In-Situ Curing Analysis of Photoreplicated Objective Lenses using Raman and IR Spectroscopy

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ABSTRACT: Optical pick-up lenses are used in optical storage devices such as CD, DVD, and Blu-Ray Disc. The production of such lenses is based on UV-induced polymerization of a mixture of a dimethacrylate monomer and an initiator on a spherical glass substrate. The shape of the polymer layer is defined with an aspherical transparent mold. This means that the coating is completely surrounded by glassy materials during processing. Raman spectroscopy is applied in situ to monitor the polymerization reaction under conditions that closely resemble the actual production process. As a result improvements can be made to the reaction conditions if necessary. Data are compared to results obtained with IR spectroscopy in an off-line approach. The value of the *in situ* characterization using Raman spectroscopy is illustrated by the observation that contrary to expectation, the local rate of polymerization is not influenced by shrinkage effects caused by local variations in volume relaxation in the wedge-shaped sample volume. Instead, even quartz glass mold plates with a thickness of 30 times that of liquid monomer were deformed to accommodate for thermodynamically required volume shrinkage. The assumption of isochoric polymerization in a confined volume turned out to be incorrect. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1287–1295, 2006

Key words: photopolymerization; Raman spectroscopy; radical polymerization; polymerization shrinkage; conversion

INTRODUCTION

The new standard for optical storage is Blu-Ray Disc (BD). It has a storage capacity of 25 GB on the surface of standard CD size. This is equivalent to 4 h of video of high definition quality. DVD has only 4.7 GB. To read and write this much information, the size of the pits and the distances between them have to be much smaller than those on a conventional CD or DVD. To realize this in practice, the so-called optical pick-up system, which includes the focusing lens, needs to focus the laser light to the smallest possible spot, limited by diffraction only (Fig. 1).

According to the theory of diffraction, the minimal spot size is $\lambda/\text{NA} = \lambda f/\wp$ where, NA is the numerical aperture, f the focal length, and $\wp$ the diameter of the lens. Therefore, a change from near IR (CD, $\lambda = 780$ nm) to red (DVD, $\lambda = 650$ nm) to blue (BD, $\lambda = 405$ nm) laser light allows an increasingly better focusing to a smaller spot size. Maximizing NA can further increase the storage capacity. To minimize aberrations, aspherical lenses are used.

Aspherical lenses with high NA can be manufactured from glass, but these are very costly to produce.[1] Alternatively, such lenses can be made through injection molding of optical-grade plastics.[2] Much more accurate and mechanically stable lenses can be made from spherical lenses of conventional optical glass, by correcting them with a thin aspheric coating of a transparent polymer.[3,4] These hybrid lenses are discussed in the current article. Herein, the spherical glass substrate will be referred to as the glass body. The coating is obtained by filling the gap between the substrate and an aspherical mold, with a liquid monomer to which a small amount of a photoinitiator has been added (referred to as replication coating). The mixture is then turned into a glassy polymer by exposure to UV light. Subsequently, the lens can be released from the mold. Figure 2 shows both the lens replication process and the finally obtained objective lens. Because a large NA is required, the asphericity of the lens is high. This gives rise to large aspect ratios with respect to the layer thickness of the coating. In the example shown in Figure 2, the layer thickness of the aspherical coating varies strongly with the radial position, between 0.7 and 22 μm. The thinnest section appears as a white ring in the SEM micrograph (here the electrons can reach the glass body). This replica
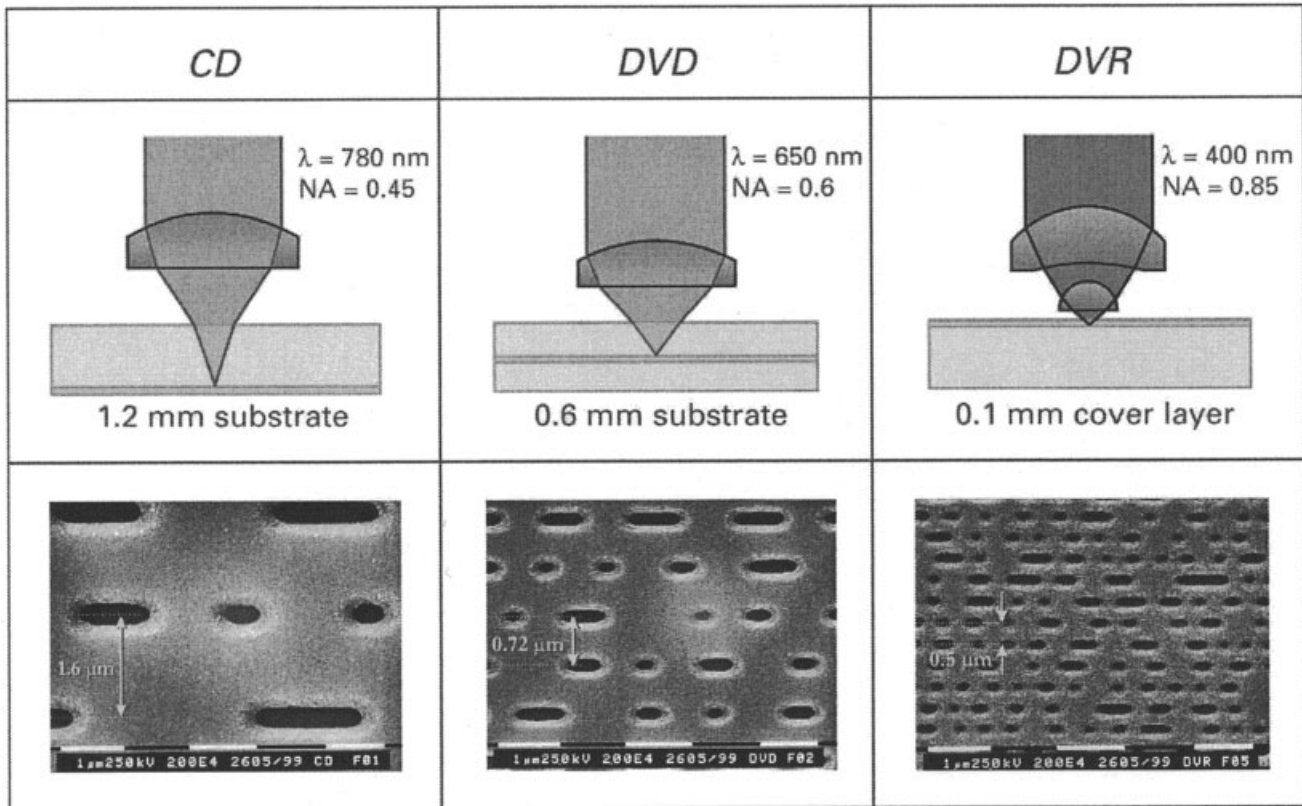
Figure 1 Optical systems as used in current optical storage systems.

layer is the positive copy of the mold cavity used during the replication.

Light-initiated polymerization relies on the formation of active species, such as radicals or cations from a photoinitiator during exposure with light, for which the initiator was designed. The concentration of the initiator has to be well chosen, to have a desirably high reaction rate combined with sufficient transparency throughout the layer to avoid excessive shielding. In the case of lenses for optical recording, a large variation in layer thickness (0.7–22 μm) is desired to combine a sufficient asphericity with easy processing. This variation could give rise to local differences in the reaction rate and final conversion of the reactive groups of the monomer.

In our case, the replication process consists of light-induced (free radical-initiated) chain crosslinking polymerization of a dimethacrylate. This yields a highly
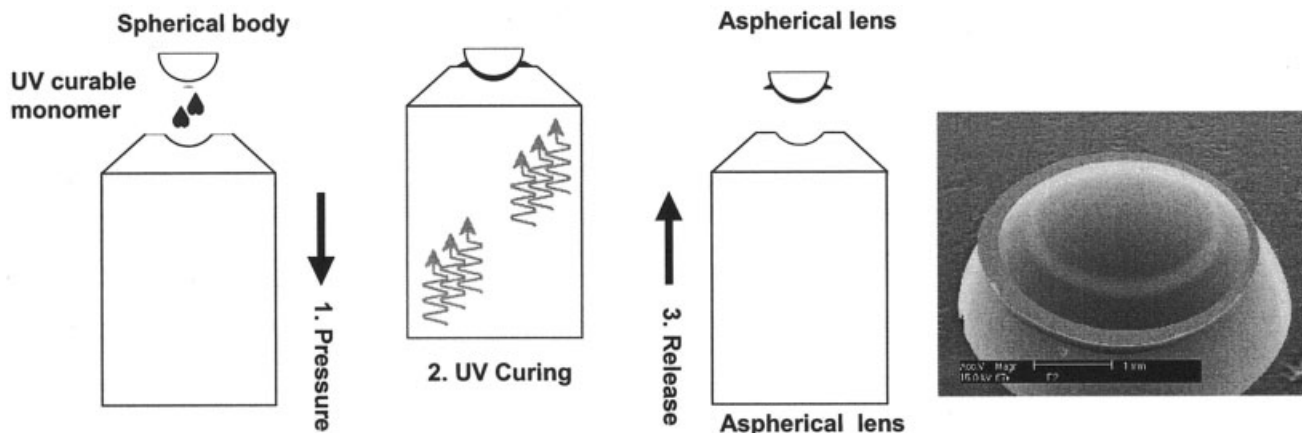

Figure 2 Production process of aspheric lenses, using photopolymerization of a coating on a spherical glass body. The final lens is shown in the SEM picture on the right.

transparent glassy product suitable for optical applications in the blue part of the visible spectrum.[5]

Polymethacrylates are known for their long kinetic chain lengths. One radical may well initiate the coupling of thousands of monomers. For example, in the photopolymerization of 1,6-hexanediol diacrylate (HDDA) carried out in bulk, kinetic chain lengths of $>10^5$ monomer units have been reported, whereas for the corresponding dimethacrylate, they tend to exceed 10^3.[6] As opposed to acrylate polymerization, chain transfer in methacrylate polymerization is almost negligible.[7]

The formation of long chains with each member having a pendent reactive group leads to early gelation and thereby to the early build-up of elasticity. By the same token, the replenishment of monomer is already suppressed at low conversion.

An ethoxylated bisphenol A dimethacrylate, like hydroxyethyl bisphenol A dimethacrylate (HEBDM), gels below 1–2% conversion and vitrifies at about 15%.[5] Almost the entire reaction takes place in the gelled state, which means that polymerization shrinkage provides a driving force for deformation of the (visco-) elastic network. Since major deformation is prevented by the geometrical constraints of the mold and the substrate, internal stress develops. This stress not only opposes shrinkage, but the formation of a continuously densifying gel also introduces a strongly increasing volume relaxation time of the polymerizing system. Relaxation of the shape will therefore mainly occur after release from the mold. Before release, the relaxation is suppressed by adhesion of the sample to the mold and the substrate. Incomplete relaxation will lead to the generation of a temporal excess of free volume, prolongation of a state of high local mobility, and a correspondingly high conversion before vitrification slows down the reaction.[4] At still higher conversion, large stresses can develop through polymerization shrinkage. Eventually rupture or void formation may occur. Proper choice of conditions, i.e., the use of a high light intensity helps in preventing such defects.

After release from the mold, partial relaxation immediately takes place. A thermal after-treatment completes the relaxation process, resulting in the desired lens shape, provided that the proper shape correction was applied to the mold.

In methacrylate polymerization, two causes of shrinkage are present. First, the number of covalent bonds increases with every addition of a monomer molecule. Since these are shorter than the Van der Waals distance between monomers, the volume decreases. Secondly, a large decrease in entropy during the polymerization reaction favors the disappearance of vacancies from the polymerizing liquid.[8,9] This results in more-dense packing.[8] At full conversion and relaxation, a shrinkage of 10% is estimated for a coating containing 96% HEBDM and 4% initiator, our model system.[5]

In addition to the overall shrinkage, the rheology of the polymerizing system is also of great importance: the earlier the system stiffens, the more difficult it will be to compensate for shrinkage by replenishment of liquid monomer from the unexposed or retarded outer rim to the central region of maximum thickness. Retardation or even suppression of polymerization at the outer rim is caused by oxygen inhibition. The thinner the gap of minimum thickness, the more difficult replenishment of monomer will be. The question is how the actual conversion takes place as a function of position with the large variations in thickness of the coating and the large variations in oxygen consumption and replenishment, in our model system. With that information, one might be able to predict shape aberrations due to differences in reaction rate and/or the final degree of polymerization as a function of radial position on the lens. Adjusting the shape of the mold until the proper shrinkage correction is obtained will then no longer be a matter of trial and error. Conversion can be examined during and after polymerization in model systems, but with the complicated structures involved in lens manufacturing, such systems have to resemble the production circumstances as much as possible. The best option is to study the conversion under real production conditions, using a remote analysis technique.

IR spectroscopy is very well suited to monitor light-induced curing reactions, using an attenuated total reflection (ATR) crystal. In the production process, the glass hemisphere is supplied with a coupling agent to prevent the release of the coating layer from the glass during and after polymerization. During polymerization, large shrinkage stresses occur, which tend to peel off the coating. The crystal used in the ATR accessory of the IR spectrometer is composed of diamond and can therefore not be modified. Therefore, to perfectly simulate the conditions used in the lens replication process, IR spectroscopy is not well suited. Moreover, the stress conditions around the probe will differ from those in the material between lens body and mold.

Raman spectroscopy is also able to monitor chemical changes during light-induced reactions. Using laser light, vibrational information can be obtained from the wavenumber shifts in the inelastically scattered light. With Raman spectroscopy, vibrational analysis is possible in a transparent but confined environment using visible light. This allows monitoring of the conversion rate of the monomer during actual lens replication. However, Raman scattering is not very intense and high laser power is required to achieve high-quality Raman spectra at a high speed, which is necessary to be able to monitor the relatively fast photochemical reaction.
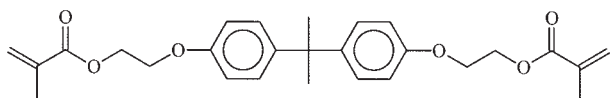
Scheme 1 Structure of HEBDM.

In our study, we monitored the conversion of a free radical-initiated polymerization by using fast Raman spectroscopy, using experimental conditions that are identical to the actual production process, with only 7 s of exposure time using 40 mW/cm^2 UV irradiation. In addition, IR measurements have been used to determine the conversion in the first few seconds of the reaction, in which the rate is so high that it is impossible to achieve Raman spectra of sufficient quality.

Raman results are compared with results obtained from IR analysis in off-line experiments.

EXPERIMENTAL

Materials

Ethoxylated bisphenol A dimethacrylate (Scheme 1) abbreviated here as HEBDM was supplied by Akzo Nobel, Arnhem, The Netherlands, under the trade name Diacryl 101.

The photoinitiator used is dimethoxyphenylacetophenone (Irgacure 651) from Ciba-Geigy, Basel, Switzerland. HEBDM was mixed with 4 wt % Irgacure 651 photoinitiator before use.

UV-induced polymerization

Exposure was carried out using an EFOS Acticure spot-curing apparatus consisting of a high-pressure mercury light source equipped with a fiber–optic waveguide and a filter transmitting wavelengths ranging from 320 to 390 nm. Several exposure doses were used for the individual monomers in both Raman and IR experiments, as indicated under Results. Standard curing involves irradiation with an intensity of 40 mW/cm^2 for 7 s. A long-pass filter ($\lambda > 500$ nm) is placed in the Raman microscope to avoid interference from the curing radiation during the in-line characterization.

IR measurements

The rate of the reactions was measured using a Bruker Equinox 55 instrument with a fast-scanning module. For the IR measurements, a layer of monomer of about 10 μm thickness was applied on an ATR crystal through which the IR light enters. A similar method has been applied by Scherzer.[10] The UV fiber was placed at a distance from the crystal (the crystal is on top of the ATR unit) sufficient to obtain the desired light intensity. Next, IR spectra were taken at a frequency of 4 Hz to allow monitoring of the reaction rate. Principal component analysis (PCA) was used to demonstrate the conversion from monomer to polymer network. Figure 3 shows part of the spectra obtained for HEBDM. The main vibration that changes upon polymerization is the C=C (next to the ester) at 1640 cm^{-1}.

Raman measurements

Inelastic scatter from an object in water or behind glass can be analyzed without removing it from its environment. This means for the UV curing reaction in
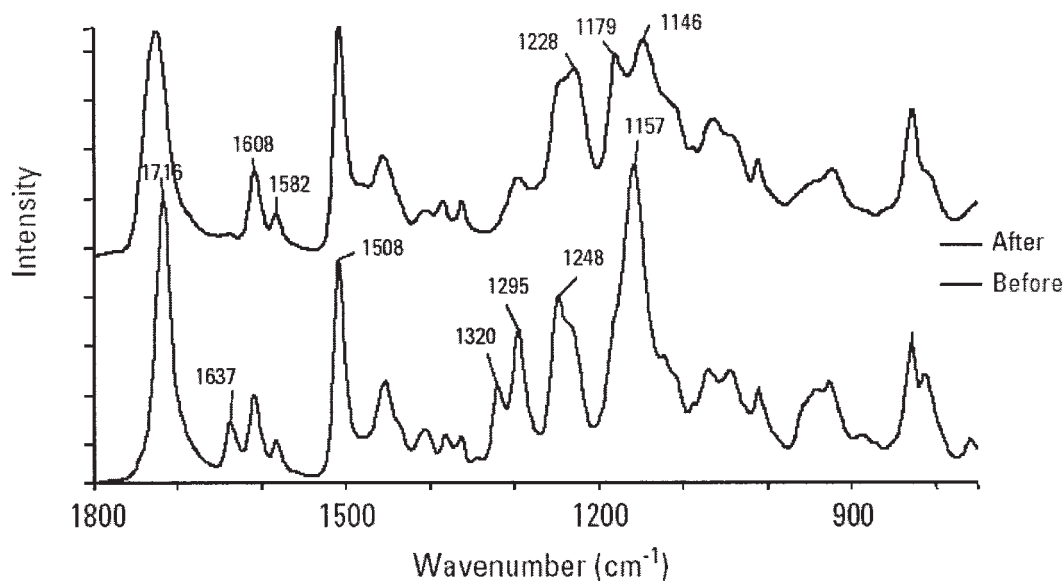

Figure 3 IR spectra before (lower) and after (upper) "full" curing of the lens coating.
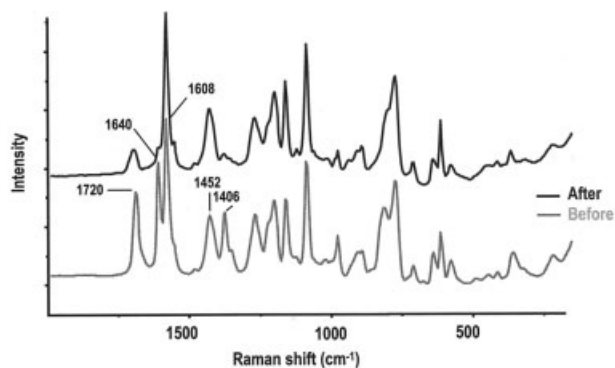
Figure 4 Raman spectra before (upper) and after (lower) "full" curing of the lens coating.

the lens replication that Raman analysis can be performed inside an actual production setup. All that is needed is an optical window through which the reaction of the coating can be monitored. As the lens is transparent, a setup as described in Figure 2 can be used to follow the UV curing reaction. This setup is identical to that used in production except for the weight, which is now mounted outside the optical region to allow access for the laser beam.

The Raman spectra of the coating contain a large amount of information about the functional groups in the material that change during polymerization. Figure 4 shows a part of the spectra, taken before and after UV-curing of HEBDM, using the same type of sample as for the IR measurements. The clearest differences between the spectra before and after UV-curing are seen in the Raman bands at 1406, 1640, and 1722 cm^{-1}. These are linked to changes in the C=C and C=O bonds that occur as a result of conversion of methacrylate groups during the polymerization.

For off-line measurements, a LabRam confocal microscope (Jobin Yvon, France) was used without significant changes to the original system. Excitation was performed at a wavelength of 633 nm (10 mW), using a 50× long-working distance objective (NA = 0.5; Olympus, Germany). Depth profiles were measured using the same setup, with a confocal aperture of 0.4 mm and the same objective. As monomer conversion was never at 100%, no oil- or water-immersion objective could be used to improve the depth resolution, as the material of interest is not sufficiently resistant to water or oil.

On-line measurements need to be performed at a much higher speed than available with the standard setup. A high-power external Kr-laser was used (647 nm, 400 mW) to allow quantitative time-resolved analysis of the curing reaction through the mold, collecting Raman spectra at 2 Hz (Fig. 5). Laser light was introduced via a home-made (Philips Research, Eindhoven) 45° notch filter for 647 nm. This filter can handle a higher laser power than that handled by

standard notch filters, and therefore, allows the collection of a higher Raman signal at 100 cm^{-1} from the laser line. No damage to the sample was observed during or after the analysis. Conversion was measured as a function of spatial position on the lens surface.

RESULTS AND DISCUSSION

IR spectroscopy for analyzing reaction kinetics

Using IR spectroscopy, the first part of the curing can be examined off-line (Fig. 6). The results confirmed the reaction rate difference, showing that the conversion rate is clearly reduced when the material is exposed in air (oxygen inhibition).

This indicates that during actual lens production—in an enclosed volume—a high conversion rate is expected, as the irradiated volume has no contact with the surrounding atmosphere. However, any additional effects on conversion yield that may occur during curing in an enclosed environment (that allows no shrinkage of the reaction volume) cannot easily be studied with IR spectroscopy. This leaves an obvious
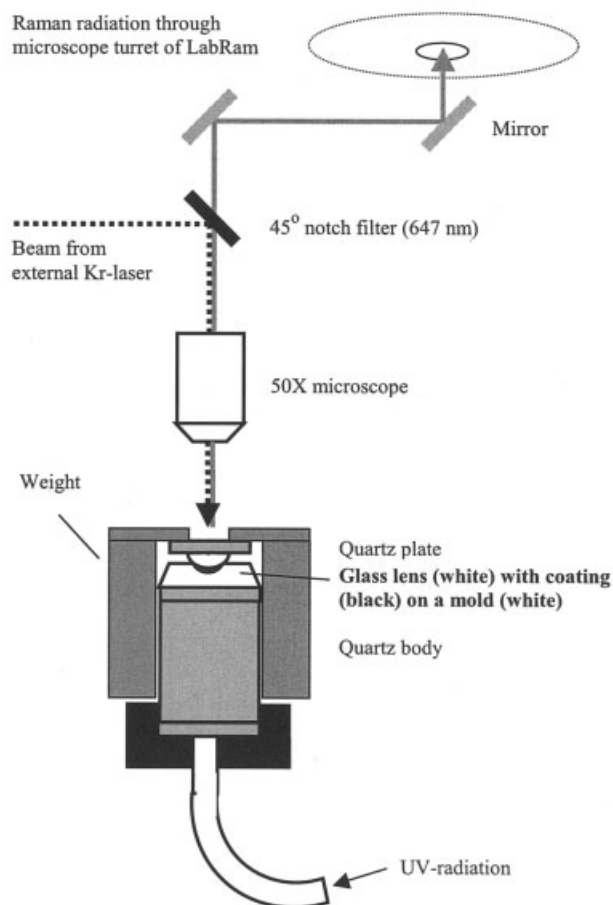

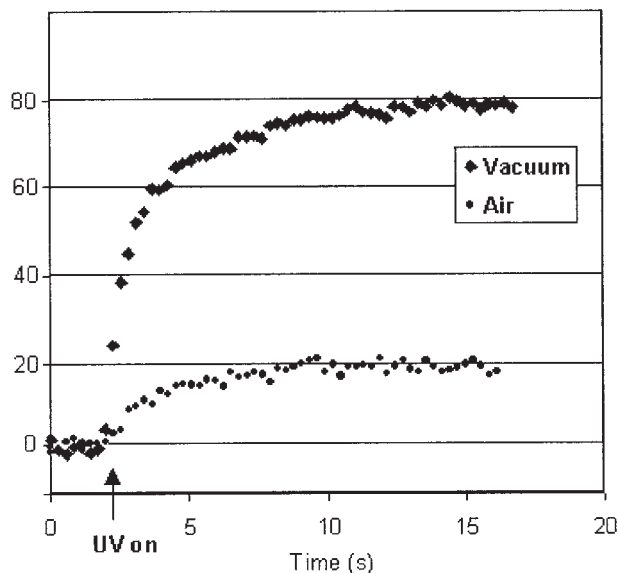**Figure 5** Raman setup for on-line time-resolved analysis of lens production.

Figure 6 IR results of UV-induced conversion of monomer to polymer as a function of time.

need to analyze the curing reaction in an on-line setup, with an alternative approach.

Raman spectroscopy for analyzing on-line reaction kinetics

A small droplet of HEBDM was UV-cured on a lens, in the setup shown in Figure 5. For comparison, a droplet of coating was UV-cured in the same setup without the lens present to give the droplet freedom to shrink. During the reaction, a large number of spectra are taken (one every 0.5 s). To obtain a quantitative and unequivocal indication of the conversion from monomer to polymer, PCA is applied to determine the degree of conversion from a larger part of the Raman spectrum. The relative double bond conversion in time is shown in Figure 7 for both the free drop in nitrogen and the confined coating on the lens. Data were scaled using 100% conversion as the maximum value, determined for a lens that was illuminated for 30 min and annealed overnight at 140°C.

The reaction is too fast to obtain a proper fit of the conversion during the first few seconds of exposure. Therefore, IR measurements were performed to specifically cover this part. However, our main interest is to investigate whether spatial and temporal variations occur. Since these parameters become more important on a longer timescale, we refrained from further IR analyses.

Remote analysis at different positions

With a coating thickness ranging from 0.7 to 22 μm, it is possible that the conversion rate and final degree of

conversion is not constant over the lens radius and thickness. To determine whether there are differences, a Raman spectrum was recorded every 0.5 s at different radial positions. Figure 8 shows the results for the conversion efficiency as an average of three experiments. The entire thickness of the coating was sampled. Little difference is seen in the first few seconds, but a major difference is seen on a timescale of 1 min. Polymerization occurs with the same rate at the lens center (thickness of 22 μm) and at the ring of minimum thickness (0.7 μm). The conversion near the edge of the lens (outside the thinnest ring region and in contact with air during exposure) is lower. Data were scaled using 100% conversion as the maximum value, determined for a lens that was illuminated for 30 min and annealed overnight at 140°C.

A depth profile was made of the lens coating conversion after release from the mold (Fig. 9). The available depth resolution is much better then, since measurements can be performed directly onto the lens coating. A depth resolution below 2 μm is available, using a 50× long working distance objective and a 0.4 mm confocal hole. A mapping of 20 × 20 points was performed over the lens surface, using an auto focus system to find the surface for each position. Data were corrected for signal drop with depth, and the relative conversion was determined using PCA. From the collected 3D datacube, it could be concluded that the degree of polymerization is the same throughout the lens within the radius of the ring of minimum thickness.

However, when we look at the "bottom" near the lens edge, the conversion is clearly lower. Previous experiments indicate that this is likely to be due to exposure to oxygen (from the air) during the polymerization at this position (Fig. 8). Oxygen clearly retards
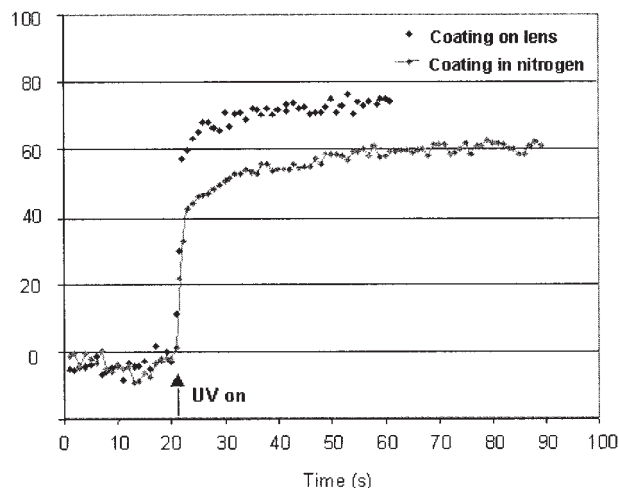

Figure 7 Conversion as a function of time in a free droplet of coating and in the actual production setup as determined with PCA. Exposure conditions: 0.7 s, 40 mW/cm².
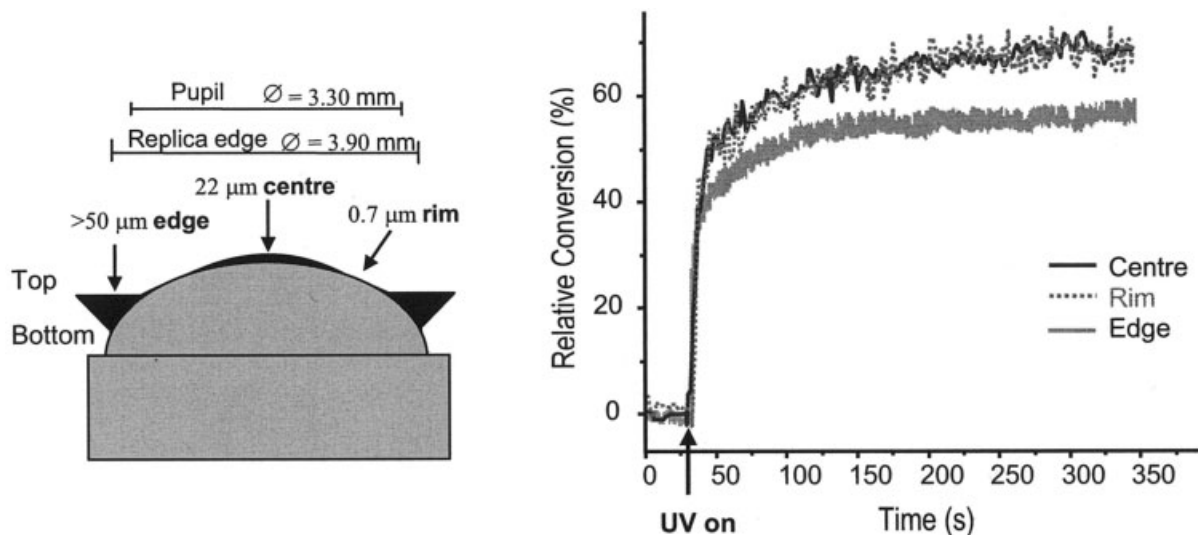
Figure 8 Conversion as a function of time at various radial positions on the lens. Data are averaged over the entire thickness of the lens.

the radical-driven polymerization and results in a lower rate at a similar intensity of UV irradiation.

This means that under production conditions, using 7 s of illumination at 40 mW/cm^2, no variation is present in the degree of conversion over the surface. This is unexpected, as the delayed shrinkage in the mold was expected to play a role in the conversion rate. The earlier data in Figure 7 suggested this. Additional measurements on lenses, using a lower UV radiation dose were performed to determine whether the rate of the reaction differs more under such conditions. However, even with 7-s UV irradiation at a power density as small as 4.5 mW/cm^2, only the top of the edge shows a decreased reaction rate. The conversion differences over the lens surface within the ring of minimum thickness were <5%.

Although the above results seem to indicate little more than that there is no difference over the lens surface, this result is of great interest. It seems to indicate that the shrinkage is not an issue and this is only realistic if the shrinkage can occur "freely" inside the mold. As no delamination from the mold is observed, a wild suggestion is that the setup actually deforms to accommodate the shrinkage effects. This
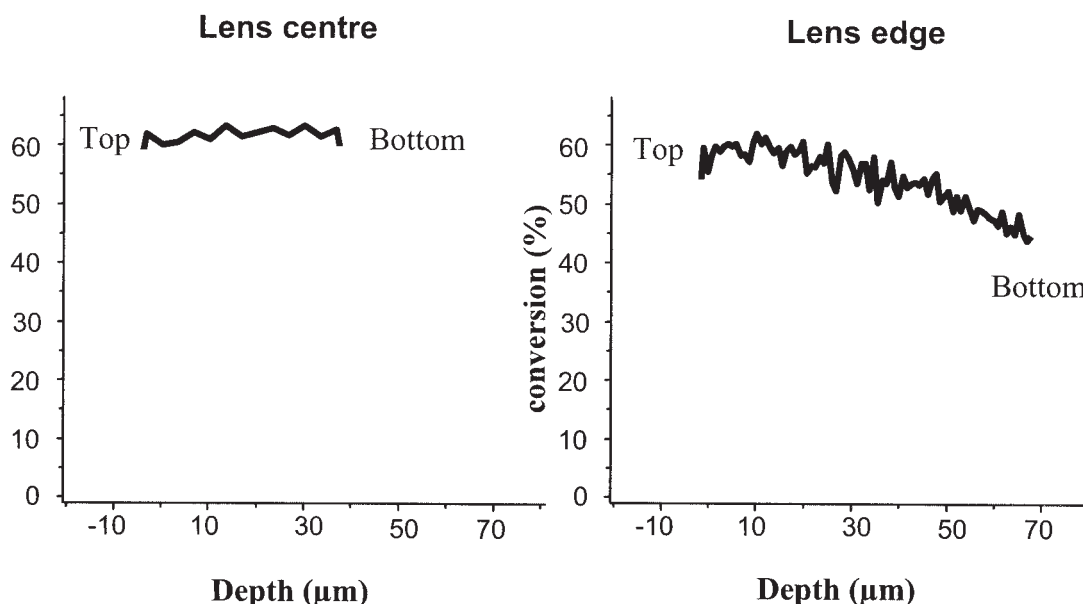

Figure 9 Conversion as a function of depth at different radial positions. Confocal Raman microscopy was applied after release from the mold, 1 h after UV curing.
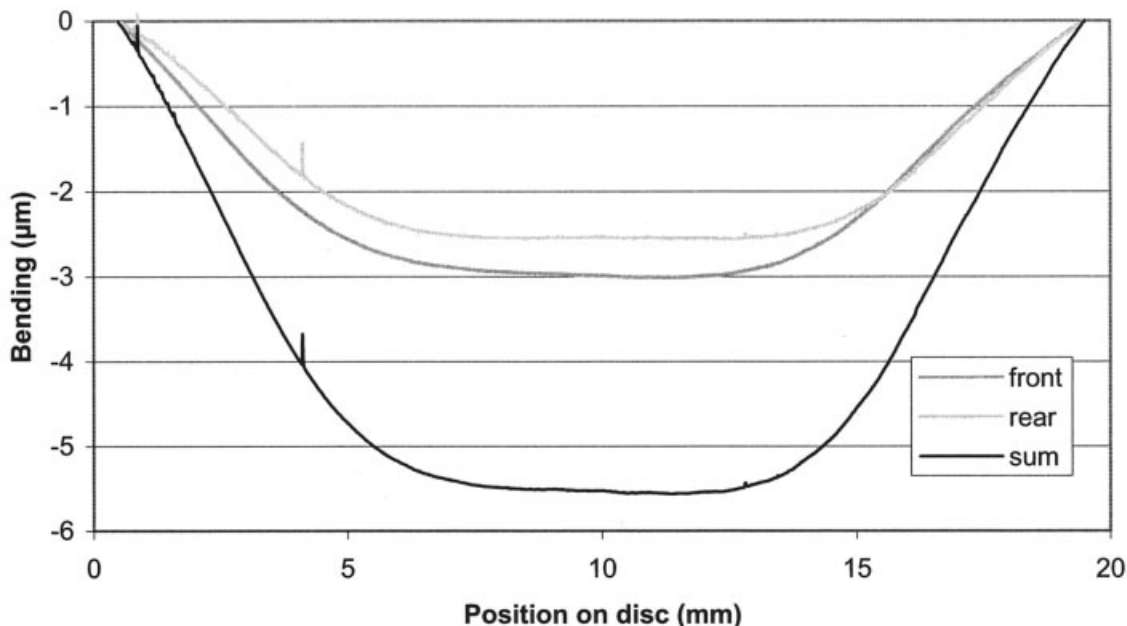
Figure 10 Profile of front and rear surfaces of the discs, and the summation of both, indicating that both the thick quartz discs move towards each other.

possibility was examined using a setup consisting of two 3-mm thick quartz plates with a diameter of 20 mm. One of these contains a cylindrical cavity with a diameter of 16 mm. The cavity was created using chemical mechanical polishing. The surfaces that will be in contact with the coating are modified with a silane coupling agent, by exposing them to the vapor of γ-methacryloyloxypropyltrimethoxysilane (A174) in a desiccator to make sure that the polymer network does not release from the quartz walls upon shrinkage. The same procedure is normally applied in the lens production. Next, the cavity is filled with replication coating and the two quartz plates are clamped together. This creates a confined volume in which one can determine the rate of polymerization in a system with parallel flat surfaces. Unexpectedly, on-line Raman analysis during the polymerization of this system revealed that the rate of polymerization and final conversion levels are identical to those observed in the lens production system. The free volume increases upon polymerization, if shrinkage cannot be realized. This will lead to a locally higher mobility of pendant reactive groups, and therefore, will lead to a higher polymerization rate and final conversion. The analysis disputes this proposition, unless the "confined" volume still decreases and shrinkage is still realized. To check this, surface flatness scans of the outer quartz surfaces were performed using a Dektak profilometer (Fig. 10).

The figure clearly indicates that the shrinkage is still realized. A bending of 5.5 μm occurs for the front and backside together. Apparently, the shrinkage stresses

are so high that it is very difficult to create a truly confined environment. Since the molds used in production are thinner than 3 mm it is likely that volume relaxation occurs already during exposure, before release.

CONCLUSIONS

Raman spectroscopy has been found to be a valuable tool for monitoring the conversion of thin acrylic lens coatings in an in-process analysis. In the dimethacrylate studied, long primary chains are formed. This leads to early gelation and almost immediate build-up of stiffness.

In combination with the very thin minimal thickness of the lens, where the coating thickness is only 0.7 μm, it was expected that a temporary excess of free volume is created at the much thicker central section during the reaction, as a result of polymerization shrinkage. In principle, this should lead to a conversion rate that is different from the rate observed for a free, nonconfined droplet of coating. However, Raman experiments showed that this is not the case. This puzzling result can be explained by a deformation of the mold. Initially, it was expected that volume relaxation occurs only after release from the mold. Experiments with flat substrates instead of lenses showed that shrinkage actually occurred during the polymerization, as the shape of 3-mm thick quartz glass substrates is distorted when a volume of monomer with a thickness

of 100 μm is photopolymerized. No release from the mold was observed during the reaction.

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