Optimized curing process for perfluorinated acrylic polymer optical waveguide

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Abstract
UV polymerization of perfluorinated acrylic polymer (ZPU12) for optical waveguide is studied by FTIR spectroscopy. With 15 \textmu m planar thickness of the polymer material ZPU12-450 and 6 \textmu m thickness of ZPU12-456 requires 8 and 3 min respectively to be fully UV cured with low intensity of 14 mW/cm\textsuperscript{2} at room temperature in the presence of nitrogen flowing. These results show the delay of curing reaction with increasing thickness or depth in the optical waveguide. Besides, a thickness of 6 \textmu m of ZPU12-456 requires about 4 min to be fully UV cured with intensity of 12 mW/cm\textsuperscript{2}. The conversion rate slows down on the decreasing of curing intensity. The polymerization also shows that the UV induced polymerization is faster than thermal curing reaction. The refractive indices of ZPU12-450 is around 1.450 and most of the refractive indices of ZPU12-456 are between 1.455 and 1.456. On the other hand, the thermooptic coefficient of ZPU12-456, $dn/dT$ is $-2.105 \times 10^{-4}/\text{C}$ and $-2.090 \times 10^{-4}/\text{C}$ for TE and TM polarization, respectively. The thermooptic coefficient of ZPU12-450, $dn/dT$ is $-2.737 \times 10^{-4}/\text{C}$ and $-2.465 \times 10^{-4}/\text{C}$ for TE and TM polarization, respectively.

Keywords: Optical waveguide; Thermal; UV curing

1. Introduction

Recently, polymeric optical waveguide have attracted much attention for use in optical interconnects and in integrated devices for optical communications in the excess network and home network areas [1,2]. Polymer materials offer a number of interesting features for fabrication of optical waveguides compared to silica glass. Silica glass has a low optical loss of below 0.01 dB/cm as well as high thermal stability. Organic polymers, by contrast, have attracted a lot of attention due to their ease of fabrication and structure flexibility. These are important factors with regard to their use in packaging and optical interconnects. In addition, the thermooptic (TO) coefficient of polymers is an order of magnitude larger than silica glass and some of non-aromatic polymers have very low birefringence. These are desirable characteristics in terms of their application to optical integrated devices such as TO switch. Classes of polymers that are used in integrated optics include acrylates, polycarbonates, polyimides and olefins.

The most simple and widely used method of polymer formation is radical-chain addition polymerization. Polymerization involves initiation, propagation, transfer and termination steps. Initiation is the step where initiating radicals are formed by external stimulation such as light, heat, gamma-radiation and redox process. UV radiation curing offers a number of advantages over other methods, such as solvent-free formulation, low energy consumption, ambient temperature operations and tailor-made properties of the photopolymer. Indeed most of the UV curing resin systems are made of acrylic monomers and oligomers due to their high reactivity and low cost. Nowadays, highly crosslinked polymers can be produced within seconds by photoinitiated polymerization of multifunctional acrylic monomers and oligomers [3]. Photocalorimetry [4] and real time infrared spectroscopy [5] are powerful tools for...
studying the complex kinetics governing crosslinking photopolymerization.

In this paper, we report on the curing time of perfluorinated acrylic resins (ZPU12-450 and ZPU12-456) for different thickness of coating in order to get the optimum curing time for the desired thickness by using FTIR spectroscopy. Insufficient curing can cause poor adhesion of the coating to the substrate and affects the properties of the layer, such as refractive index. These resins is chosen as the core and cladding materials for TO switch because of their low propagation loss, high environmental stability, precise control of refractive index, good and easy ability to process, excellent adhesion properties, and easy control of film thickness. So far, TO switch such as directional coupler switch [6] and digital optical switch [7] has been fabricated by using this material.

TO polymer waveguide switches are advantageous compared to silica-based TO switch for low-speed applications as bypass or protection switches. First, large optical devices can be made more easily because polymer waveguides are easy to fabricate compared to silica-based waveguides. Second, the TO effect of polymers is ten times larger than silica [8]. TO coefficient is \(-10^{-4}/\text{C}\) for polymers and \(-10^{-5}/\text{C}\) for silica [9]. This means that the refractive indices of polymers are highly dependent on the temperature. Therefore, using polymers instead of silica can significantly reduce the electrical power needed for switching. Conventional silica TO switches require a large amount of electrical power, 400–500 mW [10]. In contrast, switch power as low as 5 mW for a polymeric Mach-Zehnder switch has been demonstrated [11].

In UV curing, a liquid acrylic resin is transformed almost instantly into solid polymer by exposure to UV light. Scheme 1 shows the mechanism of crosslinking reaction of ZPU12-RI, where Rf represents various perfluorinated compound and Ro is free radical species. The HC=CH double bond is attacked by free radical species induced by photoinitiator and turned to become CH–CH single bond. However, it is unstable and reactive because it has radical on CH–CH single bond. Therefore, the intermediate radical species will react with other CH=CH double bond, which makes the long chain polymeric network (chain propagation reaction) occurred. The final termination reaction arises when the two reactive species bonded together.

2. Experimental conditions

Photopolymerization experiments have been carried out with perfluorinated acrylate (ZPU12-450 and ZPU12-456), which are obtained from Zenphotonics Company. These resins are used as received. The resins are dispensed onto a cleaned silicon substrate, spun to achieve desired film thickness, exposed to UV light with spectral range from 350 to 450 nm and intensity of 14 mW/cm² in an irradiation chamber with nitrogen flowing, and finally baked at 160 °C for an hour on a hotplate. Infrared spectra are recorded with a UMA 400 IR microscope attatched to the Digilab Excalibur FTS 3000 FTIR system under dry air purge. High sensitivity mercury cadmium telluride (MCT) detector with spectral resolution of 8 cm⁻¹ has been set. When the acrylate coating is exposed to UV, the absorption band will decrease slowly due to dissappearance of C=C double bond of acrylic polymer. For example, Fig. 1 shows the decrease of IR band during UV curing of acrylate coating. The degree of conversion (x) is directly related to the decrease of IR absorbance, and was calculated from equation
Conversion, \( x(\%) = \frac{A_0 - A_t}{A_0} \times 100 \quad (1) \)

where \( A_0 \) and \( A_t \) represent the area of the IR band centered at 1636 cm\(^{-1}\), before and after UV exposure at time \( t \).

3. Results

Figs. 2 and 3 show the FTIR absorption spectra of 6 \( \mu \)m of ZPU12-456 before and after curing at different intensity of 14 and 12 mW/cm\(^2\). It can be seen that the functional group of acrylate, C=O (carbonyl group, about 1700/cm) did not change before and after curing process. The HC=CH double bond with stretching vibration mode at 1636/cm was attacked by free radical species induced by photoinitiator and then turned to the CH–CH single bond. So, the C=CH double bond peak was disappeared after curing as shown in IR spectra. Besides, another peak shown in 807/cm, which was out of plane vibration mode of C=C–H (monosubstituted C–H bond) was disappeared after curing.

The main reasons for performing the UV curing of coating is not only to speed up the curing process, but also to obtain tack-free surface. Fig. 4 shows the intensity profile of conversion of acrylic polymer for 6 \( \mu \)m thickness of ZPU12-456 coating. It clearly demonstrates that 6 \( \mu \)m of coating required 3 and 4 min to be fully UV cured at 14 and 12 mW/cm\(^2\), respectively. The conversion rate considerably slows down on the decreasing of the intensity.

Homogeneous through cure of acrylic polymer is essential for attaining optimum properties. In order to achieve good through cure of the coating UV light has deeply to penetrate into the layer. Fig. 5 shows the FTIR spectra of 15 \( \mu \)m of ZPU12-456 before and after curing. Fig. 6 shows the depth profile of conversion of acrylic polymer for 6 and 15 \( \mu \)m thickness of coatings. It was obvious that the 6 and 15 \( \mu \)m coatings were fully UV cured at 3 and 8 min, respectively with intensity of 14 mW/cm\(^2\). These results reflect the delay of the curing reaction with increasing depth in the coating.

A number of factors are expected to affect the inhibitory process of acrylic resins, such as the oxygen content of atmosphere, the rate of air diffuses into the coating.
sample, which depends on the resin viscosity and on the temperature, the film thickness, and the duration of polymerization [12]. Therefore, we should define the key parameters which will affect the polymerization in order to get the best film quality.

The influence of the UV crosslinking on the polymer when polymerization takes place in the presence of air has already been investigated [13]. Oxygen inhibition causes numerous deleterious effects on free-radical formed by photolysis of the initiator are rapidly scavenged by oxygen molecules to yield peroxylradicals. These species usually abstract hydrogen atoms from the polymer backbone to generate hydroperoxide. This premature chain termination will modify the mechanical properties of the film. Consequently, higher UV energy is needed to consume the oxygen dissolved in the resin [12].

The most effective way to overcome oxygen inhibition is to work in an inert atmosphere. For example, by flushing the irradiation chamber with nitrogen and carbon dioxide. In our experiment, the nitrogen gas is used to diffuse through the film during flowing step with rate of 12 ml/min before (approximately 3 min) and during curing process. The gas replaces the oxygen dissolved in the sample. As nitrogen molecules are smaller than carbon dioxide molecules, their penetration into the sample will be easier and efficient [12]. If UV curing process is performed in an inert atmosphere, an effective polymerization can be achieved by means of low intensity UV lamps, in particular at the coating surface, which receives the most intense light. Thus, low light intensity 14 mWcm\(^{-2}\) is used to cure the polymer. This amount of intensity was acceptable according to technical data sheet provided by Zenphotonics Company, where the polymer should be cured at the range of intensity 10–16 mWcm\(^{-2}\).

The other factors that may affect the curing process is temperature. The acrylic resin has viscosity of 150–300 cps at 25 °C. At high temperature, the viscosity decreases. However, it will amplify oxygen inhibitory effect by accelerating the oxygen diffusion into the film [12]. This phenomenon competes with a higher molecular mobility which accelerates the polymerization. In contrast, the viscosity increases at low temperature, thus the polymerization proceeds significantly slower than at room temperature. Therefore, the irradiation conditions have been intentionally selected so as to overcome oxygen inhibition. The polymerization was performed at room temperature and strongly inhibited in the presence of air by flushing irradiation chamber with nitrogen.

![Fig. 6. Depth profile of conversion of the acrylic polymer for 6 and 15 µm coating at UV intensity of 14 mW/cm\(^2\).](image)

![Fig. 7. FTIR absorption spectra for 15 µm coating after 7 min of UV curing and an hour of postbaking.](image)

![Fig. 8. Refractive index of acrylic polymer under different UV curing time.](image)
In most thermally induced polymerization and curing reactions, an increase of temperature leads to an increase of both ultimate conversion and the reaction rate. Fig. 7 shows the FTIR absorption spectra of a 15 μm coating was not fully cured after 7 min of UV curing and was fully cured after an hour of postbaking. It can be seen that UV curing reaction is performed faster than thermal curing reaction. Besides, the two disappeared peaks after fully UV cured in Fig. 5 are same as after postbaking in Fig. 7. It means that the mechanism of crosslinking was terminated. The purpose of postbaking process in our work was to harden the coating.

Fig. 8 shows the refractive index of acrylic polymer under different UV curing time. It can be seen that refractive indices of ZPU12-450 are around 1.450 and most of the refractive indices of ZPU12-456 are between 1.455 and 1.456. We found that the refractive indices of acrylic polymer are not much change if the polymers are being cured at the range of intensity 10–16 mW/cm².

Fig. 9 shows the refractive index of acrylic polymer due to variation of temperature. The refractive index of acrylic polymer decreases linearly when the temperature of temperature controller of prism coupler increased. The TO coefficient of ZPU12-456, dn/dT is \(-2.105 \times 10^{-4}/^\circ C\) and \(-2.090 \times 10^{-4}/^\circ C\) for TE and TM polarization respectively. Besides, the TO coefficient of ZPU12-450, dn/dT is \(-2.737 \times 10^{-4}/^\circ C\) and \(-2.465 \times 10^{-4}/^\circ C\) for TE and TM polarization, respectively.

4. Conclusion

We have studied the curing time of perfluorinated acrylic polymer for different UV intensity and thickness of coating in order to get the optimum curing time. 6 μm of ZPU12-456 coating requires 3 and 4 min to be fully UV cured at 14 and 12 mW/cm², respectively with nitrogen flowing at room temperature. On the other hand, 15 μm of ZPU12-450 and 6 μm of ZPU12-456 required 7 and 2 min, respectively to be fully cured at intensity of 14 mW/cm². UV curing reaction is faster than thermal curing reaction. Results from FTIR spectroscopy are similar as IR spectra given by Zenphotons Company. The refractive indices of ZPU12-450 are around 1.450 and most of the refractive indices of ZPU12-456 are between 1.455 and 1.456. The TO coefficient of ZPU12-456, dn/dT is \(-2.105 \times 10^{-4}/^\circ C\) and \(-2.090 \times 10^{-4}/^\circ C\) for TE and TM polarization respectively. Besides, the TO coefficient of ZPU12-450, dn/dT is \(-2.737 \times 10^{-4}/^\circ C\) and \(-2.465 \times 10^{-4}/^\circ C\) for TE and TM polarization, respectively.

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