Measurement of Residual Stresses in Injection-Molded Polymer Parts by Time-Resolved Fluorescence

TAIJI IKAWA, TOHRU SHIGA, AKANE OKADA

Toyota Central Research and Development Laboratories, Inc., Nagakute, Aichi 480-1192, Japan

Received 16 January 2001; accepted 9 June 2001

ABSTRACT: Time-resolved fluorescence properties of 9-methylanthracene (9MAn) dispersed in film of polyvinylchloride (PVC) containing carbon black were studied under tensile loadings. The fluorescence lifetime of 9MAn decreased from 5.70 to 5.55 ns, whereas the stresses acting on the films increased from 0 to 3 MPa. The change in fluorescence lifetimes of 9MAn during the stress relaxation process showed that the fluorescence lifetimes were correlated with the stresses, not with the strains. The results suggest that 9MAn is a useful probe for monitoring stresses acting on the matrix. With the use of the fluorescence properties of 9MAn, the residual tensile stresses on the skin-layer of PVC injection-molded test pieces were estimated. The estimated residual stresses were about ~ 1 MPa. The residual stresses were relaxed to 0 MPa with annealing at 100°C. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2600–2603, 2002

Key words: detection of residual stresses; fluorescence lifetime; 9-methylanthracene; polyvinylchloride; surface

INTRODUCTION

Polymer products made by injection, extrusion, compression, and blow molding have residual stresses that may considerably influence properties such as modulus, strength, and thermal expansion.[1] Also, the stresses cause fracture,[1,2] deformation,[1] flow marks,[3] and cracking on exposure to an aggressive environment. The measurement of the residual stresses, therefore, is important in understanding the reliability of the products. The most popular method for monitoring the stresses is the layer-removal procedure[4]; whereas mechanical shears damage the polymer during the layer removal and affect the stresses. Thus far, a variety of nondestructive methods including X-ray diffraction,[5] laser Raman spectroscopy,[6] and photoelasticity[7] have been proposed. These methods, however, have some disadvantages. X-ray diffraction and laser Raman methods are utilized only for measuring the stresses > 1 GPa. The photoelastic method is only suitable for transparent materials. We need new stress-monitoring techniques for monitoring the stresses in practical analysis.

Recently, we demonstrated that the time-resolved fluorescence of some photoluminescent molecules dispersed in polymer coatings varied with applied stresses on the coatings.[8,9,10] For example, the fluorescence lifetime of 9-methylanthracence (9MAn) in coatings varies with tensile loadings.[10] With the use of such a photoluminescent molecule as a sensor, it will give information about the residual stresses in the polymer moldings. In this article, we report that the time-resolved fluorescence technique is applicable for estimating the residual stresses on the surface of opaque polymer parts made of polyvinylchloride (PVC)-containing carbon black.

Correspondence to: T. Ikawa (e1056@mosk.tytlabs.co.jp).

Journal of Applied Polymer Science, Vol. 83, 2600–2603 (2002)

DOI 10.1002/app.10212

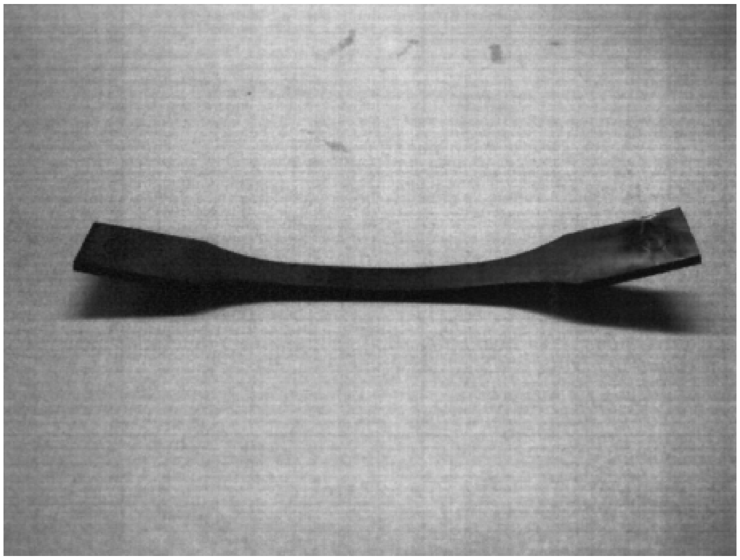

Figure 1 The dumbbell-shaped test piece.

Procedure of the Time-Resolved Fluorescence Technique

The measurement of residual stress by using the time-resolved fluorescence technique is divided into several steps. First, thin polymer films and polymer parts containing a small amount of fluorescent molecules are fabricated. Second, the fluorescence lifetimes of the molecules in the film are measured under various tensile loadings, and a stress–lifetime evaluation curve (i.e., relationship between the lifetime and the loading) is prepared. Third, the lifetime of the molecule in the polymer parts is measured, and the lifetime is reduced to residual stress by using the stress–lifetime evaluation curve.

EXPERIMENTAL

Sample Preparation

The injection-molded test piece and the compression-molded film used in this work were fabricated from PVC containing carbon black (Kaneka Co., Japan, G-408-B). 9MAn (5 mg, Tokyo Chemical Industry Co., Japan) was dissolved in spectroscopic-grade chloroform. The pellets of the PVC (500 g) were dispersed in the solution and the solvent was evaporated. The pellets were dried for > 1 day *in vacuo.* Then, the PVC pellets were molded by using an injection-molding machine (Nissei Plastic Industrial Co., Japan, PS40E2ASE), and dumbbell-shaped test pieces were fabricated. The processing conditions were as follows: cylinder temperature, 165°C; cavity temperature, 40°C; injection speed, 45 mm/s. Figure 1 shows the photograph of the dumbbell-shaped test piece. The test piece was 170 mm in length and 2 mm in thickness. The film of 300 μm in thickness was prepared from the test piece by the compression-molding machine at 165°C. The film was dried at 100°C for more than 10 h to release the residual stresses.

Spectroscopic Measurements

A schematic illustration of the measurement of time-resolved fluorescence of the PVC film under tensile loading is displayed in Figure 2. A handmade jig was used for the uniaxial elongation of the film. The given stress was obtained on a tensile tester. The time-resolved fluorescence measurements were performed by using a fluorescence lifetime measuring system with a streak

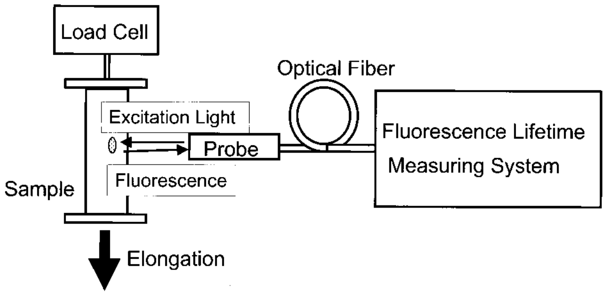

Figure 2 Schematic illustration of a fluorescence measurement under tensile loadings.

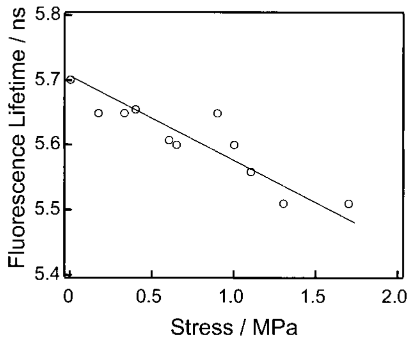

Figure 3 A fluorescence lifetimes–stresses evaluation curve.

camera (Hamamatsu Photonics, Japan, C4780). The dye laser with an average power of 150 μJ and a frequency of 15 Hz (Laser Photonics, LN120C) was used as an excitation light source. The excitation wavelength was 386 nm with pulse duration of $\sim$ 500 ps. The irradiation with excitation beam and the detection of the fluorescence were carried out by using a measurement probe through optical fibers. The excitation light was focused onto a spot the size of 1.0 mm in diameter. The transmittance of the film was measured by a UV–Vis spectrometer (Shimazu, UV-2000) which indicated that 99% of the excitation light was absorbed and/or scattered within 50 μm from the surface. The fluorescence of 9MAn, with wavelength ranging from 400 to 450 nm, was analyzed by using the following equation,

$$I(t) = \sum A_n \exp(-t/\tau_n) \qquad (1)$$

where $I(t)$ is the fluorescence intensity, A_n is the constant, and τ_n is the decay time. The deconvolution and curve fitting were performed by least-squares calculations.

RESULTS AND DISCUSSION

Figure 3 shows the relationship between the fluorescence lifetimes of 9MAn dispersed in the PVC film and the tensile stresses acting on the film. When the film was free from an external force, the fluorescence lifetime of 9MAn was 5.70 ns. The fluorescence lifetime linearly decreased from 5.70 to 5.55 ns by increasing the tensile stress from 0 to 3 MPa in the range of elastic deformation of the film. This suggested that the stress or strain, which was acting on the matrix, affected the fluorescence behavior of 9MAn dispersed in the film. To clarify which contributes to the variation in the fluorescence lifetime, we observed the change in the fluorescence lifetime on the stress relaxation process. Figure 4 shows the result. The fluorescence lifetime in the initial state was 5.70 ns. When a tensile strain of 1.5% was applied to the film, the stress became 3 MPa, and the fluorescence lifetime changed to 5.50 ns. The fluorescence lifetime extended from 5.50 to 5.65 ns, whereas the stress relaxed from 3 to 1 MPa. With the strain released, the fluorescence lifetime returned to the initial value of 5.70 ns. The result leads us to the conclusion that the fluorescence lifetime of 9MAn is not influenced by strains but by stresses.

Next, we measured the fluorescence lifetimes on the test pieces and estimated the residual stresses by using the fluorescence lifetime–stress evaluation curve displayed in Figure 3. For the estimation of the residual stress in the polymer parts, we gave the assumption that the residual stresses acting on the surface of injection moldings are tensile stresses.[1,11,12] Residual stresses of injection moldings mainly originate from two sources. The one source is the frozen-in flow-induced stresses; macromolecules are oriented along the flow direction and frozen during the filling stage of the injection-molding process. The other source is the thermal stresses, caused by differential shrinkage during postfilling stage. Computer calculations predict that tensile stresses developed at the surface because of not only the orientation of macromolecule but also the thermal stresses during the postfilling stage, whereas tensile stresses in the core are equilibrated by compressive stresses near the surface.[12] Also, some

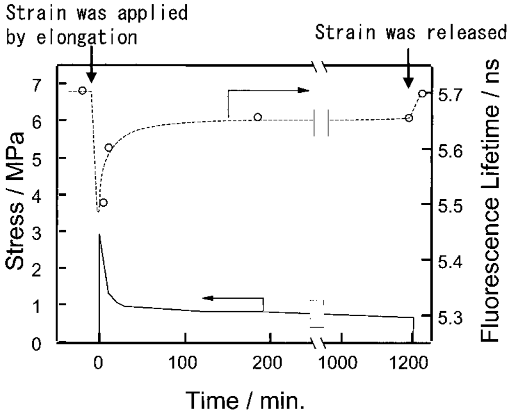

Figure 4 Temporal change in fluorescence lifetime and stress with a constant strain.

experimented results have shown that tensile stresses in the region close to the surface are found.[12,13] It should be noted that the calculations predict that the stresses near to the surface vary steeply within 200 or 300 μm. In our case, 99% of the excitation light was absorbed and/or scattered within 50 μm from the surface; therefore, it is reasonable that we measured the tensile stress very close the surface of the test pieces.

The fluorescence lifetimes and the stresses estimated by the estimation curve are shown in Figure 5. (The test piece was curved as shown in Fig. 1.) The residual stresses at the surface of the test pieces were 0.5–1.7 MPa in upsides and 0−0.5 MPa in undersides. The obtained residual stresses were larger in the upsides than in the undersides. This result might suggest the fact that the surface tensile stresses are related to the deformation of the test pieces.

The identical test piece was then annealed for 24 h at 100°C (above T_g). Figure 6 shows the fluorescence lifetimes and the residual stresses of the annealed test piece. The residual stresses estimated from the fluorescence lifetime were decreased, whereas the deformation of the sample almost disappeared during the annealing process. Thus, we concluded that the residual stresses estimated by the fluorescence lifetime are qualitatively correct.

CONCLUSION

This article describes the possibility of a new door to the nondestructive method for detecting residual stresses in polymer moldings. The obtained results suggest that 9MAn is a useful photoluminescent probe used to detect residual stresses on polymer products. The nondestructive measurement of the residual stress at the surface (even within 50 μm from the surface) is very important, because some kinds of the environmental stress cracking of injection moldings occurred at the molding's surface. We emphasize that the time-resolved fluorescence technique is useful in the application to practical analysis, such as quality inspection of polymer products of complicated shape.

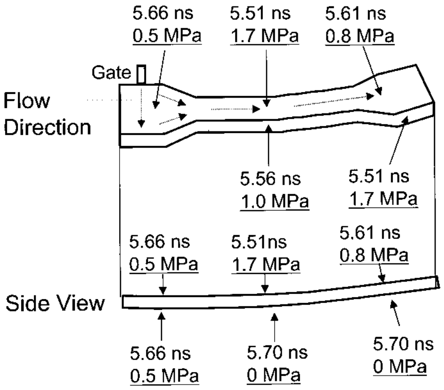

Figure 5 Fluorescence lifetimes and estimated stresses on the surface of the test piece.

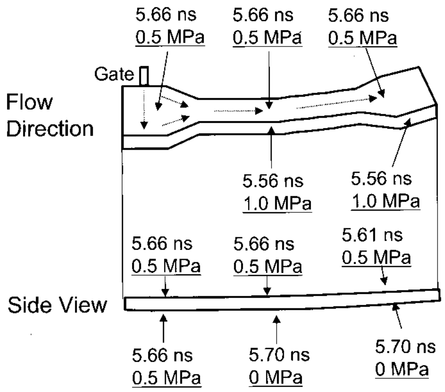

Figure 6 Fluorescence lifetimes and estimated stresses on the surface of the test pieces annealed for 24 h at 100°C.

REFERENCES

1. McKelvey, J. M. Polymer Processing; Wiley: New York, 1962.
2. Maxwell, B.; Rahm, L. F. Ind Eng Chem 1949, 41, 1988.
3. Hamada, H.; Tsunasawa, H. J Appl Polym Sci 1996, 60, 353.
4. Isayev, A. I., Ed., Injection and Compression Molding Fundamentals; Marcel Dekker: New York, 1987.
5. Gakukai, N. Z. In X-Ray Stress Analysis; Yourandou Co.: Tokyo, 1966.
6. Sato, N.; Takahashi, H.; Kurauchi, T. J Mater Sci Lett 1992, 11, 365.
7. Hetenyi, M. In Handbook of Experimental Stress Analysis; Wiley: New York, 1950.
8. Shiga, T.; Okada, A.; Takahashi, H.; Kurauchi, T. J Mater Sci Lett 1995, 14, 1754.
9. Ikawa, T.; Shiga, T. J Appl Polym Sci 1997, 66, 1569.
10. Shiga, T.; Narita, T.; Ikawa, T.; Okada, A. Polym Eng Sci 1998, 38, 693.
11. Glanvill, A. B. In Thermoplastics; Ogorkiewicz, R. M., Ed., ILIFFE Books: London, 1969, p 140.
12. Zoetelief, W. F.; Douven, L. F. A.; Ingen Housz, A. J. Polym Eng Sci 1996, 36, 1886.
13. Baaijens, F. P. T. Rheol Acta 1991, 30, 284.