Casting of Organic Glass by Radiation-Induced Polymerization of Glass-Forming Monomers at Low Temperature. II. Optical Strain of Remaining Stress Type

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Synopsis

Previously it was found that casting could be carried out efficiently without strain formation by radiation-induced polymerization of glass-forming monomers. Two types of strain were observed in casting: thermal stream type, which was studied previously, and remained stress type. In this report, the effect of various factors on the formation of remaining stress-type strain in radiation-induced casting polymerization was studied. It was found that the molecular weight of prepolymer did not affect strain formation, while prepolymer concentration and viscosity of the system had a serious influence on strain formation. It could be deduced that this type of strain formed as a result of remaining inner stress due to poor relaxation of the shrinking stress. It was realized that less volume shrinkage of glass-forming monomers accompanying casting polymerization reduced the strain formation of this type in radiation-induced casting polymerization at low temperatures.

INTRODUCTION

The authors have found various interesting characteristics in radiation polymerization of glass-forming monomers by radical mechanism[1,2] and have studied the application of these characteristics to the casting of organic glass by radiation in the supercooled phase at low temperature.[3] In the previous paper,[3] it was shown that cast polymer articles without any optical strain could be obtained by this method in a far shorter time (at a far greater rate) than in the catalytic method. It was also found that two types of optical strain formed in casting were the stream form and the block form.

The authors deduced that stream-form strain resulted from the thermal stream due to the unequal distribution of polymerization heat, and that in the polymerization at the supercooled phase this strain formation was retarded owing to a smaller thermal stream resulting from the high viscosity of the glass-forming monomers and to the low temperature of the reaction system.[4]

However, another type of strain (block-form strain) was observed in casting using aluminum plate frames or in the systems including prepolymer, crosslinking agent, or components smaller in thermoplasticity. In this report, the effect of various factors on block-type strain formation were studied using mainly hydroxyethyl methacrylate prepolymer to clarify the benefit of radiation casting at low temperature.
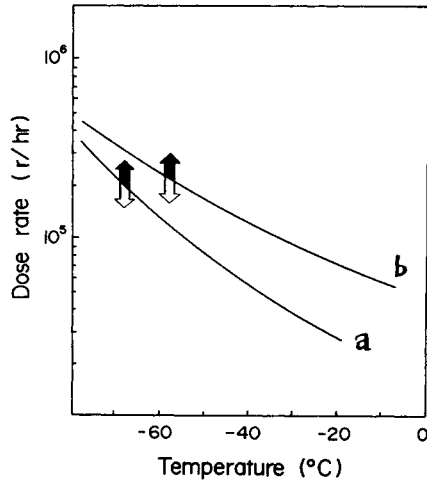
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Fig. 1. Effect of temperature on optical strain formation in casting polymerization of HEMA monomer and prepolymer systems: (a) casting of monomer; (b) casting of prepolymer; (↑) area of strain formation; (⇑) area of no strain formation. Total dose 1 × 10⁶ R/hr; sample scale: 160 × 80 × 15 mm; prepolymer concentration 10.8%.
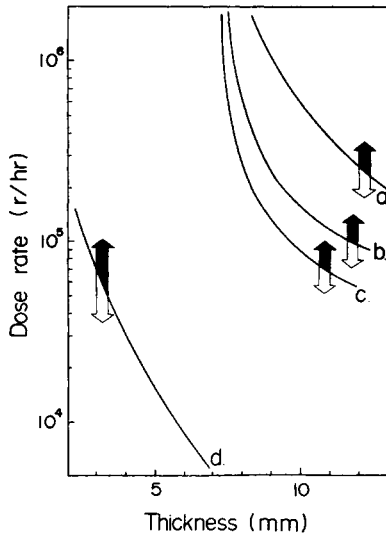

Fig. 2. Effect of thickness on strain formation in casting polymerization of HEMA monomer and prepolymer at various temperatures: (a) casting of prepolymer at −50°C; (b) casting of monomer at −50°C; (c) casting of prepolymer at 25°C; (d) casting of monomer at −25°C; (↑) area of strain formation; (⇑) area of no strain formation. Total dose 1 × 10⁶ R; sample scale 160 × 80 mm, prepolymer concentration 10.8%.

EXPERIMENTAL

Hydroxyethyl methacrylate (HEMA) and glycidyl methacrylate (GMA) (Mitsubishi Gas Chemical Co.) used in this experiment were purified by distillation under reduced pressure. Preparation of prepolymer was carried out in
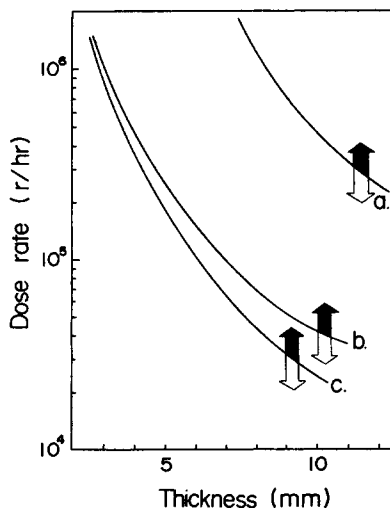
Fig. 3. Effect of thickness on strain formation in casting polymerization of GMA monomer and prepolymer at various temperatures: (a) casting of prepolymer at $-50°C$; (b) casting of monomer at $-50°C$; (c) casting of prepolymer at $25°C$; (↑) area of strain formation; (⇑) area of no strain formation. Total dose 1.5×10^6 R; sample scale 160×80 mm; prepolymer concentration 27.7%.
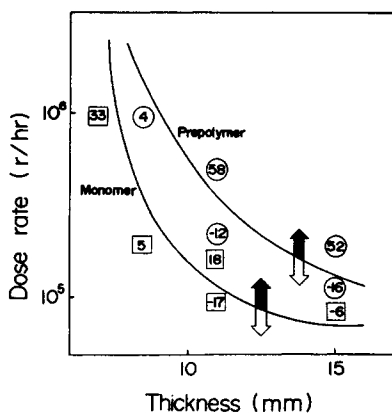

Fig. 4. Relation between boundary curve of strain formation and maximum temperature reached in center part of sample in casting polymerization of HEMA monomer and prepolymer: (O) casting of prepolymer; (□) casting of monomer; (↑) area of strain formation; (⇑) area of no strain formation. Polymerization temperature $-50°C$; total dose 1×10^6 R/hr; sample scale 160×80 mm; prepolymer concentration 10.8%.

a three-necked flasks by a catalytic method using 0.1–1.0% benzoyl peroxide at 60°–80°C.

N-Dodecyl mercaptan was added as chain transfer agent to prepare prepolymer having lower molecular weight.

The procedure of the casting polymerization, observation by photoelastic strain gauge, and measurement of the exothermic curve during polymerization were the same as previously described.[4] The viscosity of the prepolymer was measured by means of a B-type viscometer (Tokyo Keiki Co.).
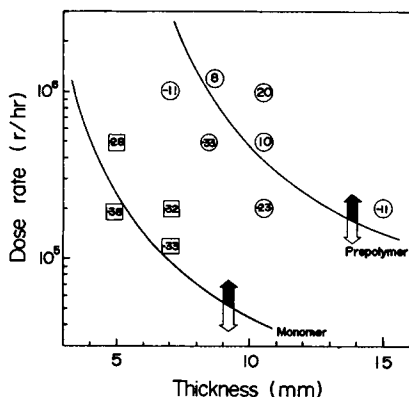
Fig. 5. Relation between boundary curve of strain formation and maximum temperature reached in center part of sample in casting polymerization of GMA monomer and prepolymer: (O) casting of prepolymer; (□) casting of monomer; (↑) area of strain formation; (⇑) area of no strain formation. Polymerization temperature −50°C; total dose 1.5 × 10⁶ R/hr; sample scale 160 × 80 mm; prepolymer concentration 27.7%.
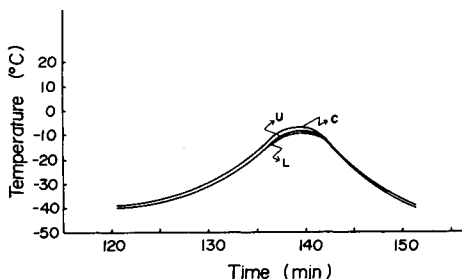

Fig. 6. Time–temperature relation curves in lower (L), middle (C), and upper (U) parts of sample during casting polymerization of HEMA prepolymer. Polymerization temperature −50°C; dose rate 2 × 10⁵ H/hr; sample scale 160 × 80 × 15 mm; prepolymer concentration 10.8%; viscosity of prepolymer system 2 × 10³ centipoises.

RESULTS AND DISCUSSION

Stress-Type Strain Formation in the Presence of Prepolymer

In the previous report,[4] stream-form optical strain (thermal stream-type strain) was investigated, and it was found that removal of polymerization heat as in casting using aluminum plate frames was effective in preventing strain formation. However, although thermal stream-type strain could be eliminated in such a system, another type of strain (block-form strain) was observed. It was also deduced that the high viscosity of glass-forming monomers was effective in retarding the stream-type strain formation. It was expected that addition of prepolymer might be effective for strain retardation owing to increased viscosity. Therefore, the effect of prepolymer on the boundary condition of strain formation was investigated, and the results are shown in Figures 1, 2, and 3.

It is evident that the boundary condition for strain formation was remarkably improved in the presence of prepolymer. Addition of prepolymer, as well as
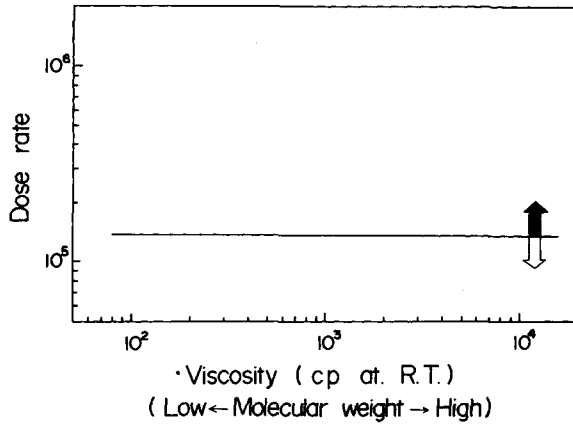
Fig. 7. Effect of molecular weight on strain formation in casting polymerization of HEMA pre-polymer: (↑) area of strain formation; (⇑) area of no strain formation. Total dose 1×10^6 R; sample scale $160 \times 80 \times 15$ mm; prepolymer concentration 13.1%; viscosity of prepolymer system 2×10^3 centipoises.
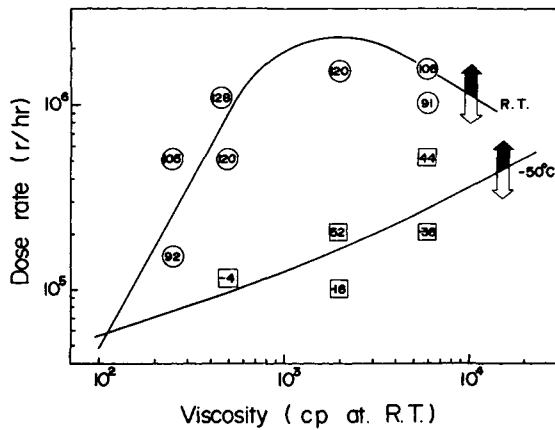

Fig. 8. Effect of viscosity on strain formation in casting polymerization of HEMA prepolymer: (↑) area of strain formation; (⇑) area of no strain formation; (O) maximum temperature reached in polymerization at 25°C; (□) maximum temperature reached in polymerization at −50°C. Total dose 1×10^6 R; sample scale $160 \times 80 \times 7$ mm; prepolymer concentration 13.1%.

removal of heat and low temperature, was demonstrated to be an effective way for preventing thermal stream strain. However, it was also recognized that thermal stream-type strain disappeared under almost all conditions in the presence of prepolymer, but block-form new strain mainly was observed in this system. This block-form strain was of the same type as observed in casting by aluminum plate frame. For example, in Figure 2, the boundary condition curves for monomer at −50°C and for prepolymer at 25°C were relatively near, but did not agree, though the viscosity of both systems was almost the same. The reason might be attributed to the difference in strain type and the mechanism of strain formation.
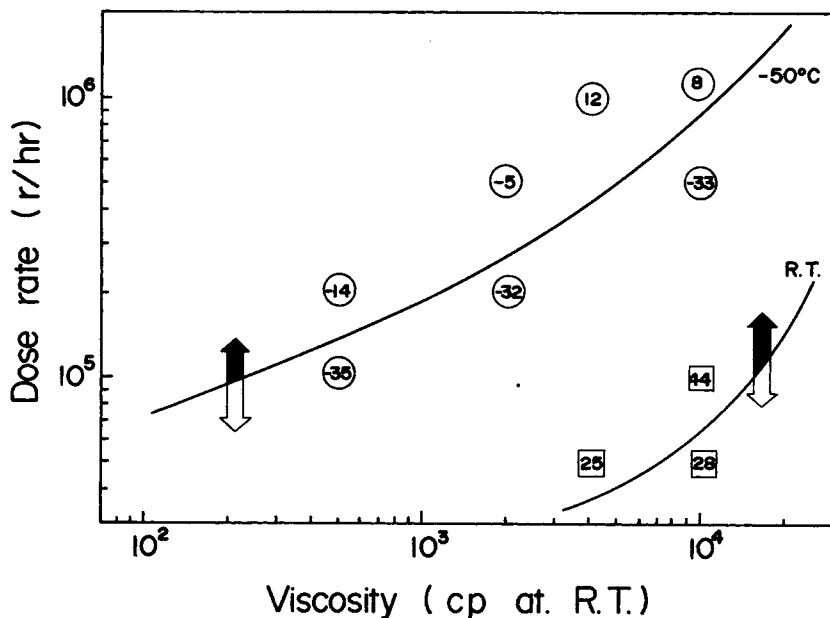
Fig. 9. Effect of viscosity on strain formation in casting polymerization of GMA prepolymer: (↑) area of strain formation; (⇡) area of no strain formation; (O) maximum temperature reached in polymerization at −50°C; (□) maximum temperatures reached in polymerization at 25°C. Total dose 1.5×10^6 R; sample scale $160 \times 80 \times 5$ mm at 25°C, $160 \times 80 \times 8.5$ mm at −50°C; prepolymer concentration 27.7%.

Relationship Between Maximum Temperature, Temperature Difference in Sample Parts, and Stress-Type Strain

In Figures 4 and 5, the maximum reached temperatures are shown in relation to the boundary condition of strain formation. It was noted that in the presence of prepolymer, no strain formed even at the relatively high maximum temperature at which thermal stream-type strain formed in the pure monomer system. For example, in casting of GMA, no strain formed under the condition of 10.5 mm sample thickness and −23°C maximum temperature in the prepolymer system, while strain formed under 7 mm sample thickness and −33°C maximum temperature in the monomer system.

The time–temperature curves in the lower, center, and upper parts of the sample are shown in Figure 6. According to the results of the figure, the temperature difference in the perpendicular direction was very small in the presence of prepolymer, even under the conditions of strain formation. All these facts suggest that the mechanism of strain formation in the presence of prepolymer differs from that of thermal stream-type strain. This type of strain could be called remaining stress-type strain, or inner stress-type strain. The effect of various factors on this type of strain formation is considered in the following section.
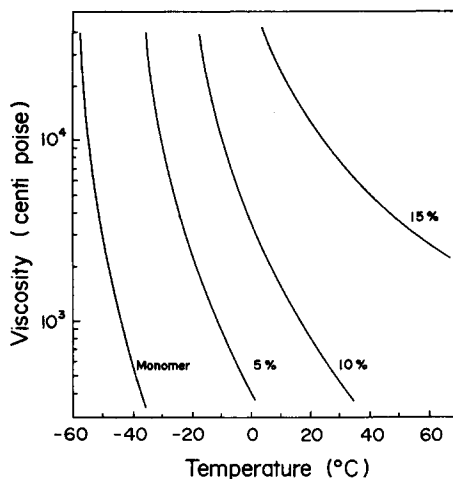
Fig. 10. Relation between viscosity of prepolymer system and prepolymer concentration in HEMA.

Effect of Molecular Weight of Prepolymer on Stress-Type Strain

The effect of molecular weight of prepolymer on stress-type strain was investigated. Three kinds of prepolymer having different molecular weights were prepared, and casting was carried out using these prepolymers at the same prepolymer concentration (13.1%) and constant viscosity which was controlled by variation of temperature in the range of −30 to −50°C. The result is shown in Figure 7.

It could be concluded that the molecular weight of prepolymer did not affect the stress-type strain formation in the studied range of molecular weights. As is well known, the glass transition temperature of polymers increases with increase in molecular weight in relatively small molecular weight polymers, but becomes constant with change in molecular weight in large enough molecular weight polymers. Of course, the glass transition temperature affects the stress relaxation; but it is considered that the change in molecular weight of the studied polymers resulted in no significant change in the glass transition temperature.

Effect of Viscosity of System on Stress-Type Strain

As it was ascertained that molecular weight has no effect on strain formation, the effect of viscosity on strain was investigated by changing the molecular weight of the prepolymer. The results are shown in Figures 8 and 9. According to the results of Figure 8, the stress-type strain formation became more difficult with increase in viscosity, at −50°C polymerization, while the boundary curve of strain formation had a maximum at room-temperature polymerization. The polymerization rate became smaller with increase in viscosity at −50°C, because no gel effect occurred at a viscosity of more than about 1000 centipoises and the polymerization rate decreased with increase in viscosity at a viscosity range higher
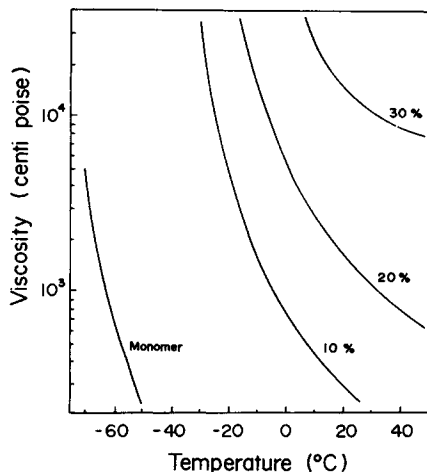
Fig. 11. Relation between viscosity of prepolymer system and prepolymer concentration in GMA.

than 1000 centipoises.[2] So, the increase in difficulty of strain formation with increase in viscosity at $-50°C$ could be attributed to the decrease in volume shrinkage velocity. But at room-temperature polymerization, the maximum polymerization temperature reached more than $100°C$ at a certain viscosity range (gel effect was possible under such conditions), and thermal stress relaxation occurred to decrease the strain formation. At room-temperature polymerization, a very high maximum temperature decrease occurred with increasing viscosity owing to a decrease of polymerization rate; and at higher viscosity range the ease of strain formation increased again due to the difficulty of stress relaxation. In GMA, the maximum temperature was low at room-temperature polymerization due to the small polymerization rate. So, the boundary curve at room temperature had no maximum in a given viscosity range, and the boundary curve at room temperature was always situated at a lower position than that at $-50°C$ polymerization.

Figures 10 and 11 show the temperature dependence of viscosity in HEMA and GMA monomers and in prepolymer-containing systems. In the presence of prepolymer, viscosity was much higher than that of the monomer, for example, the 10% prepolymer system has a large viscosity of 10^4 centipoises, even when the temperature of the system is raised to $-10°C$. Furthermore, the viscosity of the system at higher conversion would be far greater. This might be the reason why no thermal stream-type strain appeared in the presence of prepolymer even when the temperature was very high. The viscosity and its temperature dependence in GMA was much lower than that in HEMA. This probably was the reason why in Figure 5, the maximum temperature at boundary condition of strain formation was much lower and optical strain formed much easier than in HEMA.

Effect of Prepolymer Concentration on Stress-Type Strain

The effects of molecular weight and viscosity on stress-type strain were clarified. Increase in viscosity had a retarding effect on strain formation, owing to
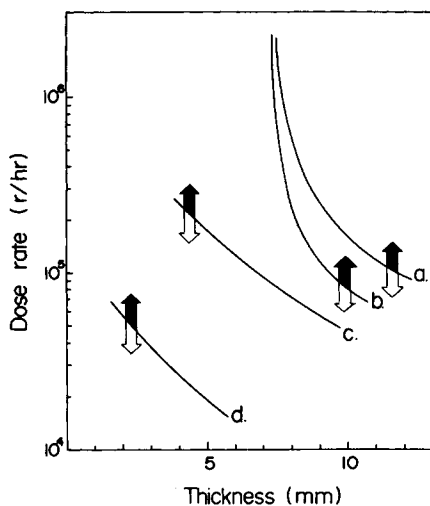
Fig. 12. Effect of prepolymer concentration on strain formation in casting polymerization of various prepolymer system: (↑) area of strain formation; (⇑) area of no strain formation; (a) prepolymer 17.8%, HEMA prepolymer system; (b) prepolymer 10.8%, HEMA prepolymer system; (c) prepolymer 42.3%, MMA prepolymer system; (d) prepolymer 12.9%, MMA prepolymer system. Polymerization temperature 25°C; total dose 1×10^6 R; sample scale 160×80 mm.

a decrease in polymerization rate and perhaps owing to a decrease in volume shrinkage rate. As shown in the previous report, volume shrinkage accompanying polymerization was much smaller in low-temperature polymerization of glass-forming monomers. It was deduced that volume shrinkage might be the essential factor of stress-type strain formation, because inner stress or remaining stress would be the result of shrinkage stress caused by volume change. Viscosity or polymerization rate could be related to quantity of shrinkage during polymerization.

The effect of prepolymer concentration on stress-type polymerization was investigated, and the result is shown in Figure 12. It was observed that the

Table I
Effect of Various Factors on Stress-Type Optical Strain Formation in Radiation-Induced
Casting Polymerization

Factor	Dependence of strain formation on the factor
Maximum inner temperature reached	Independent
Temperature difference between sample parts	Independent
Viscosity of reaction system	Dependent
Molecular weight of prepolymer	Independent
Concentration of prepolymer	Dependent
Quantity and rate of volume contraction during polymerization	Dependent

difficulty of stress-type strain formation increased with increasing prepolymer concentration. The polymerization was carried out at constant viscosity by varying the molecular weight of prepolymer. Since the polymerization rate was similar because of same viscosity and same temperature, the effect could be attributed to the decrease in volume shrinkage. This result suggested that the stress-type strain formed as a result of the freeze of shrinkage stress without enough relaxation during polymerization. The mechanism of this strain formation differs completely from that of thermal stream-type strain. The quantity and velocity of volume shrinkage are essential factors of this strain formation. It is proposed that the reason why in low-temperature casting this type of strain hardly formed might be the small volume shrinkage during casting polymerization of glass-forming monomers. More detailed analysis of this type of strain-forming conditions will be discussed in the future in relation to the effect of other factors such as dose rate distribution and crosslinking formation of polymer on the stress relaxation mechanism.

CONCLUSIONS

The effect of various factors on the formation of stress-type (block type) optical strain was studied in casting polymerization of HEMA and GMA prepolymer and monomers.

This type of strain was predominantly observed in casting polymerization of prepolymer system. The dependence of this type of strain formation on various factors was summarized in Table I. The detailed thermal and rheological analysis of optical strain formation will be discussed in the near future.

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