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Hyphenation of Rheology and Raman Spectroscopy - Investigation of epoxy curing mechanism and polyethylene crystallization

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ABSTRACT

The coupling of a rheometer and a Raman spectrometer enables a correlation between molecular structure (Raman) and macros-copic mechanical (rheometer) properties in situ. A new experimental set-up to measure simultaneously rheological properties and Raman spectra and its applications on moni-toring epoxy curing reactions and polyethy-lene crystallization is presented.

INTRODUCTION

The relationship between molecular structure and macromolecular properties is important for the better understanding of changes in chemical functionality and micro-structure of polymers and its influence on processing steps.

In polymerization reactions the information about the reaction progress in terms of increasing viscosity with monomer conversion is important in designing continuous or batch industrial reactors and to optimize polymerization conditions[1].

Gelation and vitrification time are impor-tant structural transitions for the processing of thermosets. The curing reactions can be monitored rheologically to determine the vitrification/gelation time, nevertheless in-formation about reaction mechanism and conversion cannot be obtained[2].

In polymer processing, polymers with different microstructures (crystallinity) and molecular orientation, depending on the polymer structure and thermal/processing history, respond differently to macroscopic deformation[3].

The correlation between microscopic structures and macroscopic properties are traditionally performed by separate analysis. Coupling of a rheometer with a spectrometer (RheoSpectroscopy) overcomes the problems of reproducibility related to different sample geometries/conditions and time scales when comparing measurements from different experiments.

Molecular spectroscopy (FT-IR, NIR and Raman) provides direct information about functional groups and chemical/molecular changes of a material as well as information about crystallinity. Due to the availability of fiber optical probes (for NIR and Raman) the coupling with a rheometer can be easily performed. Therefore molecular spectros-copy is a well suited technique for the hyphe-nation with a rheometer in terms of Rheo-Spectroscopy.

Coupling of a rheometer with a FT-IR spectrometer is more complicated, since fiber optical probes are not readily available. The ATR technique is an alternative approach[4]. However, the penetration depth of the infrared light is in this case only about 1-3 µm. Therefore only the sample surface can be investigated and bulk remains in-accessible for investigation, since the sample gap is much higher for rheological measure-ments. NIR and Raman provide a higher penetration depth (about 1 mm) which is in the range of the sample gap of the rheometer.

FT-IR, NIR and Raman spectra are sensitive to double bonds which allows us to monitor polymerization, curing and crosslinking reactions. Raman spectroscopy is more sensitive to the carbon backbone thus providing information about e.g. crystallinity changes or molecular changes at the glass transition. Analysis of reactions in aqueous solution and measurements through glass makes NIR and Raman a more flexible tech-nique.

In the recent years considerable progress has been made in the field of Rheo-Spectroscopy.

Feustel[4] (Resultec, Germany) developed a set-up for FT-IR (middle infrared) spectroscopy, which is commercially available from Thermo Fisher Scientific. The Thermo Fisher Scientific Rheonaut® module uses the ATR principle (an ATR crystal is implemented in the lower parallel plate geometry) and enables the Thermo Scientific HAAKE™ MARS™ III rheometer to be coupled with a FT-IR spectrometer[5].

The coupling of NIR and rheology was performed by Benali[6,7], Botella[8], Steeman[9] and Pemberger[10]. Benali[6,7] used a strain-controlled shear rheometer (RDA II from Rheometric Scientific) with an upper and lower glass plate. Using a mirror construction, the NIR spectra were collected in transmission through the upper and lower glass plate. The curing reaction of a Polyurethane system based on Polytetramethylenether-glycol (PTMEG) and Methylendi(phenyl-isocyanate) (MDI) was monitored. Botella[8] used an UV-geometry for the ARES strain-controlled rheometer (Rheometric Scientific) with upper and lower glass plate to simul-taneously measure NIR spectra via optical fibers and initiation of the reaction via UV light. The monomer conversion through gelation and vitrification was studied for the UV initiated copolymerization of an acry-late/styrene monomer system. Steeman[9] developed a parallel plate geometry setup for the simultaneous measurement of NIR spectra and reaction initiation via UV-light on a RDA II (Rheometric Scientific). The network formation of a PPG-based acrylate formulation was studied. Pemberger[10] used a FT-NIR spectrometer (Büchi) and coupled it with a stress controlled rheometer AR 2000ex (TA Instruments) via an optical fiber probe, which was attached sideways between the two measurements plates. The curing degree of the reaction of a two-component silicon adhesive was monitored.

Different set-ups for the hyphenation of a rheometer and a Raman spectrometer were developed[11-17]. Rose[11] and Farquharson[12,13] directly implemented the fiber optic into the upper measurement plate of the rheometer. Temperature dependent curing reactions of an epoxy/amine system were investigated. The disadvantage of this approach is the removal and efficient cleaning of the measurement plate and integrated fiber optics, so that it can be reused. Another approach of Chevrel[14] uses a strain-controlled rheometer ARES G2 (TA Instruments) with a glass couette cylinder geometry coupled via a Raman fiber optic probe to follow the polymerization of acrylic acid in aqueous solution[14,15] and of styrene in bulk[16], respectively in emulsion[16]. Recently ThermoScientific presented a commercial RheoRaman set-up[17], between the Haake™ Mars™ III rheometer and the DXR™ Raman microscope. The laser is introduced via a mirror and an objective system into the lower parallel plate.

In this work, we developed a new experi-mental set-up to measure simultaneously rheological properties and Raman spectra. The instrumentation can be easily set-up and customized by the usage of fiber optical probes. Beneath the lower glass peltier plate the rheometer leaves sufficient space to place different accessories. Due to the disposable glass plate system and the good temperature control it is well suited for the investigation of reactions/processes for industrial applications.

INSTRUMENTATION

The setup, see Fig. 1, consists of a stress-controlled shear rheometer MCR 302 (from Anton Paar, Austria), an UHTS 300 Raman Spectrometer (WITec, Germany), a diode laser (WITec, Germany) with excitation wavelength of 532 nm and laser power of 75 W and a Raman probe coupled via a fiber optic. The Raman probe (RamanProbe^{TM}, InPhotonics, USA) has a spectral range from 200-3900 cm^{-1} at 532 nm.

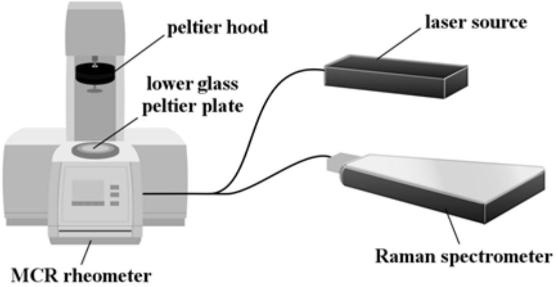

Figure 1. RheoSpectroscopy set-up consisting of a stress-controlled shear rheometer (MCR 302, Anton Paar, Austria), connected via an optical Raman fiber probe (InPhotonics, USA) to an UHTS 300 Raman spectrometer and a diode laser (WITec, Germany).

The temperature is controlled by the lower glass Peltier plate system in combination with a Peltier hood. Raman spectroscopy measurements are simultaneously performed through the lower glass plate of the rheometer using a fiber optical probe.

The Raman probe is attached below the glass plate of the Peltier plate setup and is adjusted so that the laser beam focus is within the sample, which is placed between the lower glass and upper aluminum disposable plate setup, see Fig. 2.

Rheological measurements were performed with 25 mm upper disposable aluminum parallel plates and lower glass plate (50 mm) with a gap of 1 mm and a deformation frequency of 1 Hz. During the epoxy curing experiment the normal force was kept at 0 N and the temperature constant at 25 °C. At the beginning of the measurement the deformation amplitude was set to 5% and was decreased to 0.1% when a torque higher than 90 mNm has been reached.

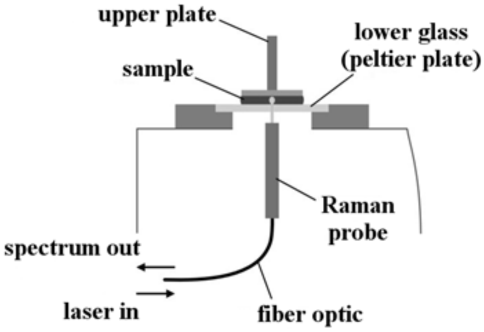

Figure 2. Raman probe attached below the glass plate of the Peltier plate setup. The Raman probe is adjusted so that the laser beam focuses within the sample. The sample is placed between the lower glass and upper aluminum disposable plate setup.

The LDPE crystallization experiment was performed at a deformation frequency of 1 Hz, the normal force was kept at 0 N with a sample gap of about 1 mm. During the first cooling step from the melt at 180 to 110 °C, at a cooling rate of 2 °C/min., a stepwise decrease of the strain from 10 to 0.05% was applied. For the second cooling step from 110 to 80 °C, at a cooling rate of 0.2 °C/min. a constant strain of 0.05% was maintained. Amplitude sweep measurements were performed before to determine the optimal strain during the experiment.

EPOXY-AMINE CURING REACTION

The reaction of an epoxy resin (Bisphenol A diglycidyl ether based epoxy resin: DGEBA, Epon^{TM} 828) with primary amine hardener (4,7,10-Trioxa-1,13-tridecanedi-amine: TTD, Baxxodur EC 130) was inves-tigated at 25 °C.

The primary, respectively the secondary amine (which is created by the primary amine reaction with the epoxy) react in a poly-addition reaction, see Fig. 3. The curing reaction of the epoxy-amine system was investigated with focus on the primary amine-epoxy reaction. To track the primary amine reaction, the decrease of the epoxy C-O stretching band at 1258 cm^{-1} and the amine N-H stretching band at 3310 cm^{-1} was analyzed.

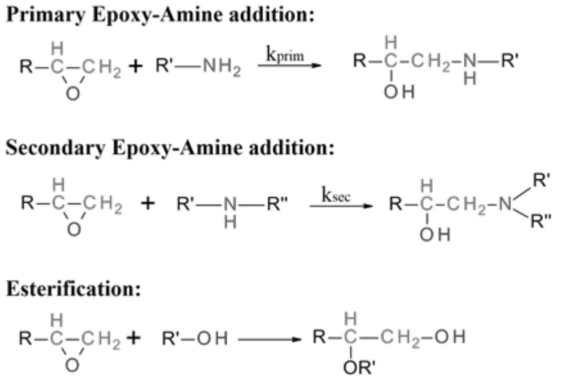

Figure 3. Mechanism of the nucleophilic addition of epoxy/amine systems. The three-dimensional network is created by the polyaddition of the secondary amine. The reaction of the primary amine is faster in comparison to the reaction of the secondary amine with epoxy.

As reference the invariant aromatic stret-ching band at 1613 cm^{-1} was used, see Fig. 4, leading to relative intensities.

The curing reaction of the epoxy-amine was monitored by the decrease of the relative intensity of the amine N-H stretching band and of the epoxy C-O stretching band with increasing G-moduli, see Fig. 5.
The decrease of the epoxy and amine band is according to the primary epoxy-amine reaction.

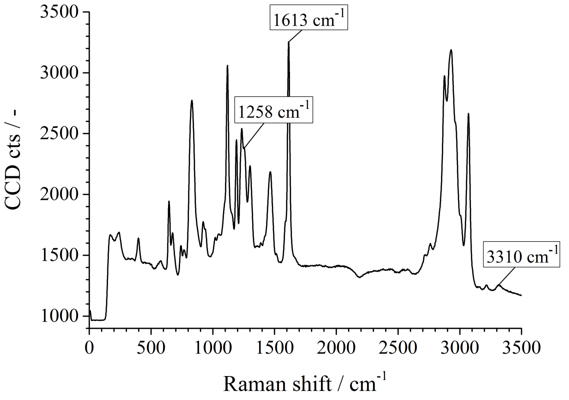

Figure 4. Raman spectrum of the epoxy-amine system, with epoxy C-O stretching band at 1258 cm^{-1}, amine N-H stretching band at 3310 cm^{-1} and the invariant aromatic stretching band at 1613 cm^{-1}, which is used as reference.

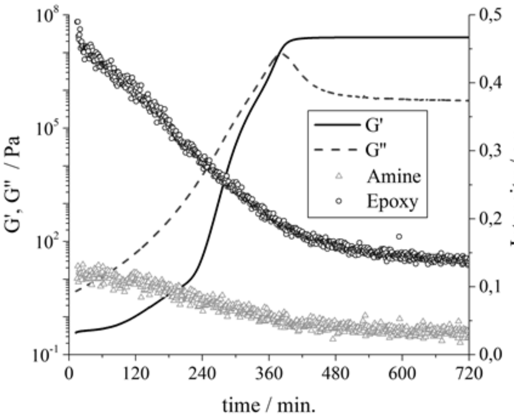

Figure 5. Comparison between peak intensities of amine and epoxy bands with trend of G-moduli. The decrease of the epoxy and amine band with increasing G-moduli is according to the primary epoxy-amine reaction.

Based on the N-H stretching band, a differen-tiation between primary and secondary amine was not possible.

LDPE CRYSTALLIZATION

The hyphenation of rheology and Raman spectroscopy offers a threefold advantage in studying semi-crystalline systems such as

LDPE. To precisely control the temperature during the crystallization of a LDPE melt, to monitor changes of the viscoelastic properties and to study the underlying molecular/morphological changes during the transition from the melt to the solid state.

For the investigation of the LDPE crystallization process via the Rheo-Spectroscopy setup, Lupolen 1800H from LyondellBasell was used. The Raman spectra of the LDPE melt acquired at 165 °C and in the solid state at 80 °C is shown in Fig. 6.

The spectral region between 1500 cm^{-1} to 1000 cm^{-1} displays bands which can be attributed to the C-C stretching vibrations (anti-symmetric: 1064 cm^{-1} and symmetric: 1130 cm^{-1}), CH_2 twisting (1297 cm^{-1} to 1330 cm^{-1}) and to bending vibrations (1419 cm^{-1} to 1470 cm^{-1}) of semi-crystalline polyethylene[18]. Bands at 1419 cm^{-1} and at 1083 cm^{-1} can be attributed to crystalline and amorphous properties.

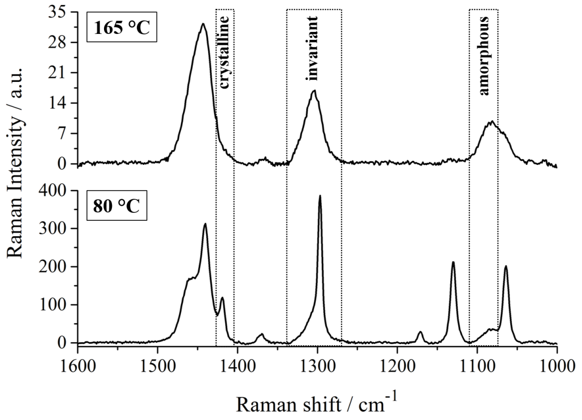

Figure 6. Raman spectra recorded from LDPE melt (at 165 °C) and solid state (at 80 °C).

Migler et al.[19] attribute bands at 1060 cm^{-1}, 1130 cm^{-1} and at 1297 cm^{-1} to a locally straight structure which is not part of an orthorhombic crystalline structure, called the non-crystalline consecutive trans (NCCT) conformation. Thus, Raman spectra allow an easy differentiation between the orthorhom-bic crystalline state and the amorphous state of LDPE.

For the Rheo-Raman experiment LDPE was heated up to 180 °C, Raman spectra confir-med that there were no crystalline parts detectable in the melt. The melt was cooled down in two steps. Firstly, the melt was cooled down with 2 °C/min down to 110 °C which is close to the melting point. From here, the cooling rate was reduced to 0.2 °C/min in order to allow the complete experimental setup to follow the temperature precisely.

Crystallization and the amount of amorphous components were monitored qualitatively by the Raman bands at 1420 cm^{-1} and 1080 cm^{-1}. In order to factor in the changes in the optical properties of LDPE during crystallization, that has a potential impact on the strength of the Raman scattering, the intensities at 1420 cm^{-1} and 1080 cm^{-1} were normalized to the area between 1270 cm^{-1} and 1350 cm^{-1} which is supposed to be invariant to changes during crystallization[20].

The Raman spectroscopic profiles for the crystalline and amorphous content in LDPE during crystallization and the corresponding G' and G'' moduli obtained from the rheological measurement are shown in Fig. 7. The transition from a molten state to a solid state can be observed to occur between 104 °C and 98 °C. Both results corroborate well with each other.

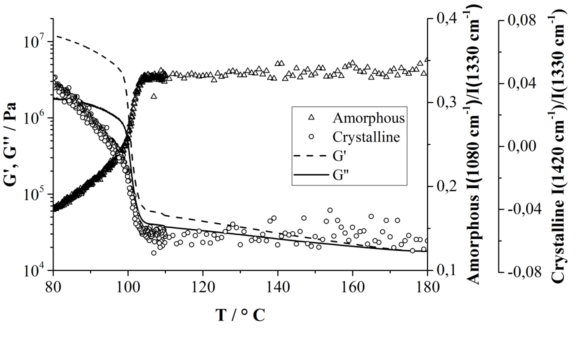

Figure 7: Correlation of rheological and NIR spectroscopic time series results of the crystallization of LDPE.

The transition from melt to solid state is a relatively fast process. As soon as crystallization starts, Raman spectra indicate that both NCCT domains and orthorhombic crystalline domains are formed quickly. Complementary to the formation of NCCT and orthorhombic crystalline domains, the amorphous content decreases. Thus it is likely, that the formation of crystalline domains is due to the consumption of the amorphous domains of LDPE.

The Raman and rheological data can be divided into three distinct zones by following the band intensities and G' and G'' respec-tively. In the temperature range from approx. 180 °C to 105 °C, Raman intensity profiles indicate a complete amorphous system. The amorphous state undergoes a dramatic transi-tion between a temperature range from 105 °C to 98 °C. Here the slope of the Raman intensity profile increases steeply. This tem-perature zone shows presence of both amor-phous and crystalline phases to be present. The rheological data in the same temperature range (105 °C - 98 °C) indicates a transition from a dominant molten LDPE state at 105 °C to a more solid like state at 98 °C. Below 98 °C, the rate of change occurring to Raman intensities or to G' and G'' reduces dramatically although some minor changes are still visible in both the profiles.

CONCLUSION

RheoSpectroscopy is a powerful technique which allows the investigation of structure-property relationships for various materials and applications. The current instrumental setup offers an advantage over existing methods by allowing disposable parallel plate geometries to be used thus enabling a faster turn-around in sample measurement. The presented setup is a unique system composed of routinely available commercial instruments. The instruments can be operated separately to carry out any specific measurement but also be combined at ease. Therefore this hyphenation approach offers advantages over a dedicated system.

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