Confocal Raman microscopy study of several factors known to influence the oxygen inhibition of acrylate photopolymerization under LED

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ABSTRACT

The free-radical photopolymerization (FRP) suffers from inhibition by atmospheric oxygen which reacts with excited species and radicals leading to inhibition period, longer irradiation time, incomplete conversion of the coating and heterogeneity in depth conversion with a possibly tacky surface. A study of the influence of several factors that affect oxygen inhibition on the depth conversion was performed by Confocal Raman Microscopy (CRM). Increasing the photoinitiator content is shown to increase the surface conversion and decrease the oxygen affected layer thickness. Interestingly, increasing the irradiance mostly affects the oxygen affected layer. The viscosity of the resin was also found to be important to reduce the depth heterogeneities in conversion. Finally, triphenylphosphine was used to highlight the decrease of the oxygen inhibition by using an oxygen scavenger. By selection of the reactive diluent, a tack-free sample surface was obtained under visible light in open-air atmosphere. This study clearly evidences the potential of CRM to assess oxygen inhibition in FRP bringing additional information – oxygen affected layer, conversion profile – which cannot be determined by commonly used experimental techniques such as real time Fourier transform infrared spectroscopy or even by attenuated total reflection spectroscopy.

1. Introduction

The free-radical photopolymerization of acrylate coatings is widely used in the automotive and wood industry, in graphic arts or electronics. Indeed, the radiation curing process is a green technology which offers many advantages compared to the conventional thermal process such as fast curing, easy industrial implementation, low energy consumption, reduction of volatile organic compounds (VOC)...[1–3]. However, upon exposure in air, the process is inhibited by oxygen which reacts with excited species and radicals [4]. Oxygen diffuses from the atmosphere into the film and leads to an inhibition period, longer irradiation time, incomplete conversion of the coating and heterogeneity in depth conversion with a possibly sticky surface [5–8]. The top first microns have minimal conversion while in lower depths the curing is almost complete. The knowledge of the depth conversion profile is of great interest to understand mechanical and surface properties of the material.

The influence of oxygen on the photopolymerization has already been thoroughly studied by Real-Time-Fourier Transform Infrared Spectroscopy (RT-FTIR) [9–12]. RT-FTIR is a technique, which allows a precise evaluation of inhibition time, rate of polymerization and conversion degree of a photocured sample. However it affords a mean value of the conversion from the whole film and does not characterize the oxygen affected layer (OAL) when used in transmission-mode. Attenuated total reflection spectroscopy (ATR-FTIR) makes possible the investigation of thin layers at interfaces (a few microns at the top and the bottom of a coating) and thus enables a rough characterization of the inhibition by oxygen. Several depth penetrations can be achieved by adjusting the measurement settings like the crystal nature or the beam incidence angle. However, the precise characterization of sticky layers is troublesome since the uncured material spreads out under the weight of the measurement set up. Nevertheless, by investigating samples of
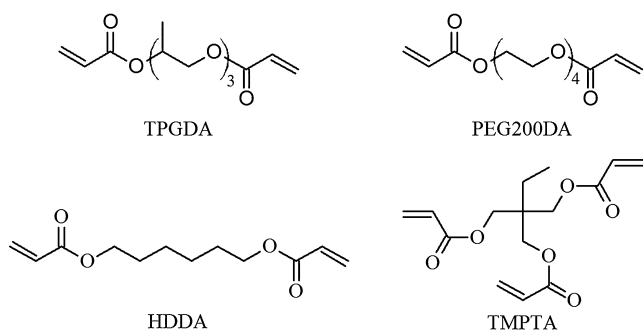
Chart 1. Reactive diluents used in this study.

different thicknesses and scanning from the sample substrate interface, a depth profile of the conversion can be obtained [13]. Taking into account the limitations of IR spectroscopy, confocal Raman microscopy (CRM) is an attractive technique for investigating variations of chemical composition of transparent materials as a function of the depth within the sample [5–8,14–16]. Indeed, CRM combines spatially resolved microscopy and Raman scattering spectroscopy. Thus, the technique enables the record of Raman spectra at different depths into a transparent sample by focusing the exciting laser light at different positions. However, when scanning in depth, optical issues such as refraction effects between air and sample should be suppressed to avoid inaccurate depth resolution [17–20].

In this paper, depth characterizations of oxygen affected layer have been studied by CRM according to an experimental procedure as described previously [6,7,21]. The influence of several physical and chemical factors known to participate in overcoming oxygen inhibition in acrylate coatings was studied. The effect of the photoinitiator (PI) concentration and light irradiance was first studied. Then, the formulation viscosity was considered. The influence of the formulation chemistry was also investigated by modifying the structure of the reactive diluent and incorporating an oxygen scavenger in the formulation to overcome oxygen inhibition. The trends that have been observed in the literature by RT-FTIR were then confirmed by CRM, a leading to a clear picture of the oxygen inhibition in free radical photopolymerization of coatings.

2. Experimental

2.1. Materials

The photoinitiator used to initiate the polymerization was the oxygen sensitive 2,4,6-trimethylbenzoyldiphenylphosphine oxide (TPO) provided by Lamberti. The sensitivity is mainly characterized by the scavenging of initiating radicals (rate constant of this reaction) [22]. The formulations were composed of the urethane acrylate difunctional resin Ebecryl 270 (Eb270, from Cytec) mixed with 50 wt% of reactive diluent tripropylene glycol diacrylate (TPGDA, from Sartomer). Eb 270 was heated up to 60–70 °C for 5 min to enable mixing. The mixture was chosen because of it is close to systems commonly employed in the coating industry. Indeed, the formulation is relatively fluid (≈600 mPa s at room temperature) and can easily be used in spreading devices for coatings in production lines. In addition, Eb270 is a urethane acrylate which exhibits good flexibility and good weathering properties in outdoor exposure [1].

The resin Eb 270 was mixed with several reactive diluent to study the influence of their backbone and functionality (Chart 1). The hexanediol diacrylate (HDDA, from Sartomer), the polyethylene glycol diacrylate 200 (PEG200DA, from Sartomer) and the trimethylolpropane triacrylate (TMPTA, from MacDermid Inc.) were used. The oxygen scavenger employed in this study is the

triphenylphosphine (TPP, from Aldrich). Dimethylsulfoxide used in Section 3.2 was received from Aldrich. All chemicals were used as received without any purification.

2.1.1. Irradiation source

The irradiation was provided by LED from Prizmatix, having a maximum irradiance peak at 390 nm (FWHM = 12 nm). The irradiance over the samples was varied from 20 to 100 mW cm^{-2}.

2.2. Techniques

2.2.1. Infrared spectroscopy

The photopolymerizations were followed by Real-Time FTIR [22] on a Vertex 70 FT-IR spectrophotometer from Bruker Optics. The machine was settled in a Rapid Scan mode and fitted with a MCT detector with a time resolution of ≈0.1 s and a spatial resolution of 4 cm^{-1} [23]. The 12 μm thick polypropylene film was used as substrate for the coatings which were applied using a spiral bar coater. Their thickness was controlled through the C=C stretching band intensity of the acrylate (νC=C) at 1636 cm^{-1}. The coating on the polypropylene film was then placed into a custom designed sample holder to fit both for IR and CRM measurements. The photopolymerization kinetic was obtained by monitoring the evolution with time of the νC=C band area (A_t) according to Eq. (1). Experimental error was found to be approximately 5% for conversion measurement.

$$\text{Conv}_{\text{IR}}\,(\%) = 100 \cdot \left(1 - \frac{A_t}{A_{t=0}}\right) \tag{1}$$

The viscosities were measured by cone/plate viscosimetry with a Brookfield Digital viscometer DV-II+ fitted with a cone CP-42.

2.2.2. Confocal Raman microscopy

Confocal Raman microscopy measurements were performed on an inVia Reflex Raman microscope from Renishaw which couples a Raman spectrophotometer with a Leica DM2500 microscope. The excitation wavelength was provided by an argon ionized laser from Spectra-Physics emitting 20 mW at 514.5 nm. This wavelength did not imply any post curing on sample during CRM measurements. 10 s of accumulation were needed at each step to obtain reasonable signal to noise ratio in buried layers. A circular polarization of the laser beam was achieved by placing a λ/4 waveplate on the optical path of the incident light to get rid of polarization effects. Two dielectric rejection filters were used to prevent the backscattered light from the laser to enter the spectrophotometer. A 600 l mm^{-1} grating optimized for the visible light and providing a spectral window of 1950 cm^{-1} was used to disperse the light on a CCD NIR deep depletion Peltier cooled detector camera. The confocal mode was defined by the spectrophotometer entrance slit opened to 20 μm in the back focal plane of the objective lens and a selection of 3 pixels perpendicular to the slit axis on the CCD camera. The spectral resolution given by the combination slit/CCD/grating was 8.7 cm^{-1}.

In this work, an immersion objective was chosen to perform depth profiling measurements with minimized refraction effects and have access to a trustworthy nominal depth [5–7,17–21]. The device was an N PLAN 100× immersion objective; its numerical aperture (NA) is 1.25 and the working distance is 0.12 mm which limits the sample thickness inferior to this distance. The objective was used in combination with a non-drying immersion oil type DF from Cargille with a refractive index of $n_D^{23} = 1.515$ close to the photopolymerized sample. The theoretical depth resolution provided by this optical configuration is 1.3 μm (≈4 λ NA^{-2}). The experimental depth resolution, determined from a depth profile on a silicon wafer beneath a 12 μm thick polypropylene film by measuring the FWHM of the Si intensity response at 520.6 cm^{-1}, was found to be