Drying dynamics of polymers films by an interferometric technique

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ARTICLE INFO

ABSTRACT

We analyze a simple laser reflectivity measurement as a tool to monitor the drying kinetics of transparent polymer films. The reflectivity signal of a laser beam at normal incidence shows oscillations due to interference arising from multiple reflection of the laser light within the drying film. We develop a model to interpret the reflectivity curves in terms of time evolving refractive indices at the top and bottom of the film. We present results of the drying kinetics of transparent alkyd films on a glass substrate of high refractive index. Data shows a clear hallmark indicating the evolution of the crosslinking process. From the reflectivity curves, the time evolution of the refractive indices at the top and bottom is obtained. Assuming a linear-gradient of the refractive index along the depth of the film the average refractive index and consequently the film thickness as a function of time are estimated. Clear features in the time evolution of the refractive indices and thickness, correlate well with qualitative "dust", "touch" and "fingerprint" drying times. Additionally, we present some preliminary results for water based latex binders, where scattering of light is present, showing that this simple optical technique could be extended for studying latex film formation.

1. Introduction

Understanding the film formation processes is of crucial importance for the coatings industry, since it plays a central role in the visual appearance of paints, their mechanical properties, pigment distribution and drying times. In general terms, the film formation of paints will depend on the nature of the binder used. In general, the evaporation process is common to both water and solvent borne binders, however, the coalescence effect is representative for the first one [1] and commonly cross linking for the second one [2]. Film formation mechanisms on both polymer binders have been studied extensively [1–12] using experimental techniques such as speckle interferometry [3,5], ellipsometry [6–9], solid-state NMR [6,10–12] and photo-acoustic techniques [13].

The understanding of the mechanism of film formation, both in latex and solvent borne binders, will help to the design of new technologies such as the emulsification of alkyds that present a lower VOC and strong structural properties [1,6,10].

For this reason, new experimental and accessible techniques to follow in real time the film formation process of polymeric binder will be helpful for chemists to design the new generation of these polymers.

In this work, we present an optical technique to monitor, in real time, the film formation process of alkyd and latex emulsion binders. This technique emerges as a requirement from production plant where a quantitative, high accuracy, drying time test of alkyd paints is needed and accomplished in minimal time. The designed technique was developed mainly for alkyds and solvent borne binders, but we will show that the technique can also be used for highly concentrated latex emulsions.

We first discuss the film formation of alkyds and the optical technique applied to this system and later we will show that some of the results can also be extended to latex emulsion. In Section 2, the alkyd film formation is discussed as well as the elements for the interference optical technique. In Section 3 the experimental procedure is explained. In Section 4 the model needed for the interpretation of the experimental data is presented. In Section 5.1 the analysis of the experiment in terms of the model is discussed and in Section 5.1.1 the technique is applied to different particle size latex emulsions. Finally in Section 6 we present our conclusions.

2. Alkyds, film formation process and optical reflectance monitoring of a drying film

Alkyd resins are the product of a condensation reaction between acids and polyols, generally modified with fatty chains [1]. These polymers are dissolved in an organic solvent. They present optical absorption (yellowish), but they do not scatter light. Film formation

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takes place, first, by evaporation of the solvent, and second, when oxygen is able to permeate into the film and the crosslinking starts by an auto-oxidative process. The most commonly accepted mechanism for the crosslinking between alkyd polymer chains consists of oxygen uptake to form a peroxide. Organo-metallic salts (dryers) are used to increase the rate of peroxide formation. Peroxides react with unsaturated bonds in the alkyd chains creating the crosslinking sites between polymers [1,6].

From the physical point of view, film formation of an alkyd resin can be pictured as follows [1]. At the beginning of the process, the film is a homogeneous mixture of polymer and solvent. Here, the dominating process is free solvent evaporation, which depends on the vapor pressure of the solvent, temperature, humidity and air flux above the film. Solvent evaporation has two regimes. First, free evaporation takes place until polymer concentration prevents it and a solvent gradient is established throughout the polymer film. It is reported that this gradient is such that the polymer concentration in the interface film-air is larger than the polymer concentration in the interface polymer-substrate [11]. Second, evaporation slows down because the solvent has to diffuse through the polymer network. When this happens, the polymer in the upper surface is exposed to the air in the ambient and crosslinking process begins, from the upper surface to the bulk. When the top surface of the film has a crosslinked layer, the diffusion of the solvent in the film is seen as forced by diffusion. At this time, there is a diffusion competition inside the film: the solvent trying to leave the film and the oxygen, required in the crosslinking process, diffusing into the film. In the final stage, all solvent is gone and the film reticulates following oxygen diffusion [11].

Besides rheological properties, optical properties of a solvent based alkyd resin also change during its drying process. If we consider a transparent resin film immediately after its application, the refractive index of the application can be approximated by a volume weighted average of polymer and solvent refractive indices (Lorentz–Lorenz model), and the value changes according to the evaporation of the solvent. In this condition, the refractive index will be a function of the spatial distribution of the solvent in the film. It is assumed that at the beginning, just after film application, the solvent is homogenously distributed in the film. However, this condition changes during evaporation because solvent flux on the top of the film produces a gradient of solvent concentration along the film and, as a consequence, refractive index will depend on the depth inside the film: $n(z)$.

To follow these changes an optical interferometric technique was used to detect changes in the optical path of a beam traveling along the film [14]. These measurements are widely applied in the study of several systems that are sensitive to diverse physical variables, such as temperature [15], light intensity [16,17] or an applied electric field [18]. In the case of a transparent alkyd film, with an initial thickness d_0, exposed to a low intensity laser beam, the interference between the reflected beam at the air-film interface and the reflected beam at the substrate-film interface allow us to follow the drying process. Similar to [19], the measured intensity of interfered beams will be time dependent, with the phase of the interference defined by the optical path difference of the beam from these two interfaces. The interference phenomena will change with time because the film thickness decreases and the refractive index changes as a consequence of composition change due to solvent evaporation and crosslinking. Because refractive index and the sample thickness contribute to reflectance, it is necessary to decouple both parameters to analyze the measured intensity data correctly [19]. Simultaneous weight measurement helps to identify and correlate solvent evaporation kinetics with reflectance data.

On the other hand, in highly concentrated latex binders (>50 wt%), it is possible to observe the interference phenomena despite the scattering of light fr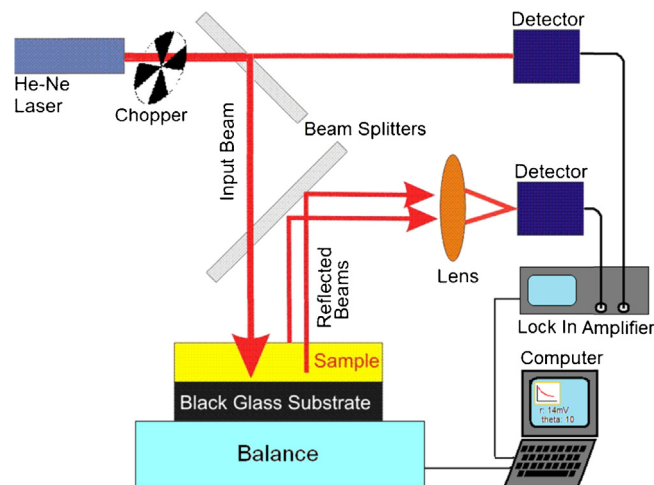om the latex particles. This is because the light scattering is diminished due to the dependent scattering effects that decrease the effective scattering cross section of the individual latex particles. This fact also allows us to use the interference phenomena for emulsion systems.

Fig. 1. Schematics of the interference technique for normal incidence.

3. Experimental methods

3.1. Samples

For transparent films, alkyd binders were used. The alkyd resin used in this work was manufactured in-house, medium oil, oxidizing type, made from soybean oil, phthalic anhydride and pentaerythritol at 26% of hydroxyl excess and an acid number less than 10. Characterization of this polymer by GPC shows Mw of about 200,000, with a PDI of 40. A conventional system of dryers based on cobalt, zirconium, and calcium was used. Its composition was a solution 50 wt% alkyd polymer with refractive index, n_p = 1.5150 in solvent naphtha with refractive index, n_s = 1.4400. A drying agent set based on soluble octoate salts of Ca, Zr and Co was added at different concentrations with respect to an optimal concentration and in the proportion 10:2:1 in weight respectively.

In the case of the acrylic polymer, this was in-house manufactured also by conventional emulsion polymerization using a premix of butyl acrylate/methyl methacrylate (56/44, w/w), potassium per sulfate as an initiator, and the system was stabilized with sodium lauryl sulphate to give a particle size of 120 nm. The theoretical Tg of this latex is around −5 °C. The emulsion has a concentration in water of 50% w/w.

Binders were applied by film applicators on a glass substrate with a refractive index of n_g = 1.5780 and nominal wet thickness varying from 50 to 200 μm. The glass substrate had its lower face sandblasted to prevent secondary reflections. The sample was placed on an analytical balance with 0.1 mg resolution.

3.2. Optical setup

A drawing of the experimental setup is presented in Fig. 1. To illuminate the sample we used a He–Ne laser beam. The beam was chopped at a frequency of 300 Hz. A beam splitter directed the reflected beams from the sample to a convergent lens that focused the reflected beams into a large area silicon photo detector, and the electrical signal was captured with a lock-in amplifier. The lock-in signal as well as the weight readings from the analytical balance was saved in a computer. Signal points are the average of 10