Calibration Curves to Measure Concentrations in Multicomponent Polymeric Coatings Using Confocal Raman Spectroscopy

Raj Kumar Arya

Abstract—Confocal Raman spectroscopy is used to measure concentration of solvents and polymer in ternary polymer – solvent –solvent coatings. A laser beam is focused through a pinhole arrangement at a location inside a sample. The scattered light is captured by a detector and its spectra are recorded in an attached computer. The spectrum is reported as intensity (in some arbitrary units) versus wave number (cm-1). Ternary and binary polymer solvent systems should be chosen in such a way that the polymer and the solvents should be distinguished by having characteristic peak at some different wave numbers. The ratio of the intensity of the polymer to that of the solvent is calibrated against known ratio of concentration of the polymer to that of the solvent.

Index Terms—Confocal raman spectroscopy, drying of polymeric coatings, diffusion, free-volume theory

I. INTRODUCTION

Many homogeneous and dense polymeric coatings are made by drying thin films cast from solutions of one polymer dissolved in two or more solvents. Multicomponent systems offer several advantages such as ability to dissolve polymer, control of drying rates and use of cheaper solvents [1]. Asymmetric membranes, having thin and dense upper layer and thick and porous bottom layer, were produced by drying of ternary systems consisting of a polymer, a solvent and a non-solvent [2]-6]. Such membranes could be also made by dissolving a solution of a polymer in a solvent and in a non-solvent. The non-solvent diffuses into the solution and the solvent out of the solution leading to phase separation. Diffusion is central to description of drying processes of homogeneous and heterogeneous coatings as internal diffusion controls the drying rate for most part of drying.

Diffusion is usually the rate controlling step during transport in many polymer solvent systems. In many cases, the transport is adequately described by Fick's law of diffusion, which states that the flux of a diffusing component at a location equals the product of diffusion coefficient and its concentration gradient there. For polymer solvent systems, the diffusion coefficient is a strong function of temperature and concentration. Free volume theory [7], [8] describes this function accurately for several

systems involving one polymer and one solvent. The theory combines thermo-dynamics and self-diffusion coefficient to predict mutual diffusion coefficient. Self-diffusion coefficient depends on free volume available for diffusion and the volume required for diffusion. The theory predicts these two volumes as a function of concentration, temperature and other properties of polymer-solvent system.

For multicomponent systems consisting of one polymer and many solvents, the volumes have been modified include the effect of all components to predict self-diffusion coefficient. Flux of the solvent at a location in multicomponent systems is determined by not only its concentration gradient but also those of others. The diffusion coefficient of the solvent, which combines with its own concentration gradient is called main-term coefficient and those that combine with gradient for other solvents are called cross-term coefficients. In fact, to describe diffusion in a N-component system, $(N-1)^2$ mutual diffusion coefficients are needed. Several theories [9]-[11] appeared in the literature that related the modified self-diffusion coefficients to mutual diffusion coefficients. All of them have basis in friction factor theory of Bearman[12] and make assumptions to simplify the expression for mutual diffusion coefficients.

Recently, Price and Romdhane[13] proposed a unified theory of which the existing theories are special cases. They mention that the theories assume that the ratio of self-diffusion coefficient of the polymer and the solvents remains constant through the diffusion process and demonstrated that such an assumption could lead to violation of material balance constraints, which was also shown by Naumann and Savoca[14]. Price and Romdhane[13] showed that the theories predict almost same average concentration of solvent in a drying ternary coating. But, they could predict different concentration profile of the solvent inside the coating. Such profiles are important in coatings that phase separate during drying as shown by Dabral[11].

The predictions of the theories have not been compared with the measured diffusion coefficients because of lack of experimental data. Instead, predictions of drying models which include the diffusion coefficient have been compared with the measured weight loss data. It was shown that, in general, the theories which include the cross-term coefficients perform better than those that do not. There is a need to know which of the existing theories are better for predicting transport in polymer solvent systems—this is especially important for practicing engineers. In other words, the theories need to be tested more rigorously than

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before.

Schabel et al. [15]-[16] reported depth profiling of solvent concentration with confocal Raman spectroscopy during drying of binary system. They showed the effect of drying temperature and air flow rate on the solvent concentration and good agreement between predictions of a drying model and measurements. The instrument has been used for a variety of researches in drying of thin film polymer coatings [16]-[18].

Comparing measurements of concentration of solvents inside a ternary coating during drying with those predicted by drying models in one rigorous test-this was also recognized by Muller et al.[19]. This paper presents such measurements with confocal laser Raman spectroscopy. In this work, a systematic calibration procedure is developed to measure the concentration in ternary polymeric coatings. Confocal Raman spectroscopy has been used to measure concentration of solvents and polymer during drying. A laser beam is focused through a pinhole arrangement at a location inside a sample. The scattered light is captured by a detector and its spectra are recorded in an attached computer. The spectrum is reported as intensity (in some arbitrary units) versus wave number (cm⁻¹). Ternary and binary polymer solvent systems should be chosen in such a way that the polymer and the solvents should be distinguished by having characteristic peak at some different wave numbers. The ratio of the intensity of the polymer to that of the solvent is calibrated against known ratio of concentration of the polymer to that of the solvent.

II. MATERIALS AND METHODS

In the present study, ternary systems consisting of one

polymer and two solvents have been considered. The system chosen for the study were: poly (styrene)tetrahydrofuran-*p*-xylene. Four binary systems; poly(styrene) – p-xylene, poly(styrene) – tetrahydrofuran, poly(methyl methacrylate) – tetrahydrofuran, and poly(methyl methacrylate) - ethylbenzene were chosen. Each binary system can be well characterized using confocal laser Raman spectroscopy due to separate characteristic peaks. Then two binary systems were mixed together to get a ternary system - poly(styrene) tetrahydrofuran -p-xylene, and poly(methyl methacrylate) tetrahydrofuran – ethylbenzene).

Proper care was taken while forming the ternary system. In each system, each species should have at least one distinct Raman peak. Figures 1 to 2 show the Raman spectra the systems. Each component can be differentiated because they have well separated characteristic peaks. For example, *p*-xylene shows a peak at a wave number of about 827 cm⁻¹, tetrahydrofuran at 911 cm⁻¹ and poly (styrene) at 1000 cm⁻¹. The properties and suppliers of materials used are listed in Table I.



Fig. 1. Raman spectra of poly (styrene) – tetrahydrofuran – p-xylene ternary system.

Name of Chemical	Supplier	Molecular Weight, $g mol^{-1}$	Density $g cm^{-3}$	Refractive Index
Poly (styrene)	Sigma Aldrich, Germany	230000	1.047	1.46
Poly (methyl methacrylate)	Sigma Aldrich, Germany	120000	1.188	1.497
Tetrahydrofuran	Qualigens Fine Chemicals, India	72.11	0.886	1.407
Ethylbenzene	Spectrochem Pvt. Ltd., India	106.17	0.886	1.495
<i>p</i> -Xylene	S.D.Fine-Chem Ltd., India	106.17	0.861	1.4950

TABLE I: SPECIFICATIONS OF MATERIALS USED



Fig. 2. Raman spectra of poly (methyl methacrylate)-tetrahydrofuran – ethylbenzene ternary system.

A. Procedure for Calibration

A number of solutions of known concentration for each binary pairs of the two systems were prepared and sealed in quartz vials of 11 mm diameter that could be fit into liquid accessory of Raman instrument.

Weight of each vial was measured every week to ensure that there is no leakage of solvent.

Dissolved polymer solution vials were kept in liquid sample accessory of the instrument.

Raman spectra were taken for a current intensity of 2mA and for a diameter of the area on which laser was focused of $400 \mu m$. Hole size can be varied from 50 microns to 400 microns; larger hole size is preferred to collect the information from the entire plan of observation. Time constant reduces the noise ratio. Therefore 5 or 10 are preferred because it reduced the noise and takes around 30 sec to 2 minutes. For liquid samples, 20X lens is usually

recommended due to weak intensity of signals. Laser is focused at several positions in the sample to ensure that the ratio of intensities of the polymer to that of the solvent remains same. Spectra were then recorded for analysis.

Calibration plots of ratios of intensities of the polymer to the solvent versus ratio of mass fraction of the polymer to the solvent were generated.

Fig. 3 and 4 show calibration plots for poly (styrene)-tetrahydrofuran and poly (styrene)–*p*-xylene.



Fig. 3. Calibration plot for poly (styrene) - tetrahydrofuran system.



Fig. 4. Calibration plot for poly (styrene) – *p*-xylene system.

III. RESULTS

Binary calibration plots were used to calculate concentration of solvents and polymer in ternary systems. Table II shows good agreement between the concentrations of solvents calculated from binary calibration plots and those of prepared solutions for poly (styrene) – tetrahydrofuran–*p*-xylene system. Confocal Raman spectroscopy is powerful technique to study the polymer solution coatings without destruction. Binary calibration curve can be used to measure concentration in ternary coatings with very great degree of confidence.

IV. CONCLUSIONS

Binary calibration curves using confocal laser Raman spectroscopy can be used to calculate concentrations in ternary polymer –solvent-solvent systems with very good degree of confidence.

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TABLE II: COMPARISON OF WT% OF POLYMER AND SOLVENTS CALCULATED FROM BINARY CALIBRATION PLOTS AND THOSE OF PREPARED TERNARY POLYMER –SOLVENT –SOLVENT SOLUTIONS.

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Sample Number	Wt% of prepared ternary solutions			Wt% calculated from binary calibration plots						
	Poly (styrene) wt%	Tetrahydrofuran, wt%	<i>p</i> -xylene wt%	Poly (styrene) Wt%	Tetrahydrofuran wt%	<i>p</i> -xylene wt%				
1	20.67	49.94	29.39	20.98	49.72	29.30				
2	12.46	65.40	22.13	11.86	64.94	23.20				
3	41.46	16.20	42.34	41.63	16.05	42.32				
4	35.97	55.43	8.60	35.45	56.89	7.66				
5	35.13	6.29	58.58	35.39	6.86	57.75				

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