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Influence of UV-curing conditions on polymerization kinetics and gloss of urethane acrylate coatings

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ABSTRACT

The photochemically curable polymer films were prepared by addition of 2,2-dimethyl-2-hydroxyacetophenone (Darocure 1173) as a radical initiator to aliphatic urethane tetraacrylate Craynor 925. Kinetic study of the UV-curing of these films by medium pressured mercury lamp was performed by means of infrared spectroscopy. The results showed that the photoinitiator concentration, the light intensity, sample coating thickness, presence of air oxygen, as well as the UV light intensity were the most significant factors affecting the polymerization course of UV-cured films. The influence of the sample coating thickness on the kinetics and final gloss were also considerable.

1. Introduction

Light induced curing in polymer coating systems has been intensively studied due to environmental protection, lower energy consumption and rapid curing even at the room temperature. One of the most effective methods of fast generation of spatial crosslinked polymers is based on a multifunctional monomer or oligomer exposed by UV light in the presence of an initiator [1–3]. Therefore, UV-curing technology has been considered as an alternative to traditional solvent-borne coatings, due to its eco-compatible process and excellent properties, such as high hardness, gloss, scratch and chemical resistance caused by high crosslink density from acrylate groups [4].

Desired ingredients in radically cured formulations are urethane acrylate oligomers providing chemical, water resistance and heat resistance and adhesion. Polyurethane acrylate resins are often used in the liquid state as precursors to produce three-dimensional networks giving high-performance final materials [5]. As UV curable resins they prove excellent adhesion, flexibility, impact property, chemical and scratch resistance and weatherability [6,7] but often suffer from the high viscosities. They are commercially available with molecular weights ranging from 600 g/mol to 6000 g/mol and with functionalities ranging from 2 to 6. Depending on molecular weight and chemical structure, hard stiff to flexible coatings can be prepared in a broad range of properties [8,9]. The photoinitiated polymerization with photoinitiator Darocure 1173 (2-hydroxy-2-methyl-1-phenylpropane-1-one) was studied and the maximal conversion was obtained at 70 °C [10]. Several authors dealt with water based urethane acrylate coatings. The advantages offered by these environment-friendly systems are partially offset by the necessity to introduce a drying step before the UV-exposure, which will increase the overall processing time. The water sensitivity of these UV-cured polymers and their hydrophilic character may also restrict their use in a humid environment and in exterior applications [11,12].

The important aspect of a coated material in terms of quality is a gloss [13–16]. It is influenced by many factors such as rheological properties and formulation of the coating, film flattening, curing rate, layer thickness, refraction index, substrate characteristics (roughness, pore size distribution), film curing behaviour (wrinkling, cratering, and yellowing), etc. In principle, the gloss is a complex phenomenon resulting from the interaction between light and the surface of the coating. Kim et al. studied the influence of coating composition and curing conditions on the final surface properties (pencil hardness and coating gloss). They found out that some gloss decrease can be caused by oxygen inhibition of polymerization. If simultaneously the lower layers are cross-linked, then shrinkage could occur resulting in puckering or wrinkling in the top layer. Consequently, the wrinkled pattern on the surface leads to low gloss since the surface is no longer smooth [17]. The influence of the curing conditions (UV light intensity, coating thickness) and coating formulation (photoinitiator type

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and concentration) on the UV-curing of 1,6-hexandioldiacrylate and final gloss of the cured surface was significant. In these low viscose formulations the gloss was decreasing during the curing process. The gloss decrease of the coatings thicker than 15 μm was considerable, which might be caused by shrinking of the sample surface during its curing [15]. Ruiz and Machado [16] discussed the behaviour of UV-clear coats submitted to degradation processes on the basis of gloss changes. The authors found that the composition of the curing system and the curing conditions effectively affect the rate of polymerization, the maximum conversion reached and the surface properties, including gloss, hydrophobicity, surface energy. Gloss is important parameter in the printing technology, providing products with a better overall look, higher chroma (greater depth of colours) [15]. UV-cured urethane acrylate clear coats are suitable to function as protective coating for prints, their advantage is an improvement in the surface properties of the coated materials such as excellent scratch and abrasion resistance, the gloss and brilliancy of print [18].

The aim of this study was to investigate the curing process of a simple varnish model system composed of urethane acrylate oligomer Craynor 925 and photoinitiator (Darocure 1173) in relation to a coating composition, curing conditions (UV light intensity, air) and coating thickness. Subsequently, the influence of these factors on the gloss evolution during the curing process as well as the influence of coating on the colour stability was studied.

2. Material and methods

2.1. Materials

Low viscosity modified aliphatic urethane tetraacrylate Craynor 925 (Sartomer, France) and radical photoinitiator, 2-hydroxy-2-methyl-1-phenylpropane-1-one (Darocure 1173, Ciba, Switzerland) were used in order to prepare a simple varnish model. The UV–vis spectrum of this photoinitiator has absorption maxima at 245 nm ($\varepsilon = 7320\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$), 280 nm ($\varepsilon = 947\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$) and 325 nm ($\varepsilon = 85\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$).

2.2. Preparation of films

The samples were applied immediately after preparation. Various amounts of initiator (from 0.5 wt.% to 5 wt.%) were added to urethane acrylate, mechanically mixed and stored in opaque bottle. The viscosity of prepared coatings was 2700 mPa s at 25 °C, the density 1.1 g cm^{-3} and the surface energy about 35 mJ m^{-2}. Photocuring reactions were realized on aluminium and glass plates. The defined sample volume (according to layer thickness) was spread on the plate by spin coating apparatus (Tesla Rožnov, Czech Republic). Different layer thicknesses were achieved by different spin velocity (2000–4000 rpm) and different amount of applied sample, while the average layer thickness was determined by gravimetric measurements. Consequently, some layers were covered with polyethylene foil (PE, Chemosvit, Slovak Republic, thickness 30 μm, molecular weight 3×10^3 kg mol^{-1}, permeability for oxygen 450 cm^3 m^{-2} day^{-1}). The PE foil reduced the sample contact with atmospheric oxygen, thus, preventing the oxygen inhibition influence. PE foil had absorbed round 40% of radiation in the spectral absorption region of the photoinitiator that was considered at the UV exposition.

2.3. UV-curing of coatings

The samples on the aluminium plates were irradiated by a medium pressure mercury lamp 250 W (RVC, Czech Republic) built into an UV-cure device constructed in our laboratory. The lamp (without any filters) emits standard medium pressure mercury radiation with narrow bands in UV and vis regions. However, the absorption regions of the used photoinitiator with maxima at 245 nm, 280 nm and 325 nm, causes that only UV radiation is photochemically active.

In order to prevent the overheating during exposure the samples were placed on the water cooled Cu plate kept at 25 °C. The intensity of incident light was changed with the varying distance of the light source from the sample (5 cm = 23 mW cm^{-2}, 9 cm = 17 mW cm^{-2}, 12 cm = 12 mW cm^{-2}, 15 cm = 7 mW cm^{-2}). The incident light intensity was measured by UVX digital radiometer (UVP, USA) with the probes for UVA and UVB region (the given values are the sum of the two measured values). Full sample area (12 cm^2) was exposed with the same light intensity. The curing process was evaluated by IR spectroscopy (FTIR spectrophotometer EXCALIBUR SERIES Digilab FTS 3000 NX, USA) based on the transmittance measurements. The degree of conversion in the cured film was determined according to the amount of acrylate double bond (twisting vibration at 810 cm^{-1}, stretching vibration at 1610–1640 cm^{-1}) by a baseline method. The internal standard was a carbonyl peak at 1725 cm^{-1}, in order to eliminate the influence of scatter in layer thickness. The degree of conversion X and relative polymerization rate R_p were calculated from well-known equation (1) [19] which were modified according to the standard peak:

$$X = \left[1 - \frac{A_{t(\lambda)}}{A_{0(\lambda)}} \cdot \frac{A_{0(1725)}}{A_{t(1725)}}\right] \times 100 \tag{1}$$

where $A_{0(\lambda)}$ and $A_{t(\lambda)}$ is the absorbance of monomers C=C bonds measured at chosen wavelength (810, 1618 or 1635 cm^{-1}) before and after the exposure to UV light for the time t, respectively and $A_{0(1725)}$ and $A_{t(1725)}$ is the absorbance of carbonyl bonds at the same exposure time. Generally, our experiences show that the absorbance at 1725 cm^{-1} did not change with irradiation.

The relative polymerization rate R_p was calculated from equation $R_\mathrm{p} = (\Delta X/\Delta t)$, where X is the conversion degree of monomer's C=C bonds, at the exposure time t. The values of maximum conversion X_max and maximum polymerization rate $R_\mathrm{p,max}$ were obtained from the plots of X and R_p vs. time in initial stage of curing. The time interval of curing steps was changed during the curing process to obtain nearly the same and noticeable change of absorbance at 1635 cm^{-1}.

2.4. Sample gloss estimation

Gloss (G) is defined as the ability of a surface to reflect light to the specular angle. Gloss (in gloss units "GU") can be measured by gloss-metres that are able to compare the amount of light reflected from the sample surface and from the gloss standard at the same geometry set-up. Glossy black glass with defined refractive index is usually used as a calibration standard (GU = 100). The sample surface appears to be matt if its gloss is less than 6 GU, if the sample gloss is in the range of 6–30 GU then the surface is semi-matt, if the surface reaches the gloss of 30–70 GU then the surface appears to be semi-glossy, and if its gloss is over 70 GU of the standard gloss then the surface is high-glossy. The gloss of coated lustrously foils is often pretty higher than 100 GU because of light reflection from 2 or more boundaries.

Gloss changes were monitored in real time during the sample curing process using a monochromatic gloss-metre constructed in our laboratory. The gloss measurements were carried out using the glass substrate samples with a matt-white surface. The sample was placed and fixed on a horizontal support, illuminated by red diode-laser light (650 nm) at the angle of 45°, and the light reflected from the sample surface was detected by a silicon photodetector with the linear amplifier. Illuminated area was 10 mm × 5 mm at the centre of the sample and the laser diode was 25 cm apart. At the