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Monitoring of photopolymerization kinetics and network formation by combined real-time near-infrared spectroscopy and ultrasonic reflectometry

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ABSTRACT

For *in situ* monitoring of fast changes of shear modulus and chemical conversion during UV radiation curing an ultrasonic (US) reflection method was combined with real-time near infrared (NIR) spectroscopy. The combined setup has been applied to study photopolymerization of different resins as acrylates, epoxy acrylates, acrylated polyurethanes and cationic epoxy resins in order to achieve a deeper understanding of the interdependence of reaction kinetics and changes of mechanical/rheological properties. The simultaneously recorded conversion–time and modulus–time curves allow differentiating between mass and diffusion controlled polymerization regime. Light curing and dark curing phases are indicated by two distinct regions in the conversion–time curves. By rescaling the curing time by chemical conversion modulus–conversion curves were constructed, which are described by combining a viscoelastic relaxation model with the conversion dependence of relaxation times. The NIR-US setup was used to study the influence of chemical composition and curing conditions on the polymer network formation.

1. Introduction

Due to short curing times, high surface quality (e.g. scratch and chemical resistance), lower energy consumption compared to thermal curing, low thermal load of the substrate, small required space for installations, minimum emission of volatile organic compounds (VOCs) and the resulting economical effects, UV curing is a very attractive technology for many applications like adhesives, printing inks or automotive coatings [1–5]. For tuning recipes to a given application, the knowledge of the relationship between chemical composition (recipe) and final material properties is often not sufficient and additional information on the time-evolution of chemical conversion and relevant physical properties is needed. Typical parameters of interest are the gelation time or the time needed to reach a sufficient degree of hardening.

Since curing involves the interplay of chemical reaction and physical mechanisms like diffusion of reactants or molecular relaxations, simultaneous measurements of conversion– and modulus–time curves are very useful for better understanding of the mechanisms of UV-initiated hardening. For thermosets, this interplay has been described by Johari et al. (see e.g. [6,7]) by the "negative feedback" between molecular diffusion, which is related to an increase in the characteristic relaxation time, and chemical reaction, which vitrifies a polymerizing liquid.

Since UV curing reactions typically proceed within seconds, experimental methods with very fast data acquisition rates are required. Widely used methods for monitoring of photopolymerization are photo-calorimetry, optical spectroscopy in the middle (MIR) or near infrared (NIR) range, Raman scattering, photo-rheology and ultrasonic (US) spectroscopy. Due to the limited heat transport in the calorimeter, photo-calorimetry [8] cannot be used for very fast reactions. The capability of MIR measurements for monitoring of fast photopolymerization reactions is well established (see [9,10] and references therein). NIR spectroscopy uses fast and robust chip spectrometers and thus is an interesting alternative for monitoring fast UV-curing [11–13], although the deconvolution of the spectra is somewhat more difficult. Ultra-fast changes in the mechanical properties can be detected by ultrasonic measurements [14,15], whereas photo-rheology is limited to slower reactions [16,17]. Osaka et al. [18] applied Raman spectroscopy and dielectric spectroscopy for monitoring of UV curing with light emitting diodes (LEDs).

In a small number of papers, simultaneous measurements of mechanical properties and chemical conversion are described. An attempt was made by Khan et al. [16] to study chemical reaction and rheological properties of thiol-ene polymers using real-time FTIR and *in situ* Fourier transform mechanical spectroscopy. In Refs. [13–15,19] we reported on the coupling of an ultrasonic (US) reflection method and NIR spectroscopy. Simultaneous rheological and NIR-measurements are described in [20,21].

The aim of this paper is to review the possibilities of ultrasonic reflection technique and its coupling with NIR spectroscopy for

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in situ monitoring of UV photopolymerization. In the first part, we summarize some experimental details concerning coupling the ultrasonic reflection method with UV a exposure unit and the extension of this setup by NIR spectroscopy. The latter allows simultaneous measurements of dynamic shear modulus and chemical conversion. In the following chapters representative examples for the application of both methods for monitoring UV curing of different acrylic and cationic epoxy systems are presented. Examples for resins with different amount of reactive diluent, photoinitiator concentration and different exposure times are given. The simultaneous measurement of conversion and shear modulus allows to determine the transition from reaction controlled to diffusion controlled polymerization kinetics and to distinguish between light and dark reaction. By rescaling the time-axis, modulus–conversion curves were constructed from modulus–time and conversion–time curves. The modulus–conversion curves are described by a model combining a viscoelastic relaxation function for the dynamic shear modulus and the conversion dependence of the characteristic relaxation time [13].

2. Experimental

2.1. Ultrasonic reflection method

The ultrasonic reflection method has been originally developed more than 50 years ago by Mason and coworkers [22] and applied to study the viscoelastic behavior of polymeric liquids in the ultrasonic frequency range. Based on the progress in high frequency digital and computer technique we adapted the measuring principle to these techniques [23], which allows now to monitor the shear modulus of coatings and adhesives during film formation or curing [23,24,14,15]. The measurement principle is depicted in Fig. 1. It is based on the reflection of ultrasonic shear waves (here 5 MHz) at the interface between sample and substrate (cell). Amorphous quartz or flint glass is used as the substrate. To each of its oblique ends an ultrasonic transducer is attached [22,23].

The complex reflection coefficient is defined by $r^* = r \cdot e^{-i \cdot \Delta\phi}$ with an absolute value of $r = |r^*|$ and a phase shift $\Delta\phi$, where r and $\Delta\phi$ are given by:

$$r = \frac{A}{A_0}, \quad \Delta\phi = \Delta t\omega. \tag{1}$$

A and A_0 are the amplitudes of the ultrasonic shear wave with and without sample, respectively. Δt is the time-of-flight difference between the corresponding shear waves and ω is the ultrasonic angular frequency. For an ultrasonic wave reflected off the substrate–air interface (substrate without sample), it can be assumed that $r = 1$ and $\Delta\phi = 0$. For isotropic and homogeneous materials r^* can be expressed in terms of the complex acoustic impedances of substrate Z_Q^* and sample Z_S^*:

$$r^* = \frac{Z_Q^* \cos\theta - Z_S^* \cos\theta'}{Z_Q^* \cos\theta + Z_S^* \cos\theta'}, \tag{2}$$

where θ (=79.03°) and θ' are the angles of the incident and the refracted waves to the normal of the interface. The acoustic impedance is defined as the ratio of the shear stress and the rate of change of displacement transverse to the direction of wave propagation. It is a complex value ($Z = R + iX$). R and X are the real and the imaginary parts of the complex dynamic shear impedance, respectively. Because of the negligible ultrasonic attenuation in quartz and flint glass, its acoustic impedance can be considered to be a real quantity. In contrast a viscoelastic sample has a complex acoustic impedance. Under these assumptions one can derive from Eq. (2):

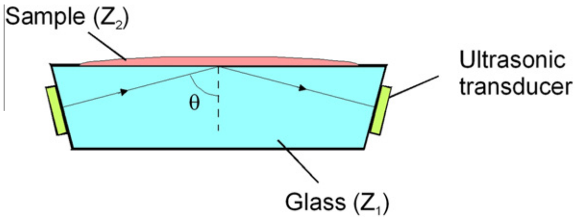

Fig. 1. Scheme of the ultrasound measurement cell.

$$Z_S^* = Z_Q \frac{\cos\theta}{\cos\theta'} \frac{1 - r^2 + i2r\sin\phi}{1 + r^2 + 2r\cos\phi}. \tag{3}$$

The complex dynamic shear impedance of the sample Z_S^* is related to the complex dynamic shear modulus G^* ($=G' + iG''$) as follows:

$$Z_s^{*2} = (R_S + iX_S)^2 = \rho(G' + iG''), \tag{4}$$

where ρ is the density of the sample, G' and G'' are the storage and the loss component of G^* which can be solved as:

$$G' = \frac{R_S^2 - X_S^2}{\rho}, \quad G'' = \frac{2R_S X_S}{\rho}. \tag{5}$$

The penetration depth of the shear waves into the sample is a function of frequency f, density ρ, velocity $\vartheta_t = \sqrt{\frac{G'}{\rho}}$ and attenuation $\alpha_t = \pi f G''/\rho\vartheta_t^3$ and can be given as $\chi_p = G'^{3/2}/\rho^{1/2}\pi f G''$ [23]. The penetration depth limits the minimum film thickness. Typical values for polymer coatings measured at frequencies of 5 MHz are 100–200 μm.

One of the main advantages of the ultrasonic reflection method is the free sample surface which allows monitoring changes of the dynamic shear modulus under exposure e.g. by humidity or radiation. For example, the method was used for monitoring latex film formation at different humidity and was implemented into a weathering chamber to monitor simulated weathering of coatings and adhesives (see [15] and references therein). In order to study radiation curing we combined the ultrasonic reflection method with a UV lamp [14,15]. A scheme of the setup is shown in Fig. 2. A UV lamp is placed above the substrate with the sample. An electrical spike pulse is transformed into an acoustic signal by an ultrasonic transducer (piezoelectric quartz). The signal propagates in the substrate, is reflected at the substrate/sample interface and then transformed to an electrical signal again by the ultrasonic transducer attached to the other end of the substrate. This signal is amplified and digitized. Pulse generator, amplifier and data acquisition card are included in a personal computer. The relevant part of the degitized echo train (first or higher reflection) is selected by a window technique and Fourier transformed in order to determine amplitude and phase shift. Details are described in Refs. [14,15,23–25].

Fig. 3 shows the experimental setup without pulse generator, data acquisition card and computer. In the lower picture (Fig. 3b) a microwave excited UV-lamp (UV Mac 6 curing System, Nordson UV) with the ultrasonic measuring cell beneath is shown. Between the UV-lamp and the cell, a fast computer-controlled shutter (Prontor magnetic E-100, Prontor) is arranged. This allows varying exposure time between 10 ms and many hours. The measuring cell (Fig. 3a, upper picture) is embedded in a temperature-controlled housing with a temperature range of 15–50 °C. The top of the housing is made of fused quartz, which is transparent to UV-light. Thus, the sample can be exposed to UV-light and inert gas (here: N_2). Up to 100 measuring points (echo trains) per second can be recorded, which allows monitoring very fast UV-initiated reactions.