polymer papers

Time-resolved determination of volume shrinkage and refractive index change of thin polymer films during photopolymerization

J. de Boer*, R. J. Visser and G. P. Melis
Philips Research Laboratories, PO Box 80000, 5600 JA Eindhoven, The Netherlands

(*Received 13 November 1990; accepted 6 January 1991*)

Polymerization shrinkage and change of refractive index have been studied on thin sample layers during photopolymerization. By using laser interferometry and special substrates it was possible to determine both parameters simultaneously. The monomer studied was bis(2-hydroxyethyl)bisphenol A dimethacrylate (HEBDM). Once the refractive index and the shrinkage were known, the double-bond conversion could be calculated using the Lorentz–Lorenz equation. It has been found that shrinkage proceeds linearly with conversion until vitrification of the system sets in. From that moment shrinkage cannot keep up with conversion and lags behind. The described model can also be used to predict changes of thickness and refractive index upon further relaxation.

(Keywords: photopolymerization; polymerization shrinkage; refractive index; interferometry)

INTRODUCTION

Thin, *in situ* polymerized films find increasing application in optoelectronic devices such as aspherical lenses, waveguides, gratings and optical fibre coatings. Their optical performance is largely determined by their thickness and refractive index. Therefore, changes of these parameters during polymerization are also of great importance. In addition, stress may play an important role. As an example, we will discuss the manufacturing of aspherical lenses.

One of the manufacturing methods of high-precision aspherical lenses used in optical disc read-out systems is a photo-replication process. In this process a methacrylate resin is applied to a spherical glass substrate and polymerized against an aspherical quartz glass mould using u.v. light[1,2]. A typical aspherical lens requires a shape accuracy better than $0.1\,\mu m$ and a surface roughness of less than $0.02\,\mu m$. A representative example of a desired layer thickness profile is shown in *Figure 1a*. As virtually all polymerization processes are accompanied by a considerable volume shrinkage, it is clear that, in order to achieve high-precision lens replication, this shrinkage has to be controlled as well as possible so that the mould can be (accurately) corrected for it. Proper correction of the mould requires accurate measurement of shrinkage.

Several methods are known to measure polymerization shrinkage. A basic, but static method is to measure densities by methods such as pycnometry or hydrostatic suspension[3,4]. Measurement of volume changes by using a dilatometer with a mercury-filled capillary is a classical method for monitoring polymerization processes[5]. In an improved version of this method a continuously recording dilatometer is used[6], but these methods are still unsuitable for measuring thin films.

Other methods suited for dynamic shrinkage measurement are based on a thin sample sandwiched between two substrates. The bottom substrate is fixed and the displacement of the flexible top substrate is monitored during polymerization[2,7]. Unfortunately, in this configuration stresses will inevitably build up in the polymer layer, notably when the system vitrifies. This will affect not only the result of a shrinkage measurement but also the optical performance.

During the polymerization of a confined layer with a thickness distribution as shown in *Figure 1a*, large stresses will arise due to the shrinkage process. At the thinnest section compression will occur, while the thicker section will be under tensile stress. *Figure 1b* shows the stress distribution obtained from a finite-element calculation[8], using an average shrinkage of 7.5%. This stress distribution manifests itself directly as a variation of actual shrinkage with radial position (*Figure 1c*). The actual shrinkage was calculated from very precise profile measurements, carried out with a stylus instrument[9]. Obviously the extent of shrinkage is influenced by geometry effects. At the edge of the lens the resin surface is open to the air, so that shrinkage can occur more freely and will be partially compensated for by transport of uncured material. The inner part of the replicated layer is a closed system. No flow of material can occur and shrinkage will immediately result in accumulation of stresses.

This illustration expresses the need for a non-perturbing

---

* To whom correspondence should be addressed. Present address: Pope Cable and Wire BV, Edisonstraat 9, PO Box 9, 5900 AA Venlo, The Netherlands

0032-3861/92/061123-04

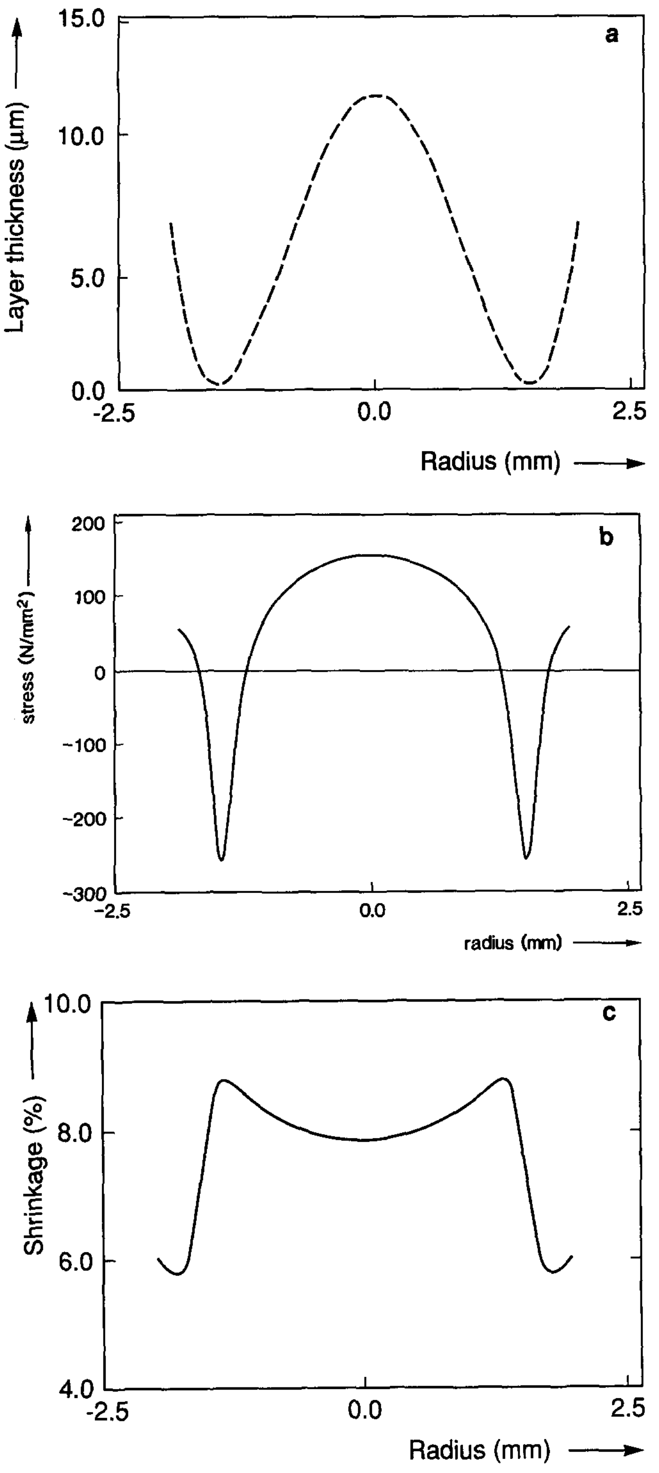

Figure 1 Measurements on an aspherical lens as a function of the radius. (a) Thickness of the polymer layer. (b) Calculated normal stress assuming an average shrinkage of 7.5%. (c) Actual shrinkage in the photopolymerization process

shrinkage measurement that does not induce stress in the measured sample. Therefore we have built an apparatus to measure shrinkage optically, without making mechanical contact with the sample. In this apparatus, to be described below, the change of the optical path length *nd* through a thin sample layer is measured using laser interferometry (*n* is refractive index, *d* is sample layer thickness).

During polymerization the optical path length will change due to decrease of thickness caused by shrinkage and increase of refractive index caused by the combined effects of shrinkage and chemical conversion. Evaluation of thickness changes therefore requires *in situ* measurement of the refractive index. Our apparatus allows the simultaneous measurement of changes in optical path length and refractive index by using special substrates.

The experimental data enabled us to establish the extent of reaction to which shrinkage and conversion proceed at the same rate and where deviations start to occur. A simple model, which correlates rates of shrinkage with rates of conversion, allows one to predict future changes of thickness and refractive index of photopolymeric films.

EXPERIMENTAL

The experimental set-up is represented schematically in *Figure 2*. A reflective substrate was spin-coated with a thin (30 μm) u.v.-curable layer and placed in a nitrogen-flushed vessel. The vessel had a quartz window to allow irradiation. A laser beam was used to measure changes in optical path length *nd* upon u.v. irradiation, using interference of light reflected at the top and at the bottom of the curable layer. Provided that there is good adhesion between sample and substrate, the large area-to-thickness ratio of the sample justifies the assumption that, although the measurement is one-dimensional, a volume shrinkage is determined.

The laser used was a 4 mW Spectra-Physics HeNe laser. The photodetector was a Centronic silicon photodetector type OSD, with a saturation level of 5 W cm^{-2}. We ensured that the detector was operating in its linear range during our experiments. The current generated was

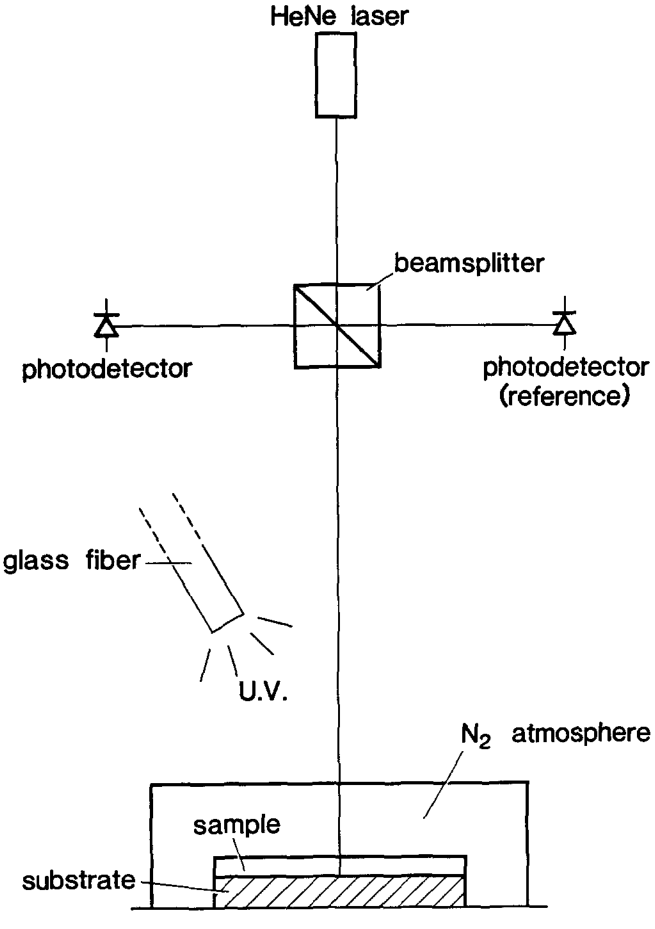

Figure 2 Experimental set-up

Table 1 The glass substrates used

Glass type	Refractive index ($\lambda = 633$ nm; 20°C)
BK3	1.49831
BK7	1.51680
F14	1.60565

converted to a voltage, which was used as input for a Philips P3102 computer. For data acquisition and control we used 'Labtech Notebook' software from Laboratory Technologies corporation. For u.v. irradiation we used a high-pressure mercury arc (Philips, HPA 400W/30S). The intensity at 350 μm was 1.2 mW cm^{-2}.

The monomer studied was bis(2-hydroxyethyl)bisphenol A dimethacrylate (HEBDM) (we used a technical batch Diacryl 101, supplied by Akzo, Deventer, The Netherlands). As a photoinitiator 4 wt% of α,α-dimethoxy-α-phenylacetophenone (DMPA) (Ciba Geigy, Basle, Switzerland) was added.

For determination of intensity variations in order to calculate changes of refractive index, we used several glass substrates (*Table 1*). After calibration with a liquid monomer and a sample of known conversion, shrinkage and refractive index, we were able to measure thickness and conversion simultaneously. The refractive index at 589 nm of HEBDM monomer (including 4 wt% initiator) was 1.5425; after 5 min irradiation the refractive index was 1.5662. (Irradiation and measurement were carried out at room temperature.)

CALCULATIONS OF THE OPTICAL PATH LENGTH AND REFRACTIVE INDEX

Optical path length

The intensity of reflected light $I(t)$ arriving at the detector at time t is modulated by interference of light reflected at the top and at the bottom of the sample. It varies according to the following equation:

$$I(t) = I_o + I_a \cos\left(\frac{2\pi 2d(t)n(t)}{\lambda}\right) \tag{1}$$

where I_a and I_o are the amplitude and offset of the signal, respectively, and λ is the wavelength of the laser (632.8 nm). The factor of 2 arises from dual passage of the laser beam through the layer. Now the product $d(t)n(t)$ can be written explicitly:

$$d(t)n(t) = \left(\frac{\lambda}{4\pi}\right)\arccos\left(\frac{I(t) - I_o}{I_a}\right) + k\frac{\lambda}{2} \tag{2}$$

with $k = 0, 1, 2, \ldots$.

Refractive index

Calculations on the variation of reflectance, due to the change of thickness of a transparent layer during etching, have been carried out by Heimann[10] and Heavens[11]. According to this work the reflected intensity (I) is proportional to $|r_e|^2$ (r_e is the (complex) ratio of reflected to incident amplitude of light), which is equal to:

$$|r_e|^2 = \frac{r_1^2 + r_2^2 + 2r_1r_2\cos(2\delta_1)}{1 + r_1^2r_2^2 + 2r_1r_2\cos(2\delta_1)} \tag{3}$$

where δ_1 is the phaseshift, given by $\delta_1 = 2\pi n_1 d/\lambda$; r_1 and r_2 are the Fresnel reflection coefficients, $r_1 = (1 - n_1)/(1 + n_1)$ and $r_2 = (n_1 - n_2)/(n_1 + n_2)$; and n_1 and n_2 are the refractive indices of sample layer and substrate, respectively. (The indices 1 and 2 refer to sample and substrate respectively.) In the case that $r_2 < 0$ ($n_1 < n_2$) this intensity will go through a maximum if $\cos(2\delta_1) = 1$. The equation then reduces to:

$$|r_e|^2 = \frac{r_1^2 + r_2^2 + 2r_1r_2}{1 + r_1^2r_2^2 + 2r_1r_2} = \frac{1 - n_2}{1 + n_2} \tag{4}$$

Thus it follows that the maximum intensity is independent of n_1, the refractive index of the sample. The change of refractive index during polymerization will only affect the minimum intensities.

In the same way it can be shown that in the case that $r_2 > 0$ ($n_1 > n_2$) the minimum intensity will be independent of n_1. Now we find the maximum intensities to be affected by changes of n_1. *Figure 3* gives the results of calculations of the reflectivity (using equation (3)), where BK7 glass is used as a substrate ($n_2 = 1.5168$) and the refractive index of the layer (n_1) is varied.

Thus the change of amplitude of the signal due to the increase of the refractive index of the sample during polymerization can be calculated. Now we are able to obtain the change of refractive index during a measurement by monitoring the change in amplitude.

RESULTS

The change in refractive index upon polymerization is caused by a change in polarizability α of the sample. According to the Lorentz–Lorenz equation, the molar refraction R_{LL} changes proportionally with α:

$$R_{\mathrm{LL}}(t) = \frac{n(t)^2 - 1}{n(t)^2 + 2}\frac{M}{\rho(t)} = \frac{4\pi N_A \alpha(t)}{3} \tag{5}$$

where M is the molecular weight of the monomer, $\rho(t)$ is the density at time t and N_A is Avogadro's number. The change of α during polymerization is due to two effects:

(i) Conversion of double bonds to single bonds, which causes α to decrease.
(ii) Shrinkage: the density will increase and therefore α will increase.

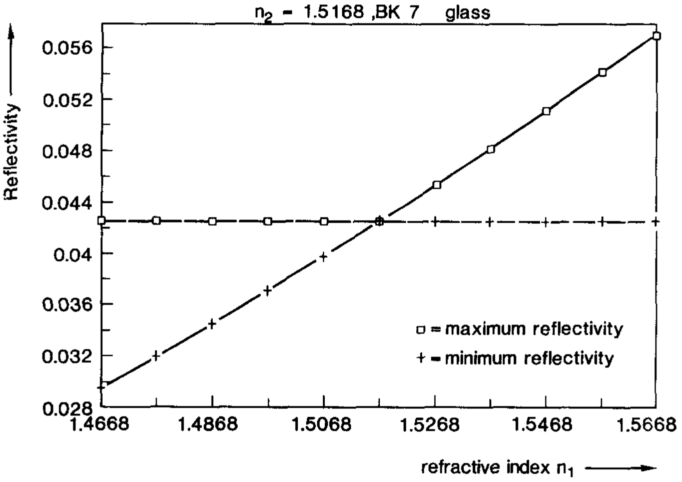

Figure 3 Calculated maximum and minimum intensities of reflected light from a BK7 glass substrate with a transparent coating of refractive index n_1 (equation (3)); n_1 is varied in an interval around the refractive index of BK7 glass

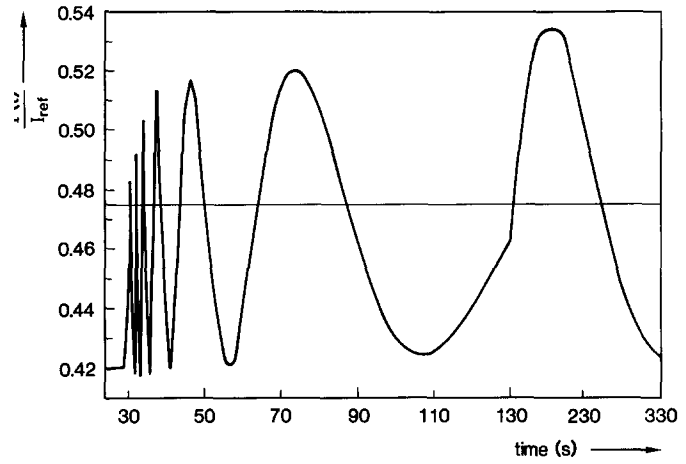

Figure 4 Intensity of reflected light from a BK7 glass substrate during the photopolymerization of HEBDM, normalized to the intensity of the reference beam (note the scale change at 130 s)

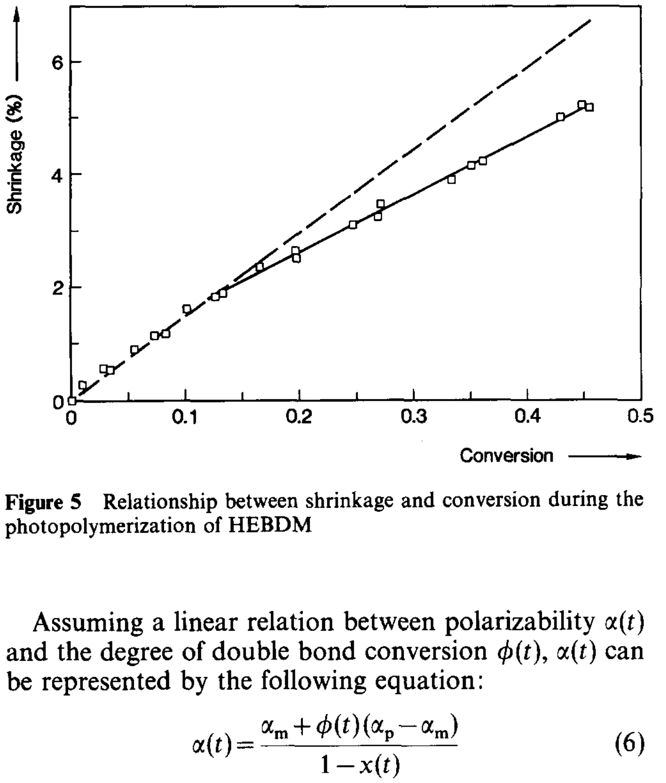

Figure 5 Relationship between shrinkage and conversion during the photopolymerization of HEBDM

Assuming a linear relation between polarizability $\alpha(t)$ and the degree of double bond conversion $\phi(t)$, $\alpha(t)$ can be represented by the following equation:

$$\alpha(t)=\frac{\alpha_m+\phi(t)(\alpha_p-\alpha_m)}{1-x(t)} \tag{6}$$

where α_m is the polarizability of monomer, α_p is the polarizability of polymer and x is the volume shrinkage For small values of $x(t)$ this equation can be approximated by:

$$\alpha(t)=\alpha_m+\phi(t)(\alpha_p-\alpha_m)+x(t)\alpha_m \tag{7}$$

If we now substitute the Lorentz–Lorenz equation in equation (7) we obtain:

$$\frac{n(t)^2-1}{n(t)^2+2}\,\frac{M}{\rho(t)}=c\alpha_m+\phi(t)c(\alpha_p-\alpha_m)+x(t)c\alpha_m \tag{8}$$

where $c=4\pi N_A/3$ and $\rho(t)=\rho_0[1+x(t)]$, with ρ_0 the density of monomer plus initiator. (For HEBDM, $\rho_0=1.1270\ \mathrm{g\,cm^{-3}}$ at 20°C.)

For $t=0$ the monomer polarizability α_m can be calculated. For HEBDM monomer (+initiator), $\alpha_m=5.397\times10^{-23}\ \mathrm{cm^3}$. Substitution of the values $x(t)$ and $n(t)$ of a sample of known conversion $\phi(t)$ yields the unknown α_p. For poly(HEBDM) (+initiator), $\alpha_p=4.608\times10^{-23}\ \mathrm{cm^3}$. Samples of known conversion were obtained from d.s.c. measurements[2,7].

Measurement of the reflected intensity now enables us to calculate refractive index, shrinkage and conversion during polymerization. *Figure 4* shows the result of an intensity measurement on BK7 glass as a substrate. similar results are obtained from measurements on different substrates (*Table 1*).

In *Figure 5* the calculated conversion is plotted against the calculated shrinkage. Obviously in the beginning of the reaction shrinkage increases linearly with conversion. However, after conversion reaches a level of about 13%, which corresponds to 2% shrinkage, an abrupt change in the slope is observed. At roughly the same conversion (10%) the rate of polymerization passes through a maximum. Here, the Trommsdorff autoacceleration is balanced by autodeceleration, caused by vitrification. It can be concluded that from this point shrinkage cannot keep up with conversion and lags behind. This phenomenon apparently occurs when vitrification of the system sets in. Diffusion of free volume generated by the chemical reaction is slowed down and finally free volume will be frozen in. The resulting material will have an excess of free volume and relaxation (delayed shrinkage) will only take place very slowly[7,12]. From this figure the amount of shrinkage that can be expected upon complete relaxation can be determined.

CONCLUSIONS

A method for measuring polymerization shrinkage, conversion and change of refractive index of u.v.-curable materials during photopolymerization has been demonstrated. The main advantage of this method is its non-perturbing character, allowing the sample to cure at a minimum of stress. In addition we mention the high speed and the extreme sensitivity (changes of 10 nm can be easily detected).

A relationship between rate of shrinkage and rate of conversion has been established. We found that shrinkage lags behind conversion from the moment the system vitrifies. The resulting system contains an excess of free volume and will slowly undergo further volume relaxation. An estimate of the amount of shrinkage that will be realized upon complete relaxation of the system can also be made by the described method.

REFERENCES

1 Smid, A. *J. Opt. Soc. Am.* (*A*) 1984, **1**, 1283
2 Zwiers, R. J. M. and Dortant, G. C. M. *Appl. Opt.* 1985, **24**, 4483
3 Bogdanova, L. M., Ponomareva, T. I., Irzhak, V. I. and Rozenberg, B. A. *Polym. Sci. USSR* 1984, **26**, 1566
4 Oster, G. and Yamamoto, M. *Chem. Rev.* 1968, **68**, 257
5 Schulz, G. V. and Harborth, G. *Angew. Chem.* (*A*) 1947, **59**, 90
6 Gee, A. J. de, Davidson, C. L. and Smith, A. *J. Dentistry* 1981, **9**, 36
7 Kloosterboer, J. G., Hei, G. M. M. v.d., Gossink, R. G. and Dortant, G. C. M. *Polym. Commun.* 1984, **25**, 322
8 Boer, J. de and van der Schee, R. to be published
9 Dil, J. G., Mesman, W. and Driessen, J. C. *Proc. Soc. Photo-Opt. Instrum. Eng.* 1980, **235**, 85
10 Heimann, P. A. *J. Electrochem. Soc.* 1985, **132**, 2003
11 Heavens, O. S. 'Optical Properties of Thin Films', Academic Press, New York, 1955, p. 56 ff.
12 Kloosterboer, J. G. and Lijten, C. F. C. M. in 'Cross-linked Polymers: Chemistry, Properties and Applications' (Eds. R. A. Dickie, R. S. Bauer and S. Labana), ACS Symp. Ser. 367, American Chemical Society, Washington DC, 1988, p. 409