluene – acetone coating is increasing faster and becomes constant earlier than poly(methyl methacrylate) – toluene – ethylbenzene coating because of less solvent present in poly(methyl methacrylate) – toluene – ethylbenzene coating. The quaternary coatings have nearly same concentration of polymer left in the coating as other ternary coatings except poly(methyl methacrylate) – toluene – ethylbenzene coating.

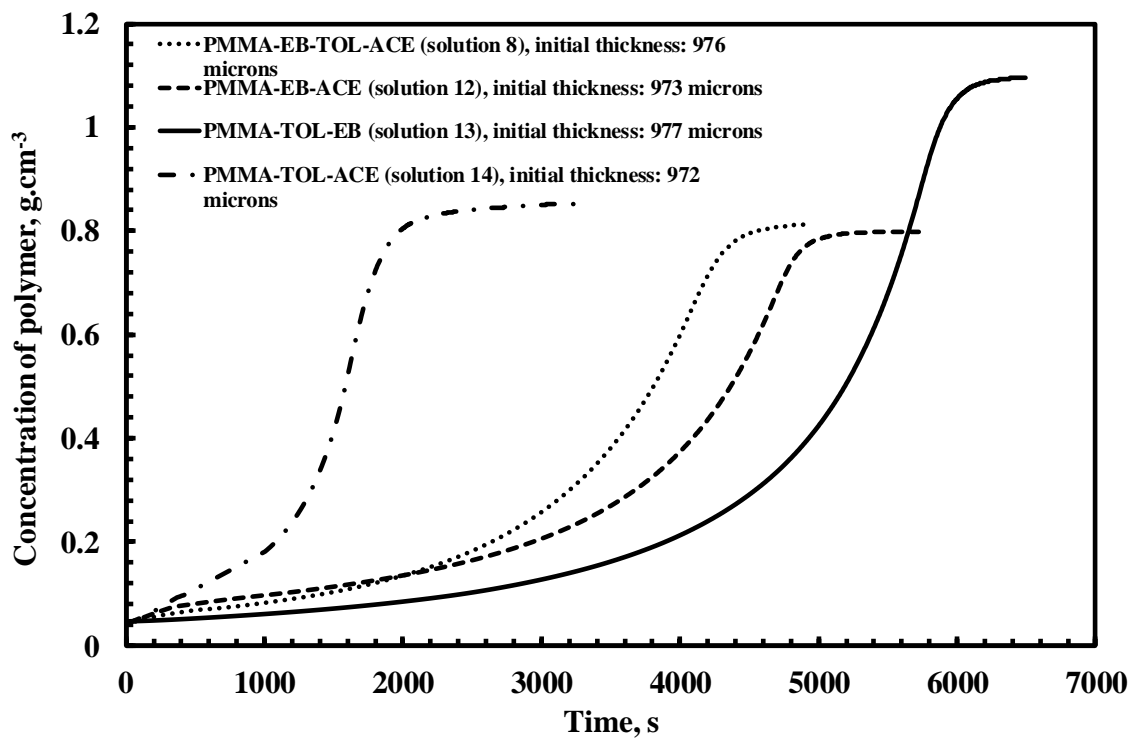


Figure 4.28: Concentration of polymer as a function of time in quaternary and ternary coatings.

4.5 Drying of poly(methyl methacrylate) – ethylbenzene – toluene - acetone coating for 1785 microns thickness

In this case, initial coating is increased to study its effect on the residual solvent, coating thickness, average concentration of poly(methyl methacrylate) and solvents

4.5.1 Residual solvent with time

Figure 4.29 shows the residual solvent as a function of time in various coatings of binary and quaternary systems containing nearly 5% of poly(methyl methacrylate). The initial coating thickness for poly(methyl methacrylate)(4.90%)-ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%), poly(methyl methacrylate)(4.96%) – toluene(95.04%), poly(methyl methacrylate)(4.98%) – acetone(95.01%), and poly(methyl methacrylate)(4.96%) – ethylbenzene(95.03%) coatings was 1785 microns, 1788 microns, 1780 microns, and 1786 microns, respectively. The removal of solvent rate was highest in poly(methyl methacrylate) – acetone and slowest in poly(methyl methacrylate) – ethylbenzene. The residual solvent left in poly(methyl methacrylate) – ethylbenzene – toluene – acetone, poly(methyl methacrylate) – toluene, poly(methyl methacrylate) – acetone, and poly(methyl methacrylate) – ethylbenzene coatings are 0.89%, 1.62%, 0.21%, and 2.25% respectively which are consuming 6362 s, 5011 s, 655 s, and 11484 s. The residual solvent removal is following the same trend in all the four coatings. However, poly(methyl methacrylate) – acetone coating is drying much faster due to high diffusion coefficient of acetone as compared to toluene, and ethylbenzene (in Table 3.1). The drying rate of quaternary system is reasonably high as compared to poly(methyl methacrylate) – ethylbenzene system but slower than poly(methyl methacrylate) – acetone and poly(methyl methacrylate) – toluene system. The residual solvent left in quaternary coating is less as compared to the other coatings because of the presence of acetone and toluene in the coating. Also, the cost of producing quaternary coating will be less as compared to others because of less composition of solvents used in it.

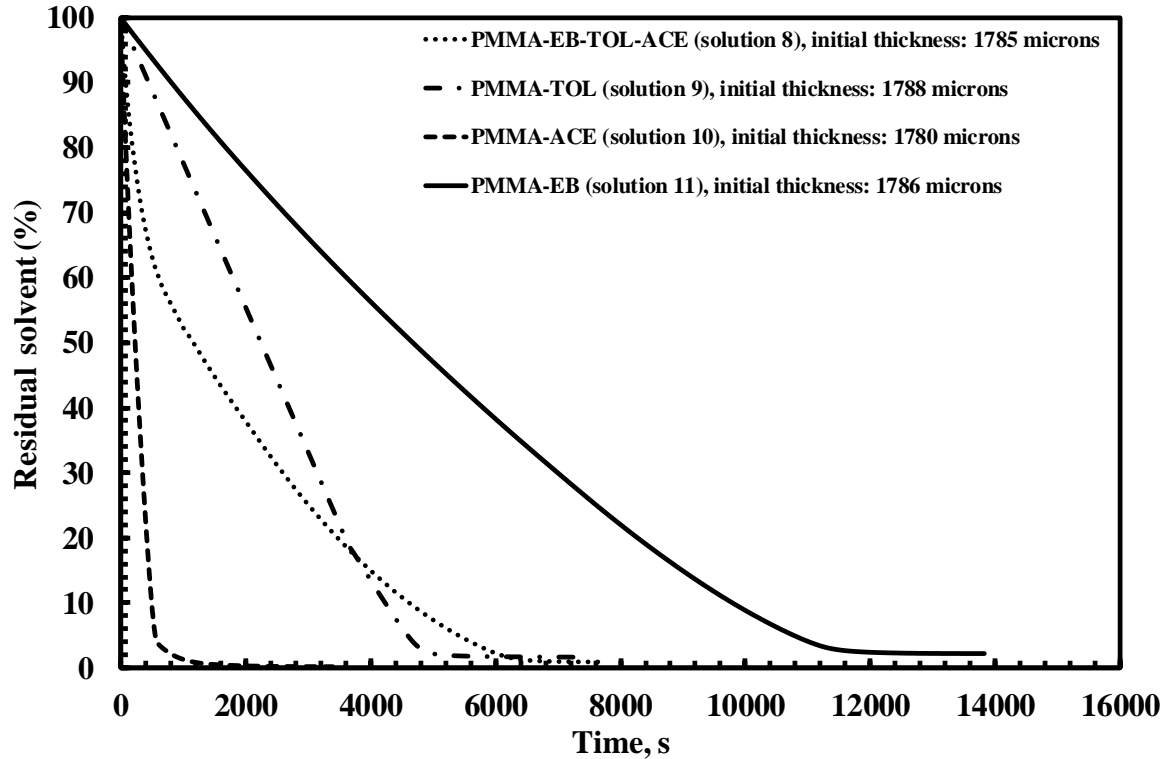


Figure 4.29: Residual solvent as a function of time in quaternary and binary coatings.

Figure 4.30 shows the residual solvent as a function of time in various coatings of poly(methyl methacrylate), i.e., ternary and quaternary systems having the percentage of nearly 5% of polymer in each coating and the initial thickness of coating for poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%), poly(methyl methacrylate)(4.97%) – ethylbenzene(47.35%) – acetone(47.65%), poly(methyl methacrylate)(5.22%) – toluene(46.08%) – ethylbenzene(48.69%), and poly(methyl methacrylate)(4.99%) – toluene(47.12%) – acetone(47.88%) was 1785 microns, 1783 microns, 1786 microns, and 1782 microns, respectively. The removal of solvent rate was highest in poly(methyl methacrylate) – toluene – acetone and slowest in poly(methyl methacrylate) – toluene – ethylbenzene. The residual solvent left in poly(methyl methacrylate) – ethylbenzene – toluene – acetone, poly(methyl methacrylate) – ethylbenzene – acetone, poly(methyl methacrylate) – toluene – ethylbenzene, and poly(methyl methacrylate) – toluene – acetone coatings are 0.89%, 1.65%, 2.53%, and 1.2% respectively which are consuming 6362 s, 7598 s, 9917 s, and 3066 s. The residual solvent removal is following the same trend in all the four coatings. However, poly(methyl methacrylate) – toluene – acetone coating is drying much faster

due to high diffusion coefficient of acetone as compared to toluene, and ethylbenzene (in Table 3.1). The drying of quaternary system is reasonably high as compared to poly(methyl methacrylate) – ethylbenzene – acetone and poly(methyl methacrylate) – toluene – ethylbenzene systems but slower than poly(methyl methacrylate) – toluene-acetone system. In this quaternary system the residual solvent left is very less as compared to the other coatings, so, defects like blisters will be less. The cost for producing this type of coating will be less as compared to other ternary coatings. This is because of less cost of acetone and toluene than ethylbenzene.

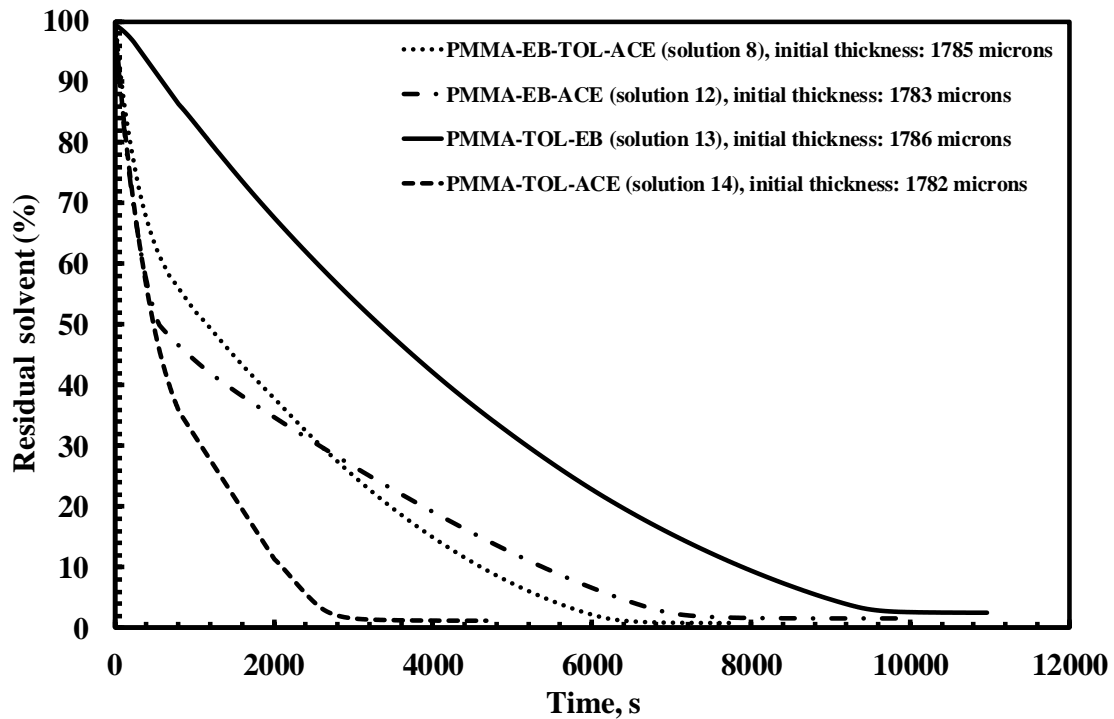


Figure 4.30: Residual solvent as a function of time in quaternary and ternary coatings.

4.5.2 Coating thickness with time

Figure 4.31 shows the coating thickness as a function of time in various coatings of binary and quaternary systems containing poly(methyl methacrylate). Each coating has the percentage of polymer nearly 5% and the initial thickness of the coating for poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%), poly(methyl methacrylate)(4.96%) – toluene(95.04%), poly(methyl methacrylate)(4.98%) – acetone(95.01%), and poly(methyl methacrylate)(4.96%) – ethylbenzene(95.03%) coatings was

1785 microns, 1788 microns, 1780 microns, and 1786 microns, respectively. The decrease in coating thickness was highest in poly(methyl methacrylate) – acetone and slowest in poly(methyl methacrylate) – ethylbenzene. The final coating thickness in poly(methyl methacrylate) – ethylbenzene – toluene – acetone, poly(methyl methacrylate) – toluene, poly(methyl methacrylate) – acetone, and poly(methyl methacrylate) – ethylbenzene coatings are 78 microns, 94 microns, 64 microns, and 105 microns respectively which are consuming 6362 s, 5011 s, 655 s, and 11484 s. The decrease in coating thickness of quaternary system is low as compared to the other systems.

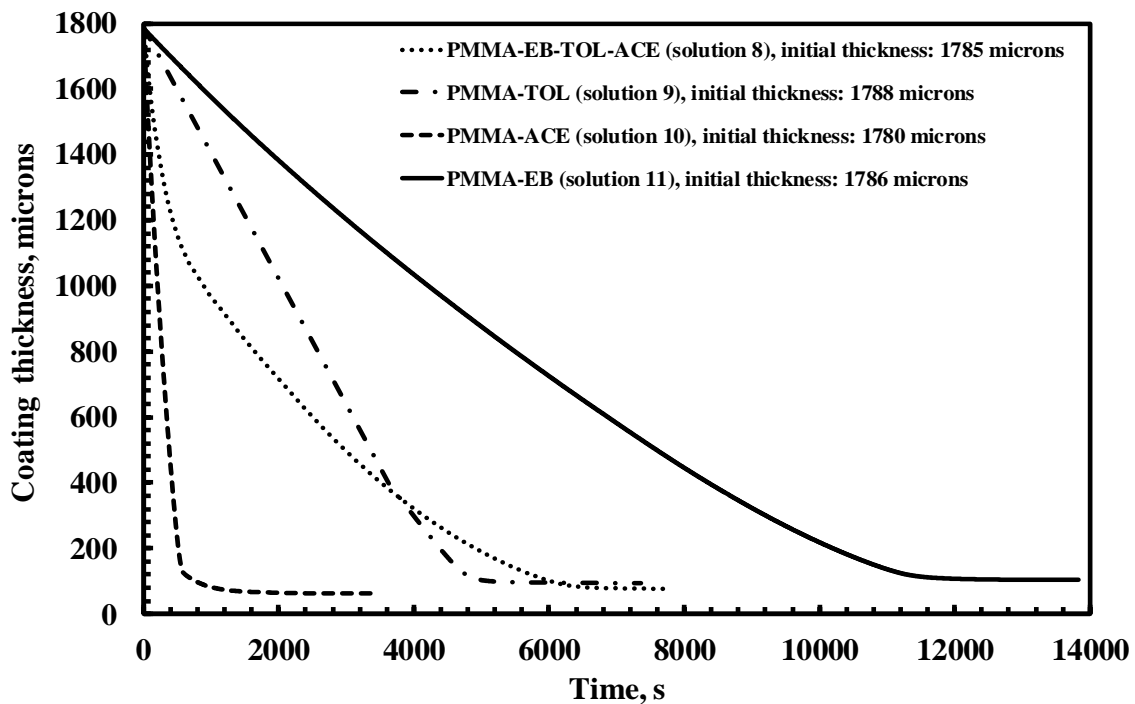


Figure 4.31: Coating thickness as function of time in quaternary and binary coatings.

Figure 4.32 shows the coating thickness as a function of time in various coatings of ternary and quaternary systems containing poly(methyl methacrylate). Each coating has the percentage of polymer nearly 5% and the initial thickness of the coating for poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%), poly(methyl methacrylate)(4.97%) – ethylbenzene(47.35%) – acetone(47.65%), poly(methyl methacrylate)(5.22%) – toluene(46.08%) – ethylbenzene(48.69%), and poly(methyl methacrylate)(4.99%) – toluene(47.12%) – acetone(47.88%) was 1785 microns, 1783 microns,

1786 microns, and 1782 microns, respectively. The decrease in coating thickness was highest in poly(methyl methacrylate) – toluene – acetone and slowest in poly(methyl methacrylate) – toluene – ethylbenzene. The final coating thickness in poly(methyl methacrylate) – ethylbenzene – toluene – acetone, poly(methyl methacrylate) – ethylbenzene – acetone, poly(methyl methacrylate) – toluene – ethylbenzene, and poly(methyl methacrylate) – toluene – acetone coatings are 78 microns, 91 microns, 113 microns, and 84 microns respectively which are consuming 6362 s, 7598 s, 9917 s, and 3066 s. The decrease in coating thickness of quaternary system is reasonably high as compared to the other ternary coatings.

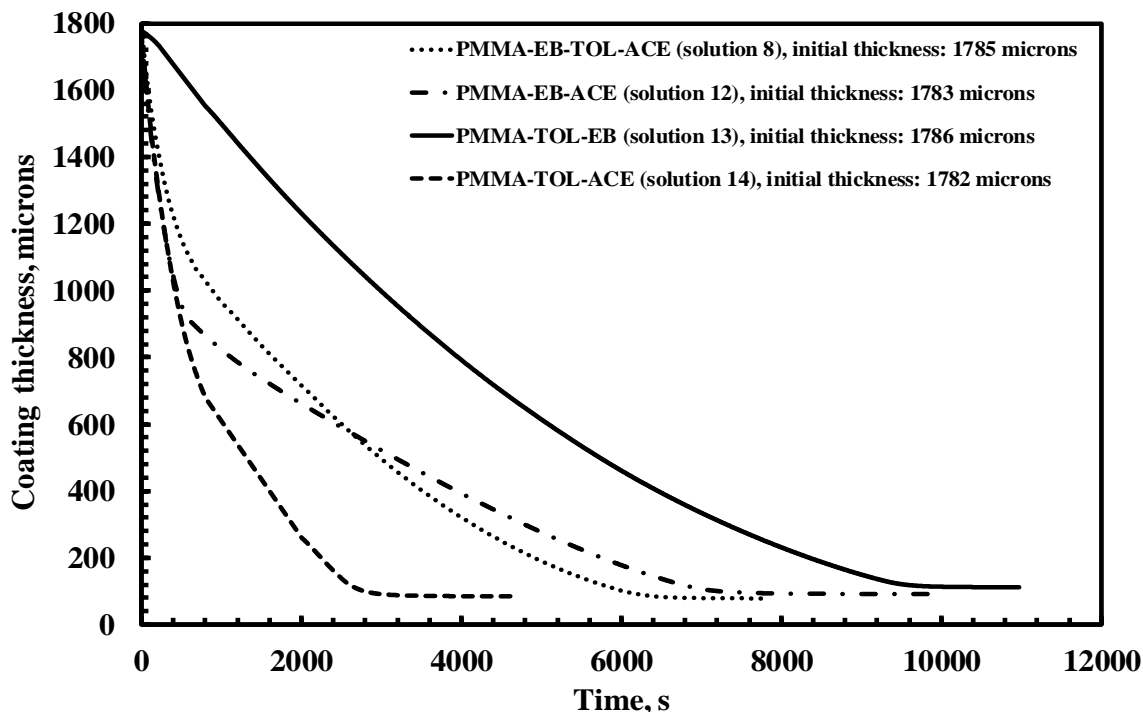


Figure 4.32: Coating thickness as a function of time in quaternary and ternary coatings.

4.5.3 Average concentration of solvent with time

Figure 4.33 shows the average concentration of solvent as a function of time in various coatings of poly(methyl methacrylate), i.e., binary and quaternary systems having polymer of nearly 5% in each coating. The initial coating thickness for poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%), poly(methyl methacrylate)(4.96%) – toluene(95.04%), poly(methyl methacrylate)(4.98%) – acetone(95.01%), and poly(methyl methacrylate)(4.96%) – ethylbenzene(95.03%) coatings was 1785 microns, 1788 microns, 1780

microns, and 1786 microns, respectively. The concentrations of solvent in poly(methyl methacrylate) – ethylbenzene – toluene – acetone, poly(methyl methacrylate) – toluene, poly(methyl methacrylate) – acetone, and poly(methyl methacrylate) – ethylbenzene coatings were 0.811 g.cm^{-3} , 0.837 g.cm^{-3} , 0.759 g.cm^{-3} , and 0.834 g.cm^{-3} , respectively. The concentration of solvent left in poly(methyl methacrylate) – ethylbenzene – toluene – acetone, poly(methyl methacrylate) – toluene, poly(methyl methacrylate) – acetone, and poly(methyl methacrylate) – ethylbenzene coatings are 0.16 g.cm^{-3} , 0.25 g.cm^{-3} , 0.04 g.cm^{-3} , and 0.32 g.cm^{-3} , respectively which are consuming 6362 s, 5011 s, 655 s, and 11484 s. The average concentration trend is exponentially decreasing in all four coatings. The concentration of solvent in poly(methyl methacrylate) – acetone coating is decreasing faster than poly(methyl methacrylate) – ethylbenzene coating. The concentration of solvent in quaternary coating is nearly same as other coatings except poly(methyl methacrylate) – acetone coating.

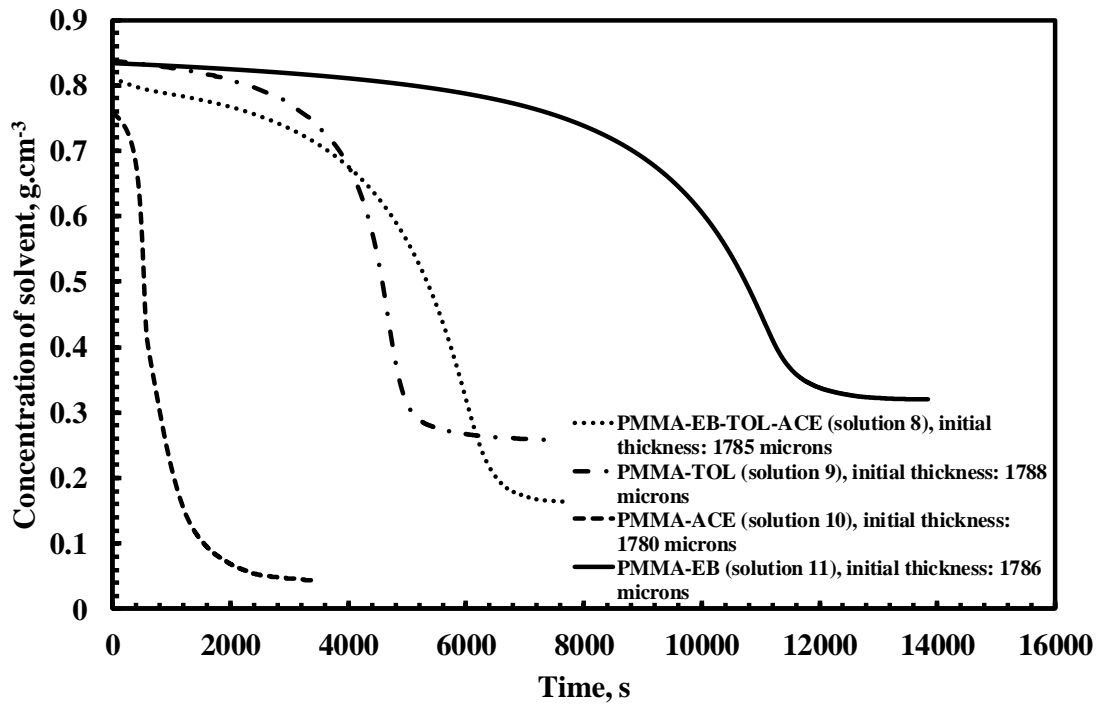


Figure 4.33: Concentration of solvent as a function of time in quaternary and binary coatings.

Figure 4.34 shows the average concentration of solvent as a function of time in various coatings of poly(methyl methacrylate), i.e., ternary and quaternary systems having polymer of nearly 5% in each coating. The initial coating thickness for poly(methyl methacrylate)(4.90%) –

ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%), poly(methyl methacrylate)(4.97%) – ethylbenzene(47.35%) – acetone(47.65%), poly(methyl methacrylate)(5.22%) – toluene(46.08%) – ethylbenzene(48.69%), and poly(methyl methacrylate)(4.99%) – toluene(47.12%) – acetone(47.88%) was 1785 microns, 1783 microns, 1786 microns, and 1782 microns, respectively. The initial concentrations of solvent in poly(methyl methacrylate) – ethylbenzene – toluene – acetone, poly(methyl methacrylate) – ethylbenzene – acetone, poly(methyl methacrylate) – toluene – ethylbenzene, and poly(methyl methacrylate) – toluene – acetone coatings were 0.811 g.cm^{-3} , 0.796 g.cm^{-3} , 0.839 g.cm^{-3} , and 0.798 g.cm^{-3} , respectively. The concentration of solvent left in poly(methyl methacrylate) – ethylbenzene – toluene – acetone, poly(methyl methacrylate) – ethylbenzene – acetone, poly(methyl methacrylate) – toluene – ethylbenzene, and poly(methyl methacrylate) – toluene – acetone coatings are 0.16 g.cm^{-3} , 0.26 g.cm^{-3} , 0.33 g.cm^{-3} , and 0.20 g.cm^{-3} , respectively which are consuming 6362 s, 7598 s, 9917 s, and 3066 s. The average concentration trend is in the form of exponential decrease in all four coatings. The concentration of solvent in poly(methyl methacrylate) – toluene – acetone coating is decreasing faster than poly(methyl methacrylate) – toluene – ethylbenzene coating. The concentration of solvent is less in quaternary coating than the other ternary coatings.

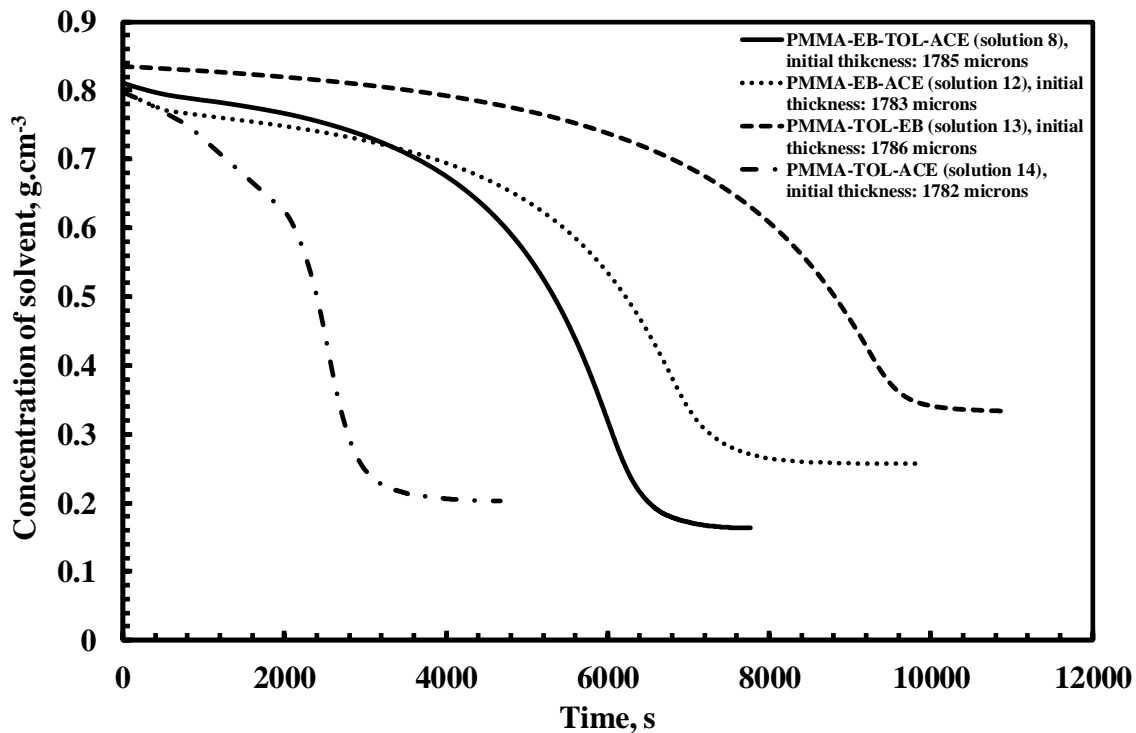


Figure 4.34: Concentration of solvent as a function of time in quaternary and ternary coatings.

4.5.4 Average concentration of polymer with time

Figure 4.35 shows the average concentration of polymer as a function of time in various coatings of poly(methyl methacrylate), i.e., binary and quaternary systems having nearly 5% of polymer in each coating. The initial coating thickness for poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%), poly(methyl methacrylate)(4.96%) – toluene(95.04%), poly(methyl methacrylate)(4.98%) – acetone(95.01%), and poly(methyl methacrylate)(4.96%) – ethylbenzene(95.03%) coatings was 1785 microns, 1788 microns, 1780 microns, and 1786 microns, respectively. The initial concentrations of poly(methyl methacrylate) in poly(methyl methacrylate) – ethylbenzene – toluene – acetone, poly(methyl methacrylate) – toluene, poly(methyl methacrylate) – acetone, and poly(methyl methacrylate) – ethylbenzene coatings were 0.0418 g.cm^{-3} , 0.0437 g.cm^{-3} , 0.0398 g.cm^{-3} , and 0.0436 g.cm^{-3} , respectively. The concentration of polymer left in poly(methyl methacrylate) – ethylbenzene – toluene – acetone, poly(methyl methacrylate) – toluene, poly(methyl methacrylate) – acetone, and poly(methyl methacrylate) – ethylbenzene coatings are 0.95 g.cm^{-3} , 0.83 g.cm^{-3} , 1.11 g.cm^{-3} , and 0.74 g.cm^{-3} , respectively which are consuming 6362 s, 5011 s, 655 s, and 11484 s. The average concentration trend is exponentially increasing in all the four coatings. The concentration of polymer in poly(methyl methacrylate) – acetone coating is increasing faster than poly(methyl methacrylate) – ethylbenzene coating. The quaternary coatings have nearly same concentration of polymer left in the coating as other binary coatings.

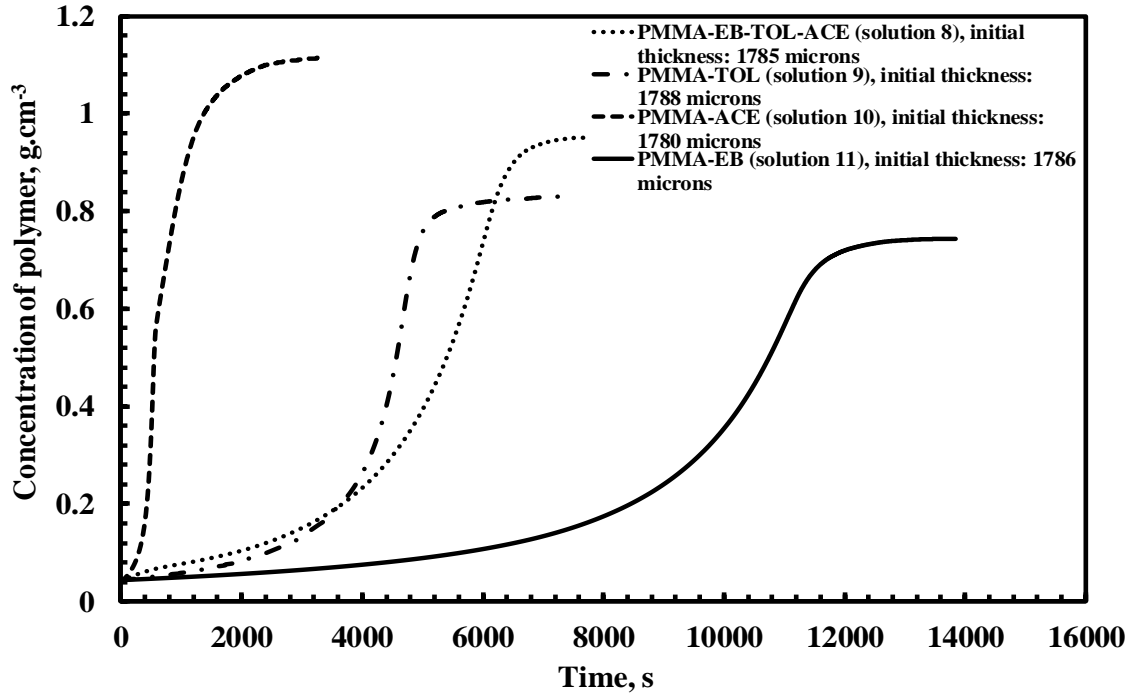


Figure 4.35: Concentration of polymer as a function of time in quaternary and binary coatings.

Figure 4.36 shows the average concentration of polymer as a function of time in various coatings i.e., binary and quaternary systems having nearly 5% of poly(methyl methacrylate) in each coating. The initial coating thickness for poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%), poly(methyl methacrylate)(4.97%) – ethylbenzene(47.35%) – acetone(47.65%), poly(methyl methacrylate)(5.22%) – toluene(46.08%) – ethylbenzene(48.69%), and poly(methyl methacrylate)(4.99%) – toluene(47.12%)-acetone(47.88%) was 1785 microns, 1783 microns, 1786 microns, and 1782 microns, respectively. The initial concentration of poly(methyl methacrylate) in poly(methyl methacrylate) – ethylbenzene – toluene – acetone, poly(methyl methacrylate) – ethylbenzene – acetone, poly(methyl methacrylate) – toluene – ethylbenzene, and poly(methyl methacrylate) – toluene – acetone coatings were 0.0418 g.cm^{-3} , 0.0416 g.cm^{-3} , 0.0459 g.cm^{-3} , and 0.0419 g.cm^{-3} , respectively. The concentration of poly(methyl methacrylate) left in poly(methyl methacrylate) – ethylbenzene – toluene – acetone, poly(methyl methacrylate) – ethylbenzene – acetone, poly(methyl methacrylate) – toluene – ethylbenzene, and poly(methyl methacrylate) – toluene – acetone coatings are 0.95 g.cm^{-3} , 0.81 g.cm^{-3} , 0.72 g.cm^{-3} , and 0.89 g.cm^{-3} , respectively which are consuming 6362 s, 7598 s, 9917 s, and 3066 s. The average concentration trend is

exponentially increasing in all the four coatings. The concentration of polymer in poly(methyl methacrylate) – toluene – acetone coating is increasing faster and becomes constant earlier than poly(methyl methacrylate) – ethylbenzene – toluene – acetone coating because of less solvent present in poly(methyl methacrylate) – ethylbenzene – toluene – acetone coating. The quaternary coatings have nearly same concentration of polymer left in the coating as other ternary coatings except poly(methyl methacrylate) – toluene – ethylbenzene coating.

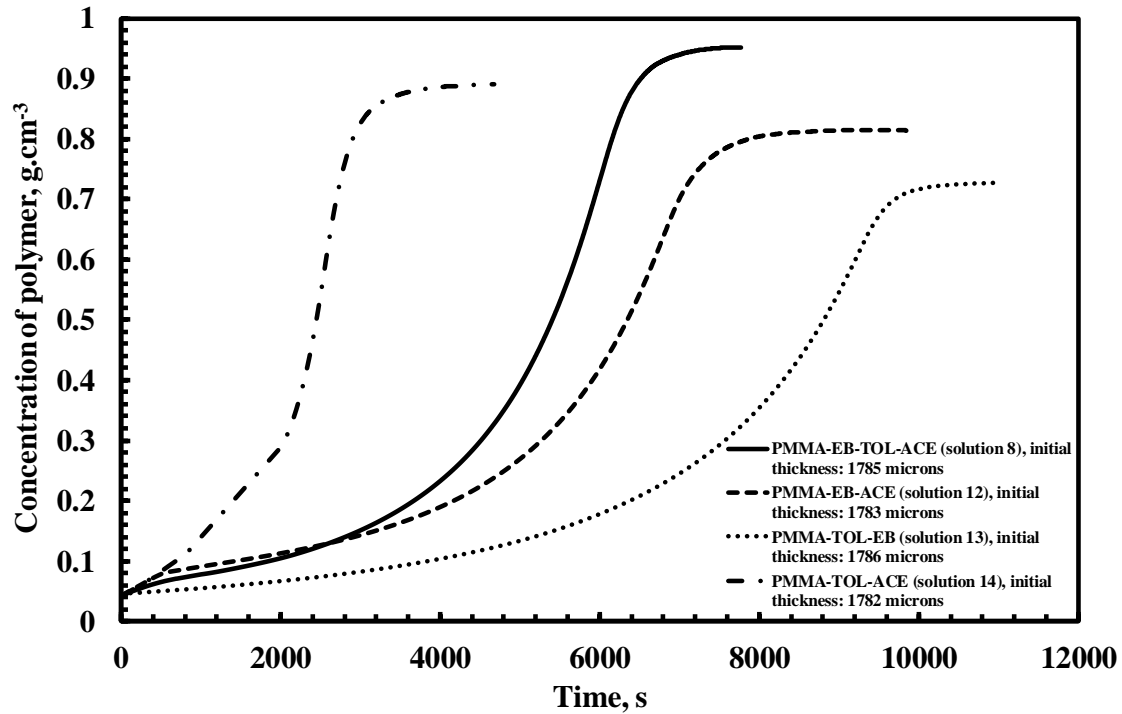


Figure 4.36: Concentration of polymer as a function of time in quaternary and ternary coatings.

4.6 Effect of coating composition on drying of poly(methyl methacrylate) – ethylbenzene – toluene – acetone coatings.

Drying of two quaternary systems of poly(methyl methacrylate) – ethylbenzene – toluene – acetone were prepared having composition, poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) and poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%) The results of both the systems are compared for different coating thicknesses, 976 microns and 1785 microns.

4.6.1 Effect of coating composition and thickness on residual solvent

Figure 4.37 shows the residual solvent as a function of time in various coatings of poly(methyl methacrylate) in poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) and poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%). The percentage of polymer in each coating was nearly 5% for both type of quaternary systems. For 976 microns thickness: The initial coating thickness of poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) and poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%) was 976 microns and 973 microns. The removal of solvent rate was highest poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%) and slowest in poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%). The residual solvent left in poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) and poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%) coatings are 2.85% and 1.66%, respectively, which are consuming 3167 s and 4271 s. For 1785 microns thickness: The initial coating thickness of poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) and poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%) was 1785 microns and 1780 microns. The residual solvent left in poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) and poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%) coatings are 0.89% and 2.3%, respectively, which are consuming 6362 s and 4257 s. The residual solvent removal trend is same in both the coatings. The quaternary poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) coating are drying faster than the other quaternary coating but the residual solvent has increased in case of poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%). Also, this is a cost-effective system because toluene and acetone are cheaper than ethylbenzene. The change in coating composition and thickness is not affecting the residual solvent at all, but the drying time is getting low in case of poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%) coating.

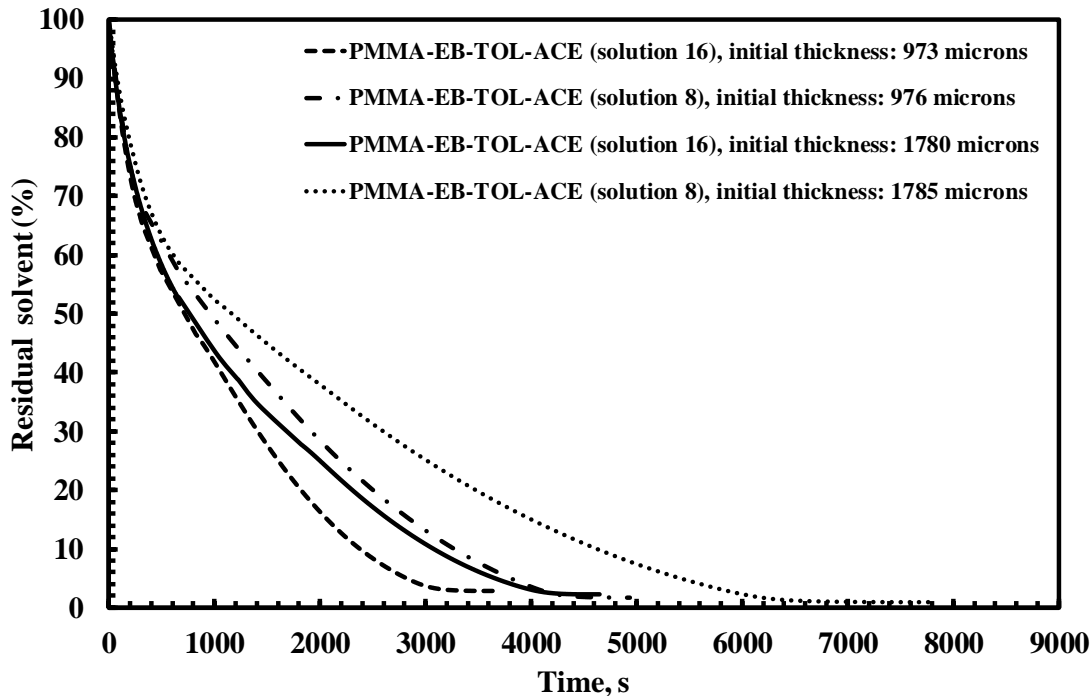


Figure 4.37: Residual solvent as a function of time in quaternary coatings of poly(methyl methacrylate) – ethylbenzene – toluene – acetone having composition and initial thicknesses: poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) and poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%), and 976 and 1785 microns, respectively.

4.6.2 Effect of coating composition and thickness on coating thickness

Figure 4.38 shows the coating thickness as a function of time in various coatings of poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) and poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone (30.92%) which are containing nearly 5% of poly(methyl methacrylate). For 976 microns thickness: The initial coating thickness of poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) and poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%) was 976 microns and 973 microns. The decrease in coating thickness was highest in poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%) and slowest in poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) –

toluene(32.29%) – acetone(31.38%). The final coating thickness in poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%) and poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) coatings are 60 microns and 50 microns respectively which are consuming 3167 s and 4271 s. For 1785 micron thickness: The initial coating thickness of poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) and poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%) was 1785 microns and 1780 microns. The final coating thickness in poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%) and poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) coatings are 100 microns and 78 microns respectively which are consuming 4257 s and 6362 s. The coating thickness in poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%) coating is nearly same as compared to the other coating. So, both coatings are good enough in case of coating thickness.

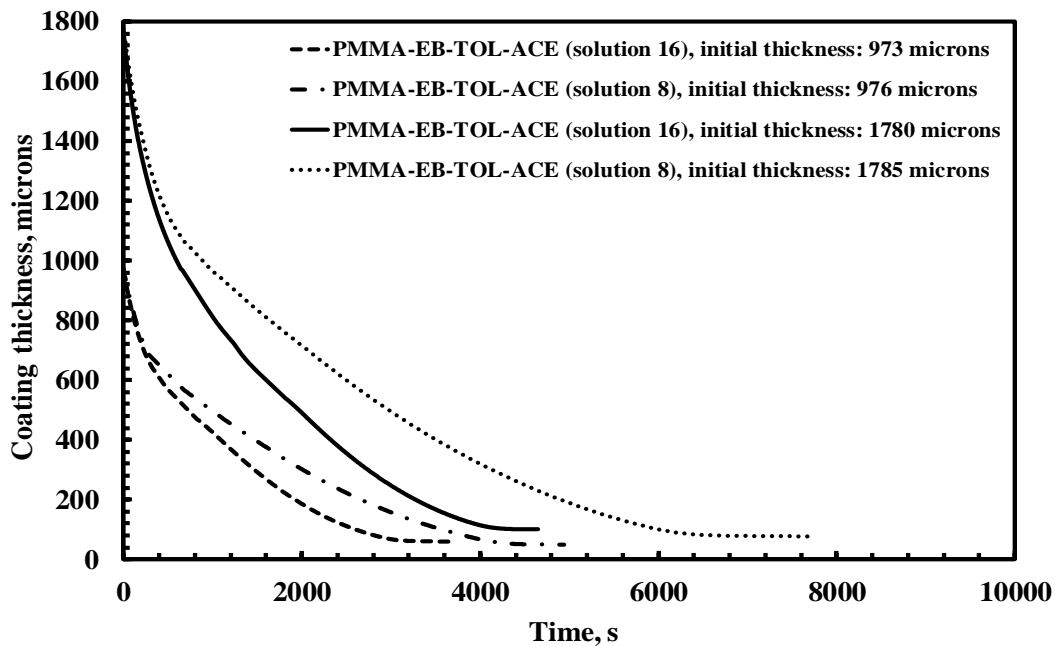


Figure 4.38: Coating thickness as a function of time in quaternary coatings of poly(methyl methacrylate) – ethylbenzene – toluene – acetone having composition and initial thicknesses: poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) and poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%), and 976 and 1785 microns, respectively.

4.6.3 Effect of coating composition and thickness on average concentration of solvent

Figure 4.39 shows the average concentration of solvent as a function of time in various coatings of poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) and poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%) contains nearly 5% of poly(methyl methacrylate). For 976 microns thickness: The initial coating thickness of poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) and poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%) was 976 microns and 973 microns. The exponential decrease in concentration of solvent was highest in poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%) and slowest in poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%). The final concentrations of solvent in poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%) and poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) coatings are 0.37 g.cm^{-3} and 0.26 g.cm^{-3} respectively which are consuming 3167 s and 4271 s. For 1785 micron thickness: The initial coating thickness of poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) and poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%) was 1785 microns and 1780 microns. The final concentrations of solvent in poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%) and poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) coatings are 0.32 g.cm^{-3} and 0.16 g.cm^{-3} respectively which are consuming 4257 s and 6362 s. The concentration of solvent in quaternary poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%) coating is higher than other coating.

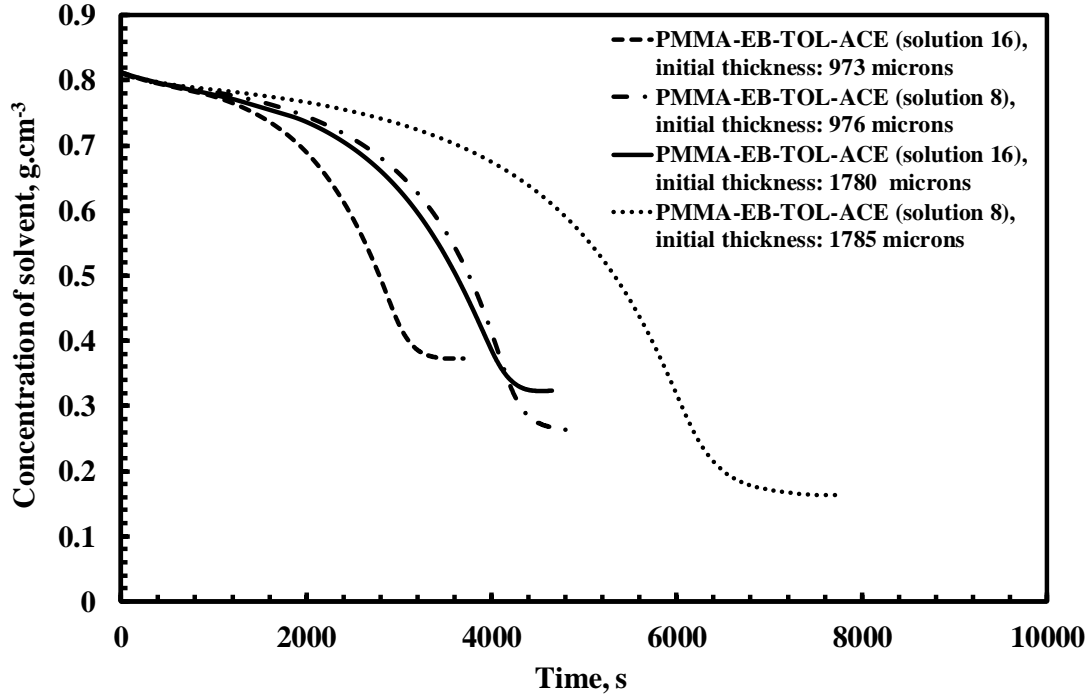


Figure 4.39: Concentration of solvent as a function of time in quaternary coatings of poly(methyl methacrylate) – ethylbenzene – toluene – acetone having composition and initial thicknesses: poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) and poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%), and 976 and 1785 microns, respectively.

4.6.4 Effect of coating composition and thickness on average concentration of polymer

Figure 4.40 shows the average concentration of polymer i.e., poly(methyl methacrylate) as a function of time in poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) and poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%). For 976 microns thickness: The initial coating thickness of poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) and poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%) was 976 microns and 973 microns. The exponential increase in concentration of poly(methyl methacrylate) was highest in poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) –

acetone(30.92%) and slowest in poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%). The final concentrations of polymer poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%) and poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) coatings are 0.65 g.cm⁻³ and 0.81 g.cm⁻³ respectively which are consuming 3167 s and 4271 s. For 1785 micron thickness: The initial coating thickness of poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) and poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%) was 1785 microns and 1780 microns. The final concentrations of polymer poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%) and poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) coatings are 0.72 g.cm⁻³ and 0.95 g.cm⁻³ respectively which are consuming 4257 s and 6362 s. The concentration of poly(methyl methacrylate) in poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%) coating is less as compared to the other coating.

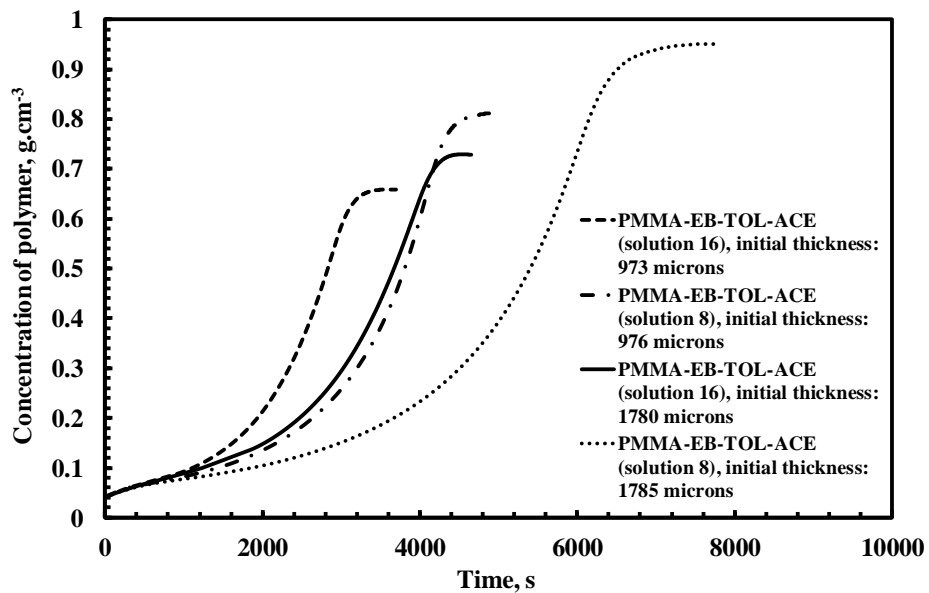


Figure 4.40: Concentration of polymer as a function of time in quaternary coatings of poly(methyl methacrylate) – ethylbenzene – toluene – acetone having composition and initial thicknesses: poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%) and poly(methyl methacrylate)(4.78%) – ethylbenzene(20.63%) – toluene(43.65%) – acetone(30.92%), and 976 and 1785 microns, respectively.

In poly(styrene) coatings, the residual solvent for 1150 microns thickness in quaternary system (poly(styrene)(5.11%) – ethylbenzene(31.89%) – toluene(31.56%) – *p*-xylene(31.44%)) is 2.39% , Table 4.1, Row 1. In comparison with quaternary system, the residual solvent in binary (poly(styrene)(5.1%) – toluene(94.94%), poly(styrene)(4.95%) – *p*-xylene(95.04%), poly(styrene)(5.29%) – ethylbenzene(94.71%)) is 0.82%, 1.78%, and 2.1%, respectively. The % residual solvent in quaternary is more as compared to binary due to the presence of three solvents but the drying time is less than other coatings. Also, for 1970 microns thickness, in quaternary system is 2.94% , Table 4.1, Row 1. In comparison to quaternary system, the residual solvent in binary (poly(styrene)(5.1%) – toluene(94.94%), poly(styrene)(4.95%) – *p*-xylene(95.04%), poly(styrene)(5.29%) – ethylbenzene(94.71%)) is 1.21%, 2.92%, and 2.47%, respectively in Row 2, 3, 4. The % residual solvent in quaternary is nearly same as other binary coatings except poly(styrene)(5.1%) – toluene(94.94%) because of high diffusion coefficient of toluene. The quaternary system is further compared with ternary system for both 1150 microns and 1970 microns thickness. The residual solvent is more as other ternary system except poly(styrene)(5.1%) – toluene(46.43%) – ethylbenzene(48.47%), Table 4.1, rows 5, 6, 7. This is because of higher diffusion coefficients of toluene and ethylbenzene than *p*-xylene. Also, quaternary system of poly(styrene) is compared with another quaternary system having varying composition of solvents to see the effect drying in the coatings. The residual solvent and drying time in quaternary system in Table 4.1, Row 8 is lesser than the quaternary system having nearly same composition of solvents in Table 4.1, Row 1. This helps the coating to dry faster and is more economical.

Table 4.1: Summary of drying data in various quaternary, binary and ternary coatings of poly(styrene).

S. No.	Coating compositions, wt%	Initial Thickness, microns	Final Thickness, microns	Residual solvent (%)	Drying time (s)
1.	PS: 5.11 wt%, EB: 31.89 wt%, TOL: 31.56 wt%, PX: 31.44 wt%	1145	75	2.39	7252
		1963	139	2.94	10603
2.	PS: 5.1 wt%, TOL: 94.94 wt%	1166	59	0.82	3226
		1959	107	1.21	5067
3.	PS: 4.95 wt%, PX: 95.04 wt%	1171	68	1.78	10594
		1975	137	2.92	13994
4.	PS: 5.29 wt%, EB: 94.71 wt%	1141	74	2.1	8813
		1958	133	2.47	12659
5.	PS: 4.99 wt%, EB: 48.17 wt%, PX: 46.83 wt%	1176	71	1.9	9578
		1964	119	1.94	14200
6.	PS: 5.1 wt%, TOL: 46.43 wt%, EB: 48.47 wt%	1107	56	0.83	6532
		1998	117	1.63	9313
7.	PS: 4.89 wt%, TOL: 48.33 wt%, PX: 46.78 wt%	1145	70	2.24	6833
		1988	136	2.85	9358
8.	PS: 4.84 wt%, EB: 21.33 wt%, TOL: 43.75 wt%, PX: 30.07 wt%	1149	58	1.04	6677
		1963	134	2.9	8483

In poly(methyl methacrylate) coatings, the residual solvent for 976 microns thickness in quaternary system (poly(methyl methacrylate)(4.90%) – ethylbenzene(31.42%) – toluene(32.29%) – acetone(31.38%)) is 1.66% as shown in Table 4.2, row 1. In comparison with binary system (poly(methyl methacrylate)(4.96%) – toluene(95.04%), poly(methyl methacrylate)(4.98%) – acetone(95.01%), poly(methyl methacrylate)(4.96%) – ethylbenzene(95.03%), the residual solvent is 2.23%, 1.26%, and 2.28%, respectively. The % residual solvent in quaternary system is less as compared to other binary systems except poly(methyl methacrylate)(4.98%) – acetone(95.01%) coating due to high diffusion coefficient of acetone, Table 1. The findings are also similar for 1785 microns thickness, the quaternary

system has less residual solvent left in the coating. The quaternary system of poly(methyl methacrylate) is further compared with the corresponding ternary system. The residual solvent is nearly same in case of 976 microns thickness shown in Table 4.2, rows 5, 6, 7. But in case of 1785 micron thickness, the residual solvent is less as compared to other system. Poly(methyl methacrylate)(4.98%) – acetone(95.01%) coating has less residual solvent because of the high diffusion coefficient of acetone, Table 2, Row 2. Now, in case of varying composition of solvent in quaternary coating, the residual solvent has increased but drying time has become even lesser than the other quaternary coating in Table 4.2, row 8. This is because of high solvent loading of acetone and toluene than ethylbenzene.

Table 4.2: Summary of drying data in various quaternary, binary and ternary coatings of poly(methyl methacrylate).

S. No.	Coating composition, wt%	Initial Thickness, microns	Final Thickness, microns	Residual solvent (%)	Drying time, s
1.	PMMA: 4.90 wt%, EB: 31.42 wt%, TOL: 32.29 wt%, ACE: 31.38 wt%	976	50	1.66	4271
		1785	78	0.89	6362
2.	PMMA: 4.96 wt%, TOL: 95.04 wt%	976	57	2.23	3065
		1788	94	1.62	5011
3.	PMMA: 4.98 wt%, ACE: 95.01 wt%	970	45	1.26	420
		1780	64	0.21	655
4.	PMMA: 4.96 wt%, EB: 95.03 wt%	980	58	2.28	7548
		1786	105	2.25	11484
5.	PMMA: 4.97 wt%, EB: 47.35 wt%, ACE: 47.65 wt%	973	51	1.75	4917
		1783	91	1.65	7598
6.	PMMA: 5.22 wt%, TOL: 46.08 wt%, EB: 48.69 wt%	977	41	0.32	5966
		1786	113	2.53	9917
7.	PMMA: 4.99 wt%, TOL: 47.12 wt%, ACE: 47.88 wt%	972	48	1.43	1881
		1782	84	1.2	3066
8.	PM: 4.78 wt% EB: 20.63 wt% TOL: 43.65 wt% ACE: 30.92 wt%	973	60	2.85	3167
		1780	100	2.3	4257

Chapter 5

Conclusions

Drying of quaternary poly(styrene) and poly(methyl methacrylate) have been studied. The results show that the binary solutions of high volatile solvents are having less drying time and less residual solvent as compared to respective ternary and quaternary systems. In case of poly(styrene) – ethylbenzene – toluene – *p*-xylene quaternary system, the presence of toluene is the governing factor to control the residual solvent and the drying time required for the coating. More the amount of the toluene, lesser would be the residual solvent and the drying time. On the other hand, presence of *p*-xylene is increasing the residual solvent and drying time significantly as compared to ethylbenzene. In quaternary system, the percentage of these three solvents can be manipulating to minimize the residual solvent to a reasonable amount. Therefore, the quaternary system would be a better option to use the multiple solvents as compared to binary or ternary systems.

In case of poly(methyl methacrylate) – ethylbenzene – toluene – acetone system, the presence of acetone in binary, ternary and quaternary coatings is the controlling factor to minimize the residual solvent and drying time. However, presence of ethylbenzene can be used to retard the drying rate depending on the applications. The acetone has very high diffusion coefficients as compared to other solvents, so, these coatings may be susceptible to skinning phenomenon which is unwanted.

Poly(methyl methacrylate) quaternary system shows the better performance as compared to poly(styrene) due to low glass transition of poly(methyl methacrylate) as compared to poly(styrene). If we calculate the total cost of two system, the cost of solvents used in poly(styrene) quaternary system would be slightly higher as compared to poly(methyl methacrylate) system due to low cost of acetone as compared to *p*-xylene. All solvent combinations cannot be used due to unstable solutions; therefore, solvent must be selected carefully to get the homogeneous solution in order to get dense polymeric film rather phase separated membranes.

So, these results confirm that each coating would have nearly same thermal property due same composition of polymer left at the end of drying. But quaternary coating might be much effective in terms of cost or drying time and hence energy required for drying.

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