Progress in Organic Coatings 95 (2016) 8–19

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Non-Fickian drying of binary polymeric coatings: Depth profiling study using confocal Raman spectroscopy

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ARTICLE INFO

Article history:
Received 31 October 2015
Received in revised form 27 January 2016
Accepted 8 February 2016
Available online 1 March 2016

Keywords:
Thin film
Non-Fickian drying
Sigmoidal profile
Polymeric films
Glassy film
Case-II diffusion

ABSTRACT

Concentration profiles in two binary polymeric coatings of poly (styrene)–*p*-xylene and poly (methyl methacrylate)–ethylbenzene system have been measured using confocal laser Raman spectroscopy. Measured profiles are very different from as shown earlier for rubbery coatings. Sigmoidal profiles are observed in these polymeric coatings because they went through the glass transition temperature during the course of drying. These coating have reasonably very high concentration of polymer in the top as compared to the concentration in the deep of the coating near the substrate. The results follow the case-II diffusion trend in glassy coatings.

1. Introduction

Several polymer coatings such as adhesives, magnetic media, audio and video tapes are made by applying a polymer solution, made by dissolving a polymer in a solvent(s), on a moving substrate and then drying it. There are numerous industrial applications of glassy polymers like primer, protective, and barrier coatings [1]. The most commonly used amorphous glassy polymers are poly(methyl methacrylate), poly(styrene), and poly(vinyl acetate). The aim of drying is to remove solvent(s) from a wet coating to desired levels without inducing any defects such as blisters, cracking and blush. Drying is usually accomplished in multi-zone dryers where in each zone hot air is blown over the coating and different temperature and residence time is maintained in each zone. They are manipulated to achieve two goals: one is to remove the solvent(s) quickly and the other is dry the coatings without creating defects such as blisters [2–4]. Drying is the last and quality controlling step in the production of polymer coatings; hence, coatings with defects lead to production losses. Due to poor choice of operating conditions, defects could be induced in the coatings: internal gradients could develop, blister could form, coatings could crack, phase separate etc.

During the drying process, the solvent evaporate from the top of the coating into the surrounding atmospheric—air or gases. These gases/air can be free from the solvent present within the coating. During initial period, rate of drying is externally controlled due to excess amount of solvent present on the surface of the coating. This is called externally controlled drying and it can be controlled by manipulating air flow rate, temperature of air and percentage saturation of the gases flowing over. Later on, drying mechanism shifts from externally controlled to internally controlled. The rate of diffusion controls the drying rate which is very strong function of temperature, weight fraction of solvent and polymers in case of rubbery solution [5,6] and stress relaxation in case of glassy films.

Solvent removal from the coatings mainly consists of two processes. First one is fast and characterized as exchange between coating and surrounding generally known as externally controlled or external mass transfer and controlled by physico-chemical properties of the system [7]. Second one is characterized within the system especially high polymer concentration region which may go to glass transition. The glass transition temperature of the coating depends on the solvent concentration in the polymer and is a strong function of solvent concentration [8]. As the solution inters into transition zone, the diffusion is coupled with stress relaxation

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http://dx.doi.org/10.1016/j.porgcoat.2016.02.004

of macromolecular chain and turns to be non-Fickian or case-II diffusion.

Case II diffusion is generally characterized by a sharp velocity front which moves with constant velocity into the polymer, just before of front there will be no solvent concentration gradient, and there will be some induction time for the movement of the front [9]. The study of these three processes in glassy polymers has been studied experimentally and theoretically specially for sorption of solvent into glassy polymers[10]. More et al. [11] have studied the stress modified case II diffusion in poly(methyl methacrylate)—methanol system. They found that the compressive stress of 0.2 MPa is sufficient enough to increase the induction time sufficiently and there were 4 fold reductions in penetration distance.

Large amount of diluent is required to dissolve the glassy polymer before converting stiff solid into the rubbery gel. There is substantial material misfit due to penetration of diluent into the glassy core[12]. The penetration front in rubbery polymer follows the time$^{1/2}$ law at constant temperature however in case of glassy transport it is sharp front which moves with a constant velocity.

Ediger et al. [13] have defined the glass transition temperature is the temperature when relaxation time is equal to 10^2 s. At glass transition the solution froze on the experimental observation time scale and specific volume decreases. The glass transition temperature reduces very significantly due the presence of solvent in the polymer [8]. This transition gives rise to non-linear behaviour for solvent diffusion in polymer–solvent systems close to or below the glass transition temperature. This non-linear behaviour is popularly known as anomalous of case-II diffusion. It is generally explained by the theory proposed by earlier researchers [14–16]. Thomas and Windle [17,18] theory is most commonly is used as basis to explain this non-linearity. Thomas and Windle [18] have proposed a theory for case-II diffusion. The diffusivity of penetrant and viscous flow rate of glassy polymer are the two main parameters for penetrant transport in glassy polymers. The rate controlling step is the activity gradient coupled with the swelling stress.

Case-II diffusion can be characterized as concentration of absorbed penetrant increases linearly with time, a sharp boundary between glassy core and swollen region, there is no concentration gradient across the swollen region, the boundary between glassy and swollen region is termed as penetration front which moves into the polymer at an independent constant penetration velocity [15,16] which means that diffusion of molecules through the swollen region up to the front is not the rate controlling process. The initial weight gain is directly proportional to the time rather than time to the power half as in case of Fickian transport [15]. The rate controlling process is at the front and can be termed as osmotic swelling stress [16,19].

Li and Lee [9] have studied the effect of solvent size on the diffusion in glassy spherical PMMA-methanol system. The PMMA beads studied here were spherical in shape. They found that induction time increases with solvent size. They have not found any significant effect on the penetration rate with the solvent size. They have also found the penetration front rate in the beginning is independent of the polymer geometry. This dependency, they have related to the stress effect since swelling will develop the compressive stress due to constraint of the underlying glassy core.

Gall et al. [20] have also studied the effect of solvent molecule size on case-II diffusion. They found that penetration front velocity and diffusion coefficient decrease exponentially with number of carbon atoms in poly(styrene). The decrement in the diffusion coefficient is nearly by a factor of 4 for each addition carbon atom to alkaline chain. They have also found exponential decrease in swelling rate with increasing number of carbon atom at the critical concentration for the case II diffusion. The calculated critical concentration for poly(styrene)—iodoalkanes remains constant at 0.12. The swelling rate is related to the osmotic pressure and decreases strongly with it. The calculated front velocity using the Thomas and Windle model was in good agreement with experimental observations.

Fick's law of diffusion, which states that the flux of a diffusing species at a location equals the product of diffusion coefficient and its concentration gradient there, describes mass transfer in solids, liquids and gases quite accurately. Transport of solvent in polymer solvent systems is no exception. It is complicated by the fact that the diffusion coefficient is a strong function of concentration and temperature as predicted by free volume theory. Free volume theory [5,6] predicts this function accurately for many polymer solvent systems. Fick's law has been used extensively to describe solvent transport during its sorption and desorption in polymer solvent systems. During sorption, Fick's law predicts that the solvent mass uptake varies as time to the exponent of one-half. During drying of coatings casted from a polymer solution, the solvent leaves the top of the coating but the polymer does not because it is practically non-volatile under conditions used for drying. There the diffusion coefficient falls by several orders of magnitude because of low solvent concentration. Consequently, a steep concentration gradient of the solvent develops so that the internal transport matches the external one described by a mass transfer coefficient.

Thomas and Windle [19] have developed a diffusion model for case-II diffusion. The case-II diffusion in generally termed as relaxation controlled transport and this relaxation is slow process in glassy polymers. In their work, they have just given the theoretical aspect involving various processes in case-II diffusion without any mathematical equations. This relaxation can be divided as rearrangement of molecules in the initial stage which is almost instantaneous and then slow process towards the final equilibrium. The diffusion coefficient in glassy polymer is in the range of 10^{-13}–10^{-16} $\mathrm{m^2\,s^{-1}}$ however in rubbery polymer it is of the order of 10^{-11} $\mathrm{m^2\,s^{-1}}$.

Hui et al. [21] developed a case-II diffusion model by considering the Thomas and Windle model with incorporation of viscosity effect of polymer matrix. The diffusivity and viscosity of the polymer is very sensitive to the concentration of penetrant due to plasticization effect. This results very large segmental relaxation time in glassy region and a very short relaxation time in rubbery region. They have studied the swelling kinetics of the polymer without diffusion. They have tested their model with Rutherford backscattering spectrometry experiments.

Duda et al. [22] have modified the Vrentas and Duda [5,6] free volume theory model to predict the diffusion in glassy polymers. The extra hole free volume gets trapped within the polymer when solution goes below the glass transition temperature. However, the molecular motion prevents this volume relaxation to reach the equilibrium state. Hence, the molecular motion cannot be eliminated in glassy region and free volume elements are redistributed continuously. This theory predicts that diffusivity is continous function of temperature through the glass transition temperature. However, actual diffusivity will be higher than the predicted by the expansion of this theory from the data above the glass transition temperature. As solvent concentration tends to zero, the solvent self-diffusion coefficient becomes equal to the binary mutual diffusion coefficient and given by

$$D = D_1 = D_{01} \exp\left(- \frac{\xi \hat{V}_2^*}{\left(\hat{V}_{FH2}^g / \gamma\right)} \right),$$

$$\frac{\hat{V}_{FH2}^g}{\gamma} = \frac{K_{12}}{\gamma} \left[K_{22} + \lambda \left(T - T_{g2} \right) \right],$$