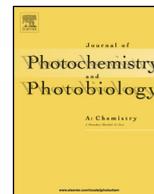




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Understanding double bond conversion using laser con-focus RAMAN spectroscopy

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ABSTRACT

The oxygen inhibition in free radical photo-polymerization is one of the big issues, because it causes the incomplete double bond conversion (DBC) of the (meth)acrylate, especially on the surface which decreases the mechanical properties of the coatings. Until now, it is still difficult to measure the effect of oxygen, because the concentration of oxygen inside the coatings depends on the penetration of oxygen and the distance from surface exposed the air. In this research, laser Con-focus RAMAN Spectroscopy was used to investigate the double bond conversion in different distance from the surface of coatings, which could provide detail information of effect of oxygen concentration on double bond conversion. At the same time, the effect of light dosage and concentration of photo-initiators on double bond conversion was investigated as well. This data could guide the end use of UV coatings to overcome the oxygen inhibition.

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1. Introduction

The two Major challenges in UV curing industry are: the oxygen inhibition at the top layer and the inner light screen effect at the bottom layer near the base material [1–3]. Most of the time, the end users concerned the double bond conversion (DBC) at the top near the air (to determine the physical properties such as surface tacky or scratch resistance) and the DBC of bottom layer close to the substrate (to determine adhesion or degree of cure) [4]. DBC of (Meth)acrylate free radical photo-polymerization have been characterized by using variety of methods, such as infrared (IR) [5,6], real-time Fourier transforms infrared (RT-FTIR) and photo-differential scanning calorimeter (photo DSC) [7,8], combination with a traditional FTIR and statistical calculation [9–12], but these approaches usually showed an average DBC throughout the film. The real-time Fourier transforms infrared attenuated total reflectance (FTIR-ATR) has been used to study the DBC at the last 2 μm near substrates in order to study inner light screen effect [13,14]. A Laser con-focus RAMAN method has been used to study the DBC in 1–2 μm depth from the air in order to study oxygen inhibition [15,16]. The Raman scattering technique is based upon change in the wavenumber (1636 cm⁻¹) of incident light interaction with the

rotation and vibrational energy levels in double bond (C=C) of (meth)acrylate molecules, this technique is perfectly suited for the detection of C=C chemical bonds and their changes before and after UV curing [17]. Laser Con-focus Raman method is a combination of microscopy and Raman Spectroscopy to provide spatial resolution and the depth resolution [18,19]. Thus, an optical slice of sample can be obtained without physical touching of the sample.

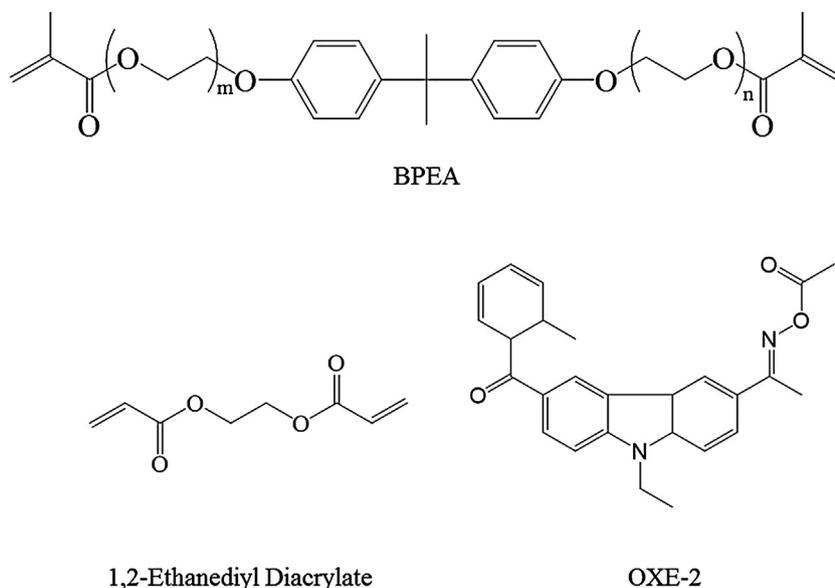
In this study, the Laser con-focus Raman spectroscopy (LCRM) was used to investigate the DBC at different depth with various UV curing condition to understand the effect of oxygen inhibition, light intensity, concentration of initiator and light dosage on DBC. The results indicated that LCRM is a very effective method to measure the DBC in different layers, proper light intensity, light dosage and concentration of initiator can improve the effect of anti-oxygen inhibition.

2. Experimental

2.1. Materials and instrumentations

Bisphenol A type epoxy diacrylate (BPEA) and 2-Propenoic acid, 1,2-ethanediyl diacrylate, which were used as oligomer and monomer, were donated by Sartomer Company, Inc. OXE-2 (9-ethyl-6-(1-(prop-1-en-2-yloxy)imino)ethyl)-4b,8a-dihydro-9H-carbazol-3-yl)(6-methylcyclohexa-2,4-dien-1-yl)methanone),

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Scheme 1. The chemical structure of the oligomer(BPEA), monomer(1,2-ethanediyyl diacrylate) and initiator(OXE-2).

which was used as initiator, was donated by Hitachi Chemical (Hitachi, Japan). The structure of the oligomer, monomer and initiator was shown in [Scheme 1](#).

UV spot source was EFOS Lite 50W miniature arc lamp, (with 5 mm crystal optical fiber, EFOS, Canada). Light intensity was recorded by the UV Light Radiometer (Photoelectric Instrument Factory, Beijing Normal University, Beijing, China). The UV absorption spectrum was recorded by a UV-vis spectrometer (UV3010, Hitachi Asia, Ltd.).

2.2. Laser con-focus Raman Microscopy

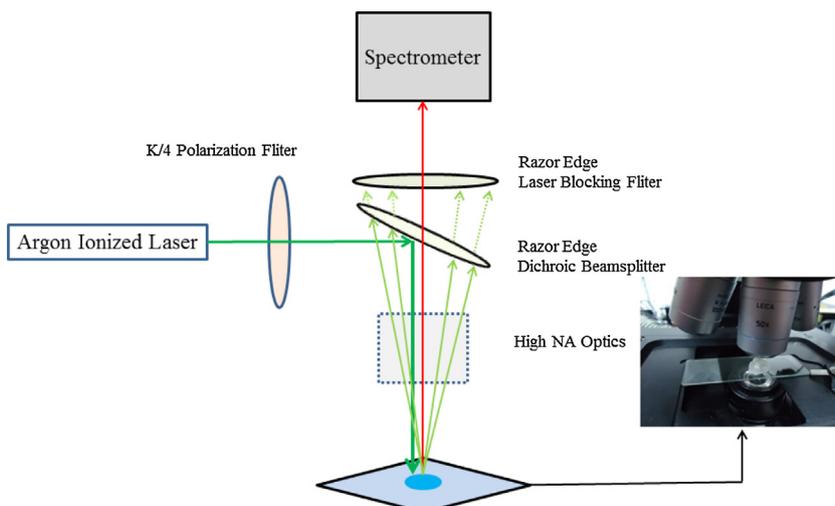
The laser con-focus Raman microscopy (LCRM) experiment was conducted by an inVia Reflex Raman microscope from Renishaw, which has been provided with a Raman spectrophotometer with a Leica TCS SP8 confocal platform. The excitation wavelength was provided by an argon ionized laser with 20 mW light intensity at 785 nm. Under this wavelength, initiator would not be initiated, post curing on sample could be inhibited. A 30 s averaging was necessary at each step to get credible experimental data in the

inner layers. A K/4 polarizing film was used to filter the unnecessary laser beam on the main optical path. Two dielectric rejection filters were used to prevent the back scattered light from the laser to enter the spectrophotometer. The principle of LCRM was shown in [Scheme 2](#).

In this work, the mixture of BPEA, 1,2-ethanediyyl diacrylate, and OXE-2 was injected into sample cells (diameter 0.5 cm, depth 0.5 cm). Then, these samples were cured with different light intensity and dosage.

The area of the C=C bond ($A_{C=C}$) at 1636 cm^{-1} was followed as function of depth. The area of the C–H bond (A_{C-H}) from the benzene ring of BPEA at 814 cm^{-1} , which was not changed during the curing process, was chosen to normalize the C=C bond to avoid data misinterpretation due to the loss in intensity with increasing depth, fluctuations of the laser intensity, or other external perturbations. The conversion as a function of depth was then calculated as follows:

$$\text{DBC}(\%) = \left(1 - \frac{A_z}{A_m}\right) \times 100\%$$



Scheme 2. The principle of LCRM (green arrow is the incident laser, red arrow is the signal of sample). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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