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Novel approach to reducing stress-caused birefringence in polymers

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Polymers have been explored extensively in fabricating planar waveguides which are playing a greater role in the telecommunications industry [1, 2]. Except for rubbery polyacrylate [3], all reported waveguide polymers occur in a glassy state and are associated with a high birefringence. In order to reduce birefringence to a level that is suitable for waveguide fabrication, researchers have modified existing polymer systems chemically to control or compensate for molecular orientation [4, 5]. This approach has significantly reduced orientation-related birefringence, although the requirement for quality waveguides has not yet been met, the reason being that, in addition to orientation-related birefringence, there is much stress-related birefringence in polymers. Unless this type of birefringence is reduced or eliminated, polymers will still not be suitable for waveguide applications. This paper describes a novel attempt to overcome stress-caused birefringence in polymers.

Three types of polymers, namely, sol-gel, acrylic and epoxy, were used. Sol-gel materials were synthesized in house for waveguide fabrication using diphenylsilanediol and 3-glycidyloxypropyltrimethoxysilane, while acrylic was used in the form of coating materials, and epoxy was formulated using bisphenol F and novolac epoxy resins. These polymers were spin coated on 4 inch-diameter (102 mm) silicon wafers to form thin glassy films, 7–20 μm thick. The resulting polymer films were exposed to compressed CO_2 at 308 K for 48 h under different pressures, namely 8.3 MPa for sol-gel materials and acrylic, and 10.3 MPa for epoxy. Following the treatment, the gas was slowly released to atmospheric pressure so that the samples could be removed for optical testing. The optical indices of the polymers were measured at a wavelength of 1550 nm using an equipment from Metricon, and the glass transition temperature T_g of the polymers under compressed CO_2 was measured by using a high-pressure DSC from Setram as described elsewhere [6]. With a careful calibration and repeating testing, an index reproducibility of better than 5×10^{-5} was achieved in the index measurement. Meanwhile, a reproducibility of 0.1°C was achieved for T_g measurement.

It is known that birefringence in polymers is related to both molecular orientation and stress. Stress-related birefringence arises from the stress sensitivity of polymeric optical properties, as follows:

$$\Delta n = C\sigma \tag{1}$$

where Δn represents birefringence, C is the photoelastic constant of polymers, and σ is the stress generated in polymers.

Stress in polymers originates from two sources, namely shrinkage and mismatched thermal expansion. Shrinkage is caused by chemical reactions occurring during waveguide fabrication, since the reactive end groups of polymer oligomers, which are used in waveguide fabrication, shrink as they react. Mismatched thermal expansion occurs when processing is carried out at high temperature and the coefficient of thermal expansion (CTE) of polymer is much higher than that of waveguide substrate, which is often silicon. Table I shows the reaction shrinkage, the CTE, and Young's modulus for some polymers. By calculating shrinkage-related and mismatched CTE-related stresses using equation $\sigma = \varepsilon E$, it is possible to estimate the birefringence caused by chemical shrinkage (Δn_{cs}) and mismatched CTE (Δn_{cte}), as shown in Table I, where $P = 4 \times 10^{-6}$ (MPa^{-1}) of acrylic [7] was used for all polymers.

As can be seen from the data, reaction shrinkage and mismatched CTE can cause a total birefringence in the order of 10^4. This value is unacceptable for applications in which a birefringence of 5×10^{-5} or less is required for waveguide materials. In fact, even if orientation-related birefringence is completely eliminated using chemical modification, the remaining stress-related birefringence is still too high for polymers to be deemed usable. The technology developed in this work was a post-treatment process conducted at low temperatures that accelerated the stress relaxation in polymers to such an extent that stress decay could

TABLE I Estimation of stress-caused birefringence in polymers

Materials	Linear curing shrinkage (%)	CTE at $< T_g$ (10^{-6}/° C)	Young's modulus (GPa)	Δn_{cs} (10^{-4})	Δn_{cte} (10^{-4})	Δn_{sum} (10^{-4})
Sol-gel	1–2	10–20	3–4	1.2–3.2	0.2–0.4	1.4–3.6
Acrylic	2–3	50–70	1.5–2	1.2–2.4	0.6–1.1	1.5–3.0
Epoxy	1–3	17–22	2–3	0.8–3.6	0.3–0.5	1.1–4.1

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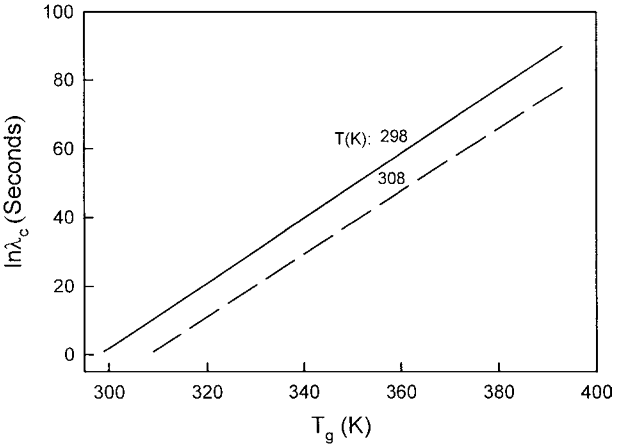

Figure 1 Relaxation time of polymers at various temperatures as a function of polymeric glass transition temperatures.

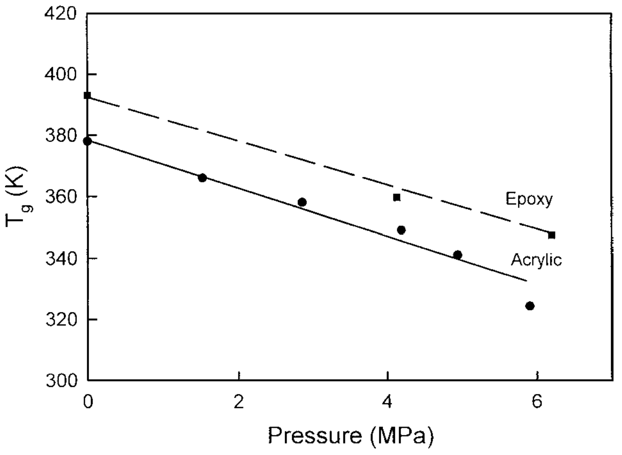

Figure 2 Effect of CO_2 pressure on the glass transition temperatures of acrylic and epoxy.

occur within a short period. Stress relaxation is well known in polymers because of their molecular structure. When polymers occur in a glassy state, stress relaxation follows [8]:

$$\sigma(t) = \frac{\varepsilon G_0}{e}\left[\frac{t}{\lambda_t}\right]^{\beta} \tag{2}$$

$$\ln \lambda_t \approx \frac{\Delta\mu^*}{k}\frac{T_g}{T_g - T_0}\left[\frac{1}{T} - \frac{1}{T_g}\right] \tag{3}$$

where σ and ε are identical to values in Equations 1 and 2, G_0 is the modulus, t is the time in seconds, λ_t, is the characteristic relaxation time, β is the Kohlrausch-Williams-Watts (KWW) parameter and is often found to be approximately 0.5 for polymers [8], Δu^* is the activation energy for rotation relaxation of one conformer without cooperativity at $T_0 = 0$ K, T_g is the glass transition temperature, and k is the Boltzmann constant. There is a relationship between t and $\lambda : t/\lambda > 1$.

Applying a Δu^* value of 117 kJ/mol with $T_g = 50 + T_0$ [8], the characteristic relaxation time as a function of T_g can be calculated as shown in Fig. 1. It can be seen that the relaxation time decreases exponentially with decreasing T_g, which is the temperature at which polymer chain segments gain full mobility. For instance, the relaxation time at 298 K is 2.7×10^{35} h when $T_g = 393$ K, but 9 h when $T_g = 309$ K. Such a decrease in relaxation time will sharply accelerate the stress relaxation process as can be seen from Equation 3, thus reducing the stress in polymers. This indicates that reducing the glass transition temperature of polymers can help decrease the stress relaxation time to a practical scale so that post-treatment can be used to reduce or eliminate polymer stress and its associated birefringence in polymers.

Plasticizing polymers using compressed gases is an easy way to achieve this goal. In this process, compressed gases dissolve into polymers and reduce their molecular interactions and thus T_g. When the pressure is released slowly, the dissolved gases escape without any trace nor any effect on physical properties [9]. Fig. 2 shows the glass transition temperature T_g of acrylic and epoxy as a function of CO_2 pressure. The T_g of sol-gel materials is difficult to measure using a DSC because of the high crosslinkage in the material. However, the material is partially acrylic based and should exhibit plasticization behavior similar to that of acrylic. The T_g of acrylic is reduced from an original value of 378 to 324 K under 5.9 MPa of CO_2, while the T_g of epoxy is reduced from an original value of 393 to 347 K under the same pressure. Increasing the above CO_2 pressure helps further reduce the T_gs to temperatures that are practical for processing. In this work, the processing temperature of 308 K was chosen to avoid gas condensation at high pressure, and the required CO_2 pressure for a targeted T_g of 318 K at that temperature was estimated using Equation 3 and the resulting relationship between the T_g and the pressure P as: 8.0 MPa for the acrylic and 10.0 MPa for the epoxy. Under these conditions, the relaxation time of the polymers could be reduced to a few hours as can be seen in Fig. 2.

The above parameters were used to treat sol-gel materials, acrylic, and epoxy with CO_2 under the designed gas pressures. Table II shows their birefringence following the treatment. The birefringence in polymers was reduced by the treatment, and the birefringence reduction was similar to the estimated stress-caused birefringence. It indicates that stress-related birefringence and thus stress can be substantially reduced or eliminated in polymers by treating them with compressed CO_2 at ambient temperatures. For highly crosslinked polymers, such as sol-gel materials, which have a low degree of molecular orientation and thus low orientation-related birefringence, the process can help reduce total birefringence to a level that is suitable for waveguide

TABLE II Effect of CO_2 on the birefringence of polymers

Materials	Treatment	n_{TM}	n_{TE}	Δn (10^{-4})	$\Delta n_0 - \Delta n_t^a$ (10^{-4})
Sol-gel	Original	1.5157	1.5161	4	–
	CO_2 treated	1.5146	1.5146	0	4
Acrylic	Original	1.5305	1.5337	32	–
	CO_2 treated	1.5309	1.5337	28	4
Epoxy	Original	1.5729	1.5734	5	–
	CO_2 treated	1.5694	1.5698	4	1

[a] Birefringence reduction after the treatment.

applications. For the polymers with a high degree of molecular orientation, the technology should include orientation-related chemical modification for waveguide applications because orientation is usually the key factor of birefringence.

The advantages of using CO_2 to reduce stress and its related birefringence are that the process can be completed at low temperature, and the processing time is controllable. Because of its compatibility with most polymers, CO_2 is usually highly soluble in polymers, and is thus effective in reducing the glass transition temperature, as well as stress and birefringence of polymers. The gas is environmentally clean and cost-effective. It can easily be removed from polymers by simply releasing the gas pressure. While the above stress technology was developed for polymer waveguide fabrication, it can actually be used in a number of areas where stress reduction is required. For instance, in the glass fiber-reinforced polymer composites, stress caused by reaction shrinkage and mismatched CTE between glass and polymer has been a problem. This technology could be used to reduce or eliminate the stress as a post-treatment process as demonstrated above or as an *in situ* treatment process for the molding in a pressured environment.

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