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Drying kinetics and segregation in a two-component anti-adherent coating studied by photoluminescence and Raman spectroscopies

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ABSTRACT

It is presented a study on the drying kinetics and segregation of a two-component solvent-based polymeric coating containing a silicon-based additive as anti-adherent. For this purpose, micro-Raman spectroscopy was employed with a two fold goal: (i) to study the kinetics of the drying process through the characterization of the fluorescence emission as a function of drying time and, (ii) to analyze the phase segregation between the polymeric resin and the anti-adherent, by using confocal Raman spectroscopy to determine the chemical composition as a function of depth in dry films. The coatings were applied on silicon wafers.

1. Introduction

Paint and coatings industry is very important because of its wide impact on a large number of goods produced by mankind, which include infrastructure, facilities, security, communications, military, transportation, and so on. In some cases a coating is used only for cosmetic purposes, although most of the times is applied to protect the surface, and the object itself, against adverse conditions or aggressive environments [1–3]. For this purpose, technological advances in the polymer and ceramic fields are applied to produce novel polymeric structures, hard ceramic nano-particles, novel coupling agents and hybrid composite materials, to mention a few [4–6].

The new generations of coatings are designed to fulfill very specific and demanding requirements, some of them relative to the surface itself and others to the bulk. An important example is the anti-graffiti (anti-adherent or easy cleaning) coating. For this specific type of coating, the best film morphology is one where the anti-adherent (AA) compound is located mainly on the external surface where it is required [7–11], while the bulk has to fulfill very different requirements such as: good adhesion to the substrate, appropriate mechanical properties, high abrasion resistance and in some cases, ease for pigmentation [12,13]. Therefore, the elaboration of good quality coatings does not only involve the use of the right constituents, but it is also required to place them in the appropriate position within the coating to perform each one their specific role, which in this particular case corresponds to place the AA on the external surface of the coating where is required. This can be done by controlling the segregation effects between the resin and the AA. The procedure employed in this work takes advantage of the fact that, right after the coating application, the solvent used provides enough molecular mobility to the constituents to attain resin–AA separation. Once the film is dry, the coating structure is defined and a useful coating can be obtained [14].

One of the most important and widely used polymers for coatings is polyurethane. Its importance is due to several properties: excellent adhesion on different substrates, highly abrasion and chemical resistance, ease for pigmentation, good mechanical properties, to mention a few [15–17]. This coating is usually a two-component material where the base consists of a high performance hydroxylated resin mixed with a poly-isocyanate to produce a

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polymer network (thermoset) with excellent properties. It is usual to add other compounds to provide this coating with some other properties that it does not possess intrinsically [18–20]. One possibility is to add, for example, a silicon-based polymer (a polysiloxane) to provide the coating with the anti-adherent property. The polysiloxane has to be chemically functionalized with hydroxyl groups to anchor it with the polyurethane network. However, the AA molecules are required only on the external (exposed) surface of the coating; to achieve this goal the resin and the AA should be partially incompatibles to segregate one phase (in this case the AA) to the surface. This phase separation can be controlled by choosing appropriately the components (resin and AA) and, to some extent, the drying conditions: the solvent (a low viscosity compound) provides enough molecular mobility to the polymers (high viscosity compounds) that allows the migration (diffusion) of the polysiloxane to the coating external surface [21]. The diffusion coefficient D depends inversely with the viscosity η_0 through the Stokes–Einstein relationship:

$$D = \frac{kT}{6\pi\eta_0 R} \tag{1}$$

where k is the Boltzman constant, T the absolute temperature and R the size of the particle (molecule) that is diffusing.

Therefore, by taking advantage of the segregation effects and the drying process it is possible to obtain an inhomogeneous film: AA-rich in at the external surface and resin-rich in the rest of the film. When the solvent is evaporating and the polymer crosslinking reaction is taking place the viscosity increases drastically, thus reducing significantly the diffusion of AA molecules towards the surface. As the drying process continues the film structure will eventually be frozen. Some other properties, like finishing (gloss), are also affected by the drying kinetics: a fast drying process may produce rough surfaces with low gloss, while high gloss can be obtained when the drying time is large enough to allow the leveling of the surface which in turn produces a flat glossy surface [22–26].

In this work an anti-graffiti coating was used to study the drying and segregation required to produce an inhomogeneous film where the AA molecules are mainly placed on the external surface. The drying process was studied through the use of the fluorescence signal in the Raman spectra as a function of the drying time. In this case the organic solvent produces the fluorescence that is reduced when the solvent evaporates. The coating morphology was characterized using a micro-Raman spectrometer in confocal mode. The segregation, produced by the incompatibility between the resin and the anti-adherent, was elucidated by determining the chemical composition as a function of depth [27–31]. Several coatings were prepared at different AA concentrations and applied to the surface of silicon wafers. This type of substrate was chosen because it produces a well known Raman band at 521 cm^{-1} with no photoluminescence.

2. Experimental

2.1. Sample preparation

The coating was prepared using a commercial hydroxylated resin, poly-isocyanate as the crosslinking agent, polysiloxane as the anti-adherent and an organic solvent. The resin was a commercial saturated, hydroxylated, polyol-polyester, alkyd resin (Alquireme 13/42160 Reichhold, Mex) with a reported molecular weight of 2000 Da, an OH equivalent weight of 243, an OH percentage of 6.99 and a number of OH groups of 64. The crosslinking agent was an aliphatic hexamethylene diisocyanate (HDI) (Desmodur N75 Bayer, Ger) with a NCO equivalent weight of 218, a NCO percentage of 19.29 and a number of NCO groups of 16. The stoichiometric ratio NCO:OH was 1.0. The anti-adherent was dihydroxy-polydimethyl siloxane (Tego 5000 Degussa, Ger.); the molecular weight, determined indirectly by dynamic light scattering, was between 1000 and 2000 Da with an OH equivalent weight of 322 and an OH percentage of 23. Several samples were prepared at different AA concentrations (0, 2, 4, 6 wt%) to determine the segregations effects.

Ten grams of alkyd resin was mixed, at room temperature during 10 min, with 5.5 g of toluene (solvent) and with the corresponding amount of polysiloxane to produce samples with: 0, 2, 4, 6 wt% of AA respect to resin. When the anti-adherent is added the solution becomes white due to the segregation effects. Separately, the 2.5 g of poly-isocyanate were mixed with 2.5 g of toluene. These two blends were mixed together during 5 min. At these conditions, the final mixture takes about 3 h to form a network. No catalyst was added to the final mixture to accelerate the curing process.

Once the final mixtures were prepared, these were immediately applied by brushing on flat pieces of silicon wafers previously cleaned to improve adhesion. The final films thicknesses were determined using a micrometer (Mitutoyo Series 227) with a resolution of 1×10^{-4} cm resulting (50 ± 5) μm. In all cases the Raman spectra were obtained using a Dilor Micro-Raman Spectrometer model Labram, operated at room temperature (25 °C), using a He–Ne laser ($\lambda = 632.8$ nm) as a light source and a 50× objective. The observed wavenumber region was from 500 to 3000 cm^{-1}. For the segregation experiments the Raman apparatus was working in the confocal mode to obtain in-depth resolution.

2.2. Drying analysis by Raman spectroscopy

The coating with 0% siloxane was used for the drying test. As soon as this coating was applied to the silicon surface, a series of Raman spectra were obtained as a function of the drying time: every minute during the first 5 min, every 5 min for the next 25 min, every 30 min for the next 2 h and every hour for the next 4 h giving a total measuring time of 6.5 h. Additionally, a Raman spectrum was obtained every day during the following 3 days. These last spectra are no further discussed here since no appreciable changes were observed.

2.3. Segregation analysis by confocal Raman spectroscopy

The films were dried for 5 days at ambient conditions to allow the curing reaction to take place completely. After this drying period, a series of Raman spectra were taken in the confocal mode, starting from the surface and then into the film in 2-μm steps, until the Si substrate surface was reached. In addition, a reference slab of polymethyl metacrylate (6 mm thick) was used to obtain the dependence of the bands intensity as a function of depth for the confocal mode measurements in a thick homogenous sample.

3. Results

3.1. Coating drying results

In Fig. 1(a) and (b) is possible to observe a typical series of Raman spectra taken immediately after the coating application: from 0 to 30 min (Fig. 1(a)) and from 30 to 210 min (Fig. 1(b)). These experiments were repeated five times in systems equally prepared, obtaining always the same characteristic behavior. From these data, the average and the standard deviation (SD) were calculated; these averages are reported in most of the plots with the corresponding errors bars provided by the SD. A plot of