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NOTE

Effects of molecular weight on the local deformation of photo-cross-linked polymer blends studied by Mach–Zehnder interferometry

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INTRODUCTION

Material processing using light at the microscopic scale has been widely exploited for designing specialty polymers. Photoresist, photolithography or photocalligraphy are among the popular technologies used for this purpose.[1] From the viewpoint of polymer physics, depending on the experimental temperature, the photocured materials can undergo a liquid-to-glass transition via which the physical properties, such as glass transition temperature (T_g), and consequently the materials' moduli can be greatly modified. As a consequence, local deformation or shrinkage often accompanies this modification of polymer chemical structures. Typical examples can be found in the hardening process of dental materials.[2]

Several experimental techniques have been used to monitor the thickness of polymers. Among them, ellipsometry has been developed to measure the sample thickness down to nanometer scales by detecting the changes in amplitude and phase of incident polarized light.[3] Alternatively, a prism coupler[4] and neutron reflectometry[5] can also be utilized to measure the sample thickness, taking advantages of reflection phenomena. However, these techniques do not result in easier monitoring of the deformation process of a polymer under photocuring. Recently, we have developed the Mach–Zehnder interferometric (MZI) technique, which enables in situ monitoring of the deformation in the submicrometer scales associated with photo-cross-linking reactions in polymers.[6–8] Depending on the kinetics of the hardening process and the resulting glass transition temperature of the sample, the deformation process could lead to a shrinkage or a recovery from shrinkage during the reaction time. This process might affect the physical properties of the photocured polymers afterward. In this note, we will experimentally show that photocuring of polymers can lead to a shrinkage because of the decrease in sample volume. Effects of the glass transition temperature (T_g) of the photo-cross-linked blends, the center-of-mass diffusion of polymer chains, as well as the entanglement networks of the matrix polymer imposed on the recovery process of the cross-linked blends are discussed.

EXPERIMENTAL PROCEDURE

Sample preparation and characterization

Polymers used in this study are poly(ethyl acrylate) (PEA) and anthracene-labeled PEA (PEA-A). The former was used as a matrix in which the cross-linking reaction of the later was induced by ultraviolet (UV) irradiation. The chemical synthesis of these polymers has been described in detail elsewhere.[7,8] Briefly, to label PEA with photoreactive anthracene, ethyl acrylate monomers were polymerized in the presence of a small amount of chloroethyl acrylate and the resulting functionalized polymer was subsequently coupled to potassium salt of anthracene carboxylic acid. The PEA labeled with anthracene (PEA-A, $M_w = 1 \times 10^5$, $M_w/M_n = 2.4$) was blended with PEA to achieve the composition PEA-A/PEA(40/60) and was used as a sample. The average anthracene-labeled content of PEA-A is 1.0 mole%. This PEA/PEA-A combination was chosen to avoid the phase separation caused by the formation of semi-interpenetrating polymer networks.[9] By fluorescence microscopy, it was determined that a PEA-A/PEA(40/60) blend after 420 min of photo-cross-link remains structureless for 3 h of annealing at 80 °C. The chemical structure of PEA-A is illustrated in Figure 1. As for the matrix, PEAs with different molecular weights ranging from 2.3×10^4 to 9.0×10^4 were obtained by fractionation of the original PEA ($M_w = 10^5$, $M_w/M_n = 2.4$) prepared by free radical polymerization using acetone as a solvent and water as a non-solvent. The characteristics of these PEAs are summarized in Table 1. The mixture was dissolved in toluene and thin films with a thickness of 18 μm were cast from the toluene solution. Subsequently, all films were dried in vacuo at 65 °C for a week before the experiments.

Mach–Zehnder interferometry

In brief, a He–Ne laser beam[6] (10 mW, 632.8 nm), after collimation, was passed through a MZI unit composed of reference and test arms. The patterns generated by the interference between the laser beams from these two arms were detected and recorded on a charge-coupled device camera. The procedure for these in situ experiments and the data analysis using Hilbert transform have

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a

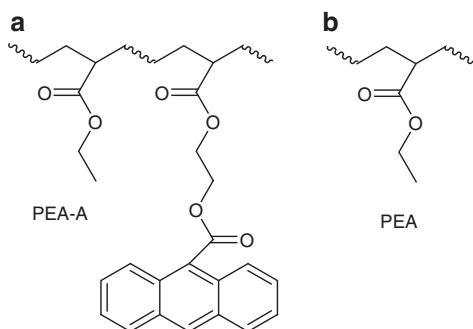**PEA-A**

b

PEA

Figure 1 Chemical structure of (**a**) anthracene-labeled poly(ethyl acrylate) (PEA-A) and (**b**) poly(ethyl acrylate) (PEA).

Table1 Codes and characteristics of polymers used in this study

Polymers	M_w	M_w/M_n	Sample	Blends	Composition
PEA-A	10^5	2.4			
PEA (1)	2.3×10^4	1.07	A	PEA-A/PEA (1)	40/60
PEA (2)	3.2×10^4	1.16	B	PEA-A/PEA (2)	40/60
PEA (3)	4.6×10^4	1.15	C	PEA-A/PEA (3)	40/60
PEA (4)	9.0×10^4	1.2	D	PEA-A/PEA (4)	40/60

Abbreviations: PEA, poly(ethyl acrylate); PEA-A, anthracene-labeled PEA.

been described in detail elsewhere.[6–8] Irradiation was performed using a high-pressure mercury lamp (350 W, Moritex, Saitama, Japan).

Dielectric relaxation experiments

The glass transition temperature of the cross-linked and non-cross-linked PEAs was measured by dielectric relaxation. Briefly, the dielectric measurements were performed using an impedance analyzer (Alpha AKB analyzer, Novocontrol Technologies, Montabaur, Germany). The frequency of applied electric field ranged from 0.1 Hz to 1 MHz. The data of real and imaginary parts of the electric capacitance (C' and C'') were converted to dielectric permittivity (ε' and ε'') using the relationships $\varepsilon' = C'/C_o$ and $\varepsilon'' = C''/C_o$ with the geometrical capacitance, C_o. The detailed procedures of the dielectric measurements are provided elsewhere.[10,11] The temperature of the dielectric relaxation was controlled with a precision[11] of $\pm 0.1\,^{\circ}$C.

Photo-cross-linking kinetics

The reaction kinetics was monitored by following the variation of the optical density of anthracene using a UV-Vis photometer (Shimadzu, UV-1600, Kyoto, Japan). The irradiation intensity used for irradiation was set at 4.0 mW cm^{-2}. All the curve fittings were performed by the IGOR software (Wave Metrics, Portland, OR, USA) using nonlinear least square with regression as described previously.[6]

RESULTS AND DISCUSSION

The photodimerization kinetics of anthracene moieties (Figure 2) labeled on the PEA-A chains monitored by UV-Vis spectrophotometry at 365 nm illustrates the irradiation-time dependence of the cross-link density $\gamma\,(t_{irr})$ calculated from the absorbance of anthracene using the following equation:[8]

$$\gamma(t_{irr}) = \frac{\alpha}{2}\frac{OD(0) - OD(t_{irr})}{OD(0)} \qquad (1)$$

where $OD(0)$ and $OD(t_{irr})$ are, respectively, the absorbance observed before and after t_{irr} minutes of irradiation. Integer 2 on the right hand side indicates that two anthracenes are involved in the
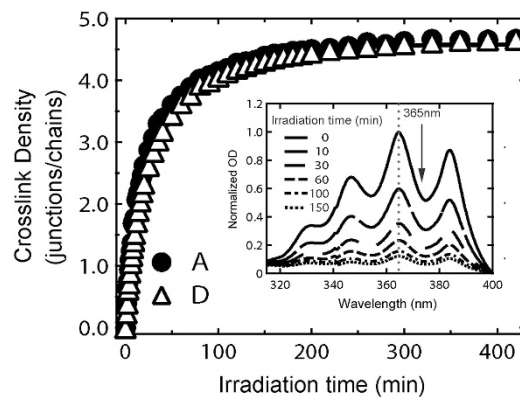

Figure 2 Irradiation-time dependence of the cross-link density observed at 25 °C for PEA-A/PEA blends (samples A and D) irradiated using 365 nm ultraviolet light with $I = 4.0$ mW cm^{-2}. The irradiation-time dependence of the normalized absorption spectra of anthracene is shown in the inset for sample D.

photodimerization. α, the average number of anthracene moieties labeled on one PEA-A chain, is 10.2 per average.

It was found that the cross-link density between the two PEA-A chains increases with increasing irradiation time and subsequently approaches a limiting value of ∼4.6 junctions per chain at a long irradiation time. The irradiation-time dependence of the cross-linking reaction can be well fitted to the modified Kohlrausch–Williams–Watts function,[7,8] revealing the inhomogeneity dynamics of the reaction in the bulk state. The inhomogeneity index (β) in the modified Kohlrausch–Williams–Watts function for samples with the lowest molecular weight ($M = 23\,000$) and highest molecular weight ($M = 90\,000$) is, respectively, 0.7 and 0.8 for samples A and D. The almost negligible difference in the cross-linking kinetics shown in Figure 2 for samples A and D with different molecular weights reveals the local aspect of the photopolymerization of anthracene. (See Supplementary Figure S1 in the Supplementary Information.) Namely, the reaction can only occur within the excited life time (4–5 ns) of anthracene and is controlled by segmental motions of PEA-A. However, the dependence of the absorption of anthracene on irradiation time is illustrated in the inset, revealing that only 90.2% of anthracene was consumed by irradiation.

The deformation (or strain) ε is defined as $\varepsilon(t_{irr}) = [\Delta d(t_{irr})/d_0]$ where $d(t_{irr})$ and d_0 is the thickness measured at $t = t_{irr}$ and $t = 0$. $\Delta d(t_{irr})$, the change in the sample thickness after t_{irr} min of irradiation, was calculated from the difference in the optical path length measured by MZI.[7,8] The result is illustrated in Figure 3, where the elastic strain ε is plotted versus irradiation time. It was found that for the blends B, C and D, the elastic strain gradually increases with increasing irradiation time and eventually approaches a stationary value, ε_∞. In this molecular weight range for the PEA matrix, the equilibrium deformation (ε_∞) decreases with increasing molecular weight of the PEA matrix. However, for the blend containing PEA with smallest molecular weight $M = 2.3 \times 10^4$ in the series, which is smaller than the entanglement molecular weight $M_e = 26\,000$ of the PEA matrix,[12] the shrinkage generated by photo-cross-linking recovers after ∼120 min of irradiation, revealing the role of chain entanglements of the matrix imposed in the deformation of PEA-A networks. This behavior suggests that the resulting strain ε observed for a photo-cross-linked PEA-A/PEA(1) blend is a combination of the shrinkage induced by photo-cross-linking and the swelling due to the recovery after cross-linking when the sample is in the rubbery state
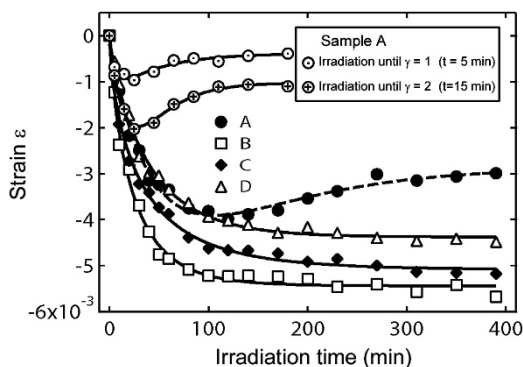
Figure 3 Irradiation-time dependence of the deformation ε observed for four blends A, B, C and D. Recovery after shrinkage under the conditions shown in the inbox is also depicted in the figure for sample A.

after cross-linking. (For details, see Supplementary Figure S2 in the Supplementary information.)

To confirm this speculation, a PEA-A/PEA(1) blend (sample A) was photo-cross-linked at 25 °C and irradiation was halted, respectively, at $t_{irr} = 5$ and 15 min. From Figure 2, the density of the cross-linked polymer at these irradiation times is $\gamma = 1$ and 2 junctions per chain, respectively. Subsequently, the behavior of the blend was *in situ* monitored by MZI. It was found that as soon as irradiation was halted, the recovery process took place. Longer irradiation times (higher cross-linked polymer density) and PEA matrices with larger molecular weights (samples B, C and D) give rise to larger deformation. For longer irradiation time, the recovery after shrinkage was not observed within the time scales of the experiments because of the strong kinetic effects arising from the high cross-link density (see Supplementary Figure S3 in the Supplementary Information for additional data).

To verify the rubbery states of the samples after photo-cross-linking, the glass transition temperature, T_g, of samples (A) and (D), which contain PEA with smallest and largest molecular weights, respectively, were measured using dielectric relaxation.

The experiments were performed for the PEA-A/PEA (40/60) blend before and after cross-linking over a sufficiently long period of time, that is, 420 min, which corresponds to the limiting cross-link density shown in Figure 2. The relaxation time τ_α of the α-process was calculated from the peak of the complex part of the relative dielectric permittivity, ε'', using the relation $\tau_\alpha = 1/(2\pi f_{max})$, where f_{max} is the frequency corresponding to the peak of the permittivity, ε''. The results are shown in the inset of Figure 4, as an example, for sample A without cross-linking together with the temperature dependence of $\log_{10}[\tau_\alpha^{-1}]$. It was found that the peaks of ε'' shift to higher temperatures on increasing frequency as expected for relaxation phenomena. However, the temperature dependence of the relaxation time τ_α can be well fitted to the Vogel–Fulcher–Tammann relation equation[13]

$$\tau_\alpha(T) = \tau_{\alpha o} \exp\left(\frac{U}{T - T_v}\right) \tag{2}$$

where U is the activation energy of the corresponding relaxation process, T_v is the Vogel temperature and $\tau_{\alpha o}$ is the pre-exponential factor.

The glass transition temperature (T_g) of the PEA sample was determined as the temperature at which the relaxation time τ_α becomes 100 s.[14] It was found that the T_g of the blend containing PEA with a high molecular weight (sample D) increases ~ 4 °C and
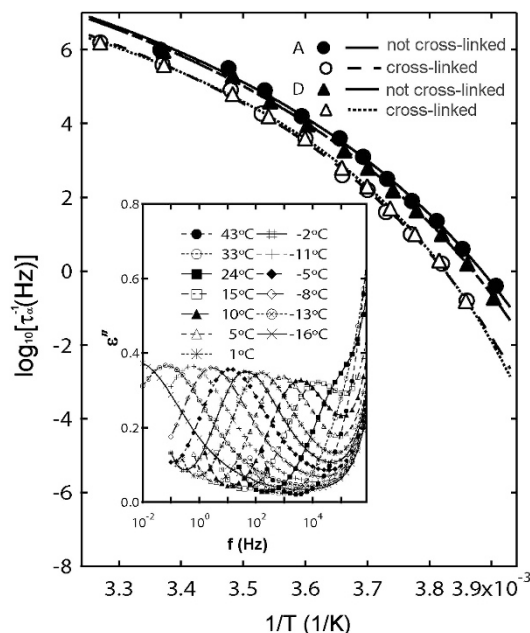

Figure 4 Temperature dependence of the dielectric relaxation time observed for the α-process of the blends A and D, with and without cross-linking. Shown in the inset is the frequency dependence of the complex component ε'' observed for sample A at different temperatures before cross-linking.

changes from 252.8 K before cross-linking to 256.2 K after cross-linking in 420 min. The glass transition temperature of the blend containing PEA with a lower molecular weight ($M = 23\,000$) also increases 4 °C after cross-linking. As expected, the T_g of the cross-linked blends is still below the experimental temperature (25 °C), supporting the recovery-after-shrinkage behavior. However, the Vogel temperature T_v also increases on cross-linking for both samples A and D, reflecting the modification of the local structures of the cross-linked PEA-A networks. (For details, see Supplementary Table S1 in the Supplementary Information).

CONCLUSIONS

Shrinkage associated with photo-cross-linked polymer blends was observed *in situ* for PEA blends in the bulk state by MZI. It was found that on photocuring, the blends deform, exhibiting shrinkage that strongly depends on the molecular weight of the non-cross-linked matrix. The entanglement networks of the polymer matrix would impose strong constraints on the recovery after shrinkage. The dependence of the sample thickness on irradiation time suggests that the recovery-after-shrinkage process is controlled by self-diffusion of the PEA component in the matrix. (Additional details are provided in Supplementary Figure S4 in the Supplementary Information). The information described here would be useful for the microscale processing and photocuring of polymers.

1 Madou, M. J. *Fundamentals of Microfabrication-The Science of Miniaturization* (CRC Press, Boca Raton, FL, 2002).
2 Lu, H., Stansbury, J. W., Dickens, S. H., Eichmiller, F. C. & Bowman, C. N. Probing the origins and control of shrinkage stress in dental resin composites. II. Novel method of simultaneous measurement of polymerization shrinkage stress and conversion. *J. Biomed. Mater. Res. B Appl. Biomater.* **71,** 206–213 (2004).
3 Azzam, R. M. A. & Bashara, N. M. *Ellipsometry and Polarized Light* (North Holland, Amsterdam, 1988).
4 Tien, P. K. Light waves in thin films and integrated optics. *Appl. Opt.* **10,** 2395–2413 (1971).
5 Russell, T. P. X-ray and neutron reflectivity for the investigation of polymers. *Mater. Sci. Rep.* **5,** 171–271 (1990).
6 Inoue, K., Komatsu, S., Trinh, X.-A., Norisuye, T. & Tran-Cong-Miyata, Q. Local deformation in photo-crosslinked polymer blends monitored by Mach-Zehnder interferometry. *J. Polym. Sci. B Polym. Phys.* **43,** 2898–2913 (2005).
7 Van-Pham, D.-T., Sorioka, K., Norisuye, T. & Tran-Cong-Miyata, Q. Physical aging of photo-crosslinked poly(ethyl acrylate) observed in the nanometer scales by Mach-Zehnder interferometry. *Polym. J.* **41,** 260–265 (2009).
8 Van-Pham, D.-T., Sorioka, K., Norisuye, T. & Tran-Cong-Miyata, Q. Formation and relaxation of the elastic strain generated by photocuring in polymer blends monitored by Mach-Zehnder interferometry. *Polymer* **52,** 739–745 (2011).
9 Kataoka, K., Harada, A., Tamai, T. & Tran-Cong, Q. Phase behavior and photo- cross-linking kinetics of semi-interpenetrating polymer networks prepared from miscible polymer blends. *J. Polym. Sci. Polym. Phys. Ed.* **36,** 455–462 (1998).
10 Fukao, K. & Miyamoto, Y. Dielectric relaxation of isotactic polystyrene above the glass transition temperature. *Polymer* **34,** 238–246 (1993).
11 Fukao, K. & Miyamoto, Y. Glass transitions and dynamics in thin polymer films: dielectric relaxation of thin films of polystyrene. *Phys. Rev. E* **61,** 1743–1754 (2000).
12 Andreozzi, L., Castelvetro, V., Faetti, M., Giordano, M. & Zulli, F. Rheological and thermal properties of narrow distribution poly(ethyl acrylate)s. *Macromolecules* **39,** 1880–1889 (2006).
13 Richert, R. & Blumen, A. in *Disorder Effects on Relaxational Processes* (eds Richert, R. & Blumen, A.) Ch. 1, 1–7 (Springer-Verlag, Berlin, 1994).
14 Kremer, F. & Schonhals, A. in *Broadband Dielectric Spectroscopy* (eds Kremer, F. & Schonhals, A.) Ch. 4, 99–129 (Springer-Verlag, Berlin, 2003).