Next-Generation Polymers for High Power UV Replicated Optics

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1. Abstract

Several polymers were evaluated as candidate materials for UV laser optics. The manufacture of glass optics such as distributed phase plates and diffractive axicons by conventional optical fabrication techniques is costly and time-consuming. The use of moldable polymers instead of glass in these applications would greatly decrease cost and production time.

For a polymer optic to be viable, it would need to have high transmission at an optical path length of several hundred microns and a high laser damage threshold (>2 J/cm^2) at 351 nm. Polymers were blade-coated onto glass substrates at varying film thickness, and their optical transmission was measured in the UV. Two polymers (Sol Epoxy NB2908-51C and Resin Design 071607-D2) were found to have absorption coefficients that correspond to a transmission of > 98% at 351 nm for a 20 μm thick polymer layer. The Resin Design material was found to have a laser damage threshold of 2.8 J/cm^2 at 351 nm; the laser damage threshold of the Sol Epoxy material has yet to be determined. Both polymers have been shown to release cleanly from Teflon®. Future research will look more closely at the moldability of current materials and expand the search for additional new materials.

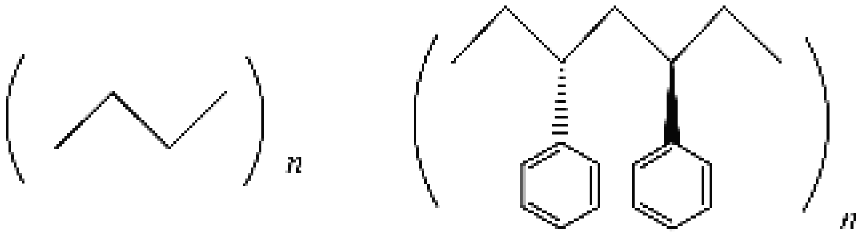
2. Introduction

The concept of a polymer-based optic is not a new idea. Over 20 years ago, an effort was made at LLE to fabricate distributed phase plates (DPP's) for use on the OMEGA laser at 351 nm using thermosetting epoxy materials, but these devices suffered from insufficiently high laser damage threshold upon scale-up to large aperture fabrication for a variety of reasons [1]. Advances in materials technology in the area of UV-transparent polymers now make it feasible to re-examine the viability of making such devices for diffractive/refractive optics for use in the Omega Laser Facility.

There are many methods for patterning optics; one of the fastest and cheapest is optical replication. This process involves patterning an optic from a master mold. Patterning of glass-based optics is accomplished by techniques such as laser writing, multiple mask lithography, or small-tool deterministic polishing, all of which utilize a piece-by-piece process that is costly and time consuming. Polymer-based optics can be produced by optical replication, which is a process that lends itself well to rapid and cost-effective manufacture of optics on a large scale [2]. The ideal polymer material for such an application needs to have a number of important physical properties: (1) as high a transmission at 351 nm as possible at long optical path lengths (up to several hundred microns); (2) excellent laser damage resistance in the UV; (3) mechanical properties amenable to surface pattern generation and replication by molding or stamping, and (4) commercial availability with low raw materials cost. This work concentrated on a survey of commercially available materials for the purpose of identifying which candidates were capable of meeting these key requirements.

3. Background

There are many chemical classes that can undergo polymerization reactions; some typical examples include carbonates, urethanes, epoxides, alkenes, and halogenated alkenes. To achieve high UV transparency, polymers need to have certain chemical properties. Most polymers are composed of long chains of carbon-carbon bonds, which can differ in bond order (e.g., single, double, or triple- bonds between each carbon atom). Molecular structures composed entirely of carbon-carbon single bonds (C-C) are highly UV transmissive down to ~ 200 nm; carbon-carbon double bonds (C=C) that are isolated from each other in a carbon chain by multiple intervening carbon-carbon single bonds (e.g., -C=C-C-C-C-C=C-) also absorb deep in the UV (~204 nm) [3]. However, when C=C bonds are separated by only one C-C unit, (e.g. –C=C-C=C-) they are termed to be in "conjugation" and the absorption spectrum is shifted to longer wavelengths. From the quantum chemistry viewpoint, conjugation of double bonds is manifested by the overlap of available p-orbitals across a sigma bond. When a double bond exists only one sigma bond away from another double bond, the p-orbitals can overlap. This overlap allows the electrons in the overlapping orbitals to be delocalized between each other, forming a π-bond. This electron delocalization results in stabilization of the molecule; the more extensive the delocalization, the more thermodynamically stable the molecule is. However, this more extensive electron delocalization also results in an increased optical absorption in the UV, which would be undesirable for the intended application. Ideally, a completely aliphatic (free of double bonds) material would be the most desirable [3]. Two examples of these cases are shown below in Fig 1. Polyethylene (structure "a") is aliphatic and has almost no absorption in the UV, whereas polystyrene (structure "b") has benzene rings that contain double bonds in conjugation, and has an appreciably higher UV absorbance.



(a) Polyethylene

(b) polystyrene

Fig. 1: The molecular structures of polyethylene (a) and polystyrene (b). The fully saturated (aliphatic) carbon skeleton of polyethylene makes it absorb significantly less in the UV than does polystyrene.

Materials with carbon-halide bonds are also to be avoided, as many of these bonds absorb in the UV. The very common commercial polymer polyvinyl chloride (PVC), shown in Fig. 2, is prepared by polymerization from a halogenated alkene. The carbon-chlorine bond is sensitive to UV light, and breaks down to form chlorine as a free radical, which is highly reactive and causes structural rearrangements and degradation of the polymer. These molecular rearrangements produce an increase in both UV and visible absorption, causing the material to become yellow.

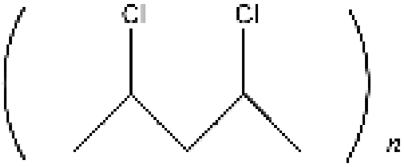


Fig. 2: The molecular structure of polyvinyl chloride.

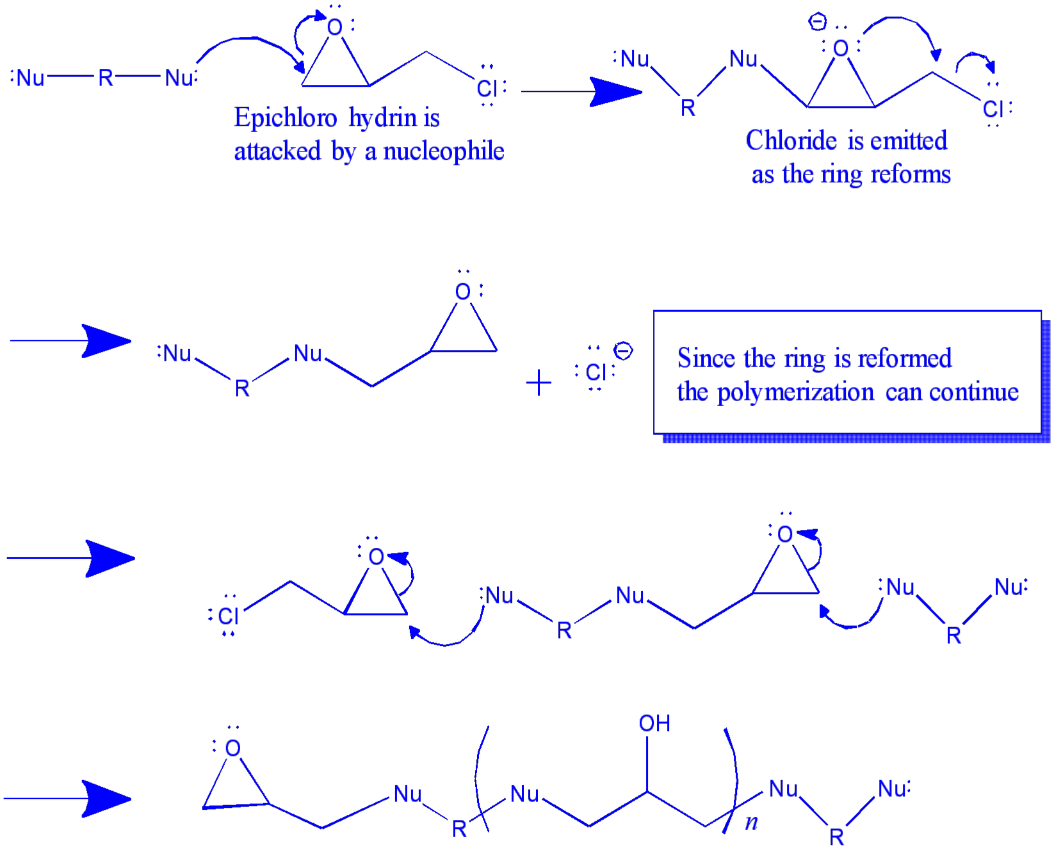
The polymers evaluated in this study were all commercially available epoxide and urethane formulations. Urethanes are produced by the reaction of an isocyanate [Fig 3(a)] and a *polyol* (a hydrocarbon chain containing a large number of –OH groups as substituents); epoxy materials are formed by polymerization of an epoxide ring [Fig 3(b)] with an amine or similar nucleophile. The properties of both types of polymers are highly dependent on the molecular structure of the reactants [3].

(a) (b)

Fig. 3: The molecular structures of some of the monomeric “building blocks” used to prepare urethanes and epoxy materials: (a) an isocyanate; (b) an epoxide.

Ordinary polymers are formed from only two reactive species (e.g., one type of isocyanate and one type of polyol). When a mixture of two or more of one reactive species is used (e.g., one type of isocyanate and two different polyol structures), co-polymers are formed. Co-polymers are often employed to make further adjustments to the properties of the desired polymer (e.g., mechanical, thermal, chemical) than would be possible from using only two reactants.

Figure 4 shows the reaction mechanism for the formation of an epoxy polymer. Epichlorohydrin, a common epoxide, polymerizes with a nucleophilic monomer (e.g., an amine). The reaction occurs at room temperature and is exothermic (releases heat), and thus proceeds by a thermal mechanism. The extent to which the reaction proceeds to completion to form a solid polymer is termed the *degree of cure*.


Epichloro hydrin is attacked by a nucleophile

Chloride is emitted as the ring reforms

Since the ring is reformed the polymerization can continue

Fig. 4: Polymerization mechanism for reaction of an epoxide with a nucleophile to form an epoxy polymer.

Most thermal-curing systems will proceed to an 85% degree of cure on their own, but as the concentration of reactants begins to drop off, the rate of reaction decreases to a point where additional heat may be required to achieve a fully-cured system with all of the desired physical properties. Employing reactants with multiple functional groups that can participate in the same reaction (e.g., a di-isocyanate) results in a polymer that is *cross-linked* (i.e., bonds are formed laterally between adjacent polymer chains) to form a polymer network. The degree of cross-linking controls the stiffness and rigidity of the polymer network, and is an important element often used when designing engineering materials and optical polymers. Figure 5 compares the molecular packing of a normal polymer network to a cross-linked one.

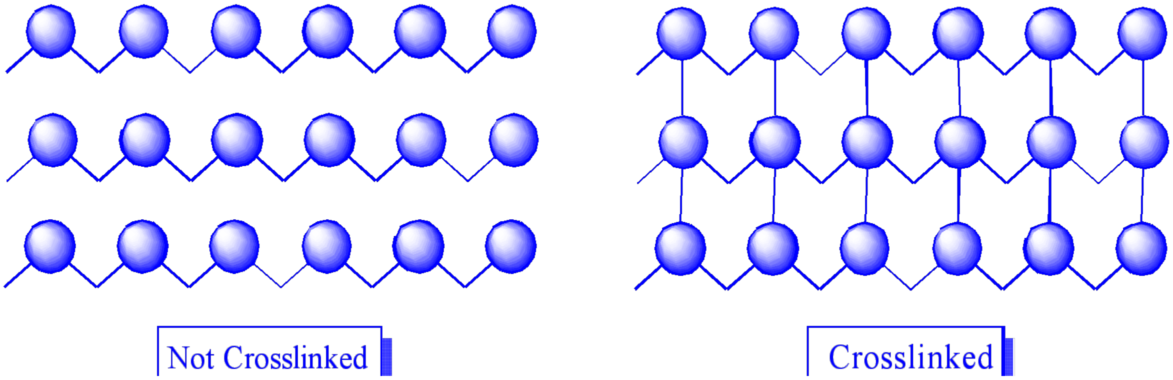


Fig 5: Comparison of a non-crosslinked polymer network to one that is cross-linked.

Certain co-polymer systems can also be cured using UV light. Because these materials contain UV chromophores by necessity in order to initiate the photoreaction (either intrinsically as part of the monomers or in the form of photoinitiators that have been added to produce transient species to initiate the reaction), they are not good candidates for high peak power laser applications in the UV, as there is always the possibility that not all traces of these UV chromophores will be converted into the desired product and some may remain behind to initiate laser damage. For this reason, only materials following a thermal cure route were considered at this time.

4. Sample preparation

Three commercially available thermosetting polymer materials, Masterbond EP21LSC1 Epoxy, Sol Epoxy NB2908-51C and Resin Designs 071607-D2 (urethane), were chosen for evaluation after an exhaustive search of available materials. After samples were obtained from the respective manufacturers, the relative rate of cure for each polymer system was tested. The curing protocol supplied by the manufacturer of each polymer formulation was used as a starting point, with some variations applied in order to produce samples that were as completely cured as possible. The cure schedules developed involved heating a sample that had been coated qualitatively onto a piece of glass using a spatula from 30 min to 3 hrs at various temperatures, depending on the material's formulation. Once the right cure method was found, the samples were coated onto a glass substrate in a Class 10,000 clean room using a knife coater equipped with micrometers for controlling the coating layer thickness. The thickness of the coatings was determined using a Taylor-Hobson Talysurf stylus profilometer; the optical transmission at 351 nm was determined using a UV-VIS-near IR spectrophotometer (Perkin Elmer Lambda 900). These two values were used to calculate the absorption coefficient μ using the formula

$$I = I_0 e^{-\mu x}$$

where

I = light intensity after passing through the sample
I_0 = Initial intensity of light
μ = linear absorption coefficient
x = sample thickness (optical pathlength)

The absorption coefficient values were then used to calculate the expected transmission for a 20 μm path length, which is the minimum desired film thickness for this application.

5. Laser Damage Testing

Laser damage testing was conducted on cast sample films of the three thermosetting polymer formulations described in Section 4 at 351 nm with a 0.9 ns pulse width. Only the 1-on-1 testing protocol (where different sites are tested at increasing laser fluence levels until damage is observed) was used for these samples. Damage testing was also conducted on a fourth polymer formulation supplied by Rochester Photonics Inc. (RPC) that had already been deposited on a substrate. This proprietary material is reported to have a laser damage threshold at 351 nm of 6.2 J/cm^2 (in very thin films) and originally was intended as a benchmark. Optical absorption measurements on the supplied sample showed that this material had an absorption coefficient of 1.6 X 10^{-3} μm^{-1}, which indicates that at the targeted 20 μm film thickness the resulting transmission would be only 96.9%. Because the material is proprietary, RPC would not release any information on its composition without a signed agreement to purchase parts made with this material.

6. Results

The sample processing conditions, linear absorption coefficients, optical transmission calculated from the optical absorption coefficients, and laser damage thresholds for the three candidate materials are shown in Table 1, along with relevant available information for the material from RPC. Figure 6 shows typical optical absorption spectra for the two best candidate materials (Sol Epoxy NB2908-51C and Resin Designs 071607-D2) in the UV-visible region between 265 nm and 450 nm. These spectra are shown for qualitative comparison of absorption coefficients, as it was not possible to make coatings of identical film thicknesses repeatedly with existing coating equipment.

Material	Chemical class	Cure method/ conditions	Absorption coefficient (μm^{-1})	Calculated transmission (20 μm)	Laser damage threshold	
					J/cm^2 (351 nm, 0.9ns)	Test path (μm)
MasterBond EP21LSCL-1	Epoxide	Thermal 65°C, 3 hrs	1.7 X 10-2	64%	0.14 ± 0.01	100
Resin Design 071607-D2	Urethane	Thermal 65°C, 1 hr	5.9 X 10-4	98.8%	2.8 ±0.50	34
SolEpoxy NB2908-51C	Epoxide	Thermal 150°C, 30 min	9.4 X 10-5	99.8%	TBD	
RPC	Proprietary	Unknown	1.6 x 10-3	96.9%	6.2 ±0.05	< 5

Table 1: A compilation of the data generated for the polymer formulations tested. The data for the RPC material is also included as a qualitative benchmark. Note that the damage threshold data for the RPC material was for a very thin path length on a device supplied by RPC

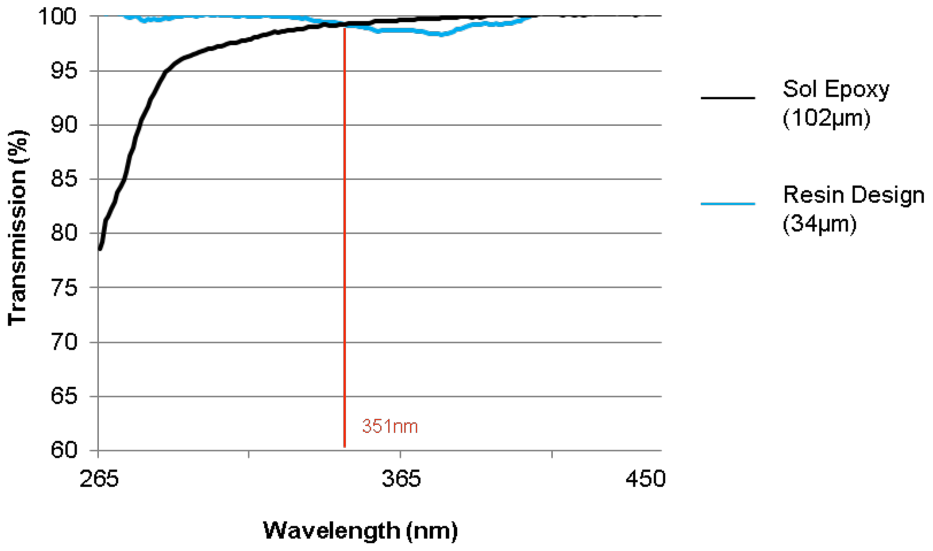


Fig. 6: Optical transmission of Sol Epoxy NB2908-51C and Resin Designs 071607-D2 in the UV-visible region. These spectra are shown for qualitative comparison of absorption coefficients, as it was not possible to make coatings of identical film thicknesses repeatedly with existing coating equipment. The high transparency of the Resin Designs urethane extending down to nearly 265 nm is remarkable.

Examination of the data in Table 1 reveals that only the Resin Designs and Sol Epoxy materials have sufficiently high transparency to be viable candidates for applications at 351 nm. The Masterbond material can be eliminated from consideration due to its relatively low 351 nm transmission (64%) and poor laser damage threshold (~0.14 J/cm^2). The Resin Design material has a higher laser damage threshold (2.8 J/cm^2) for a 20 μm path length than the 2.0 J/cm^2 required for the application. Due to insufficient time and schedule conflicts on the damage test system, it was not possible to determine the laser damage threshold for the Sol Epoxy during the time frame of this project; this data will be pursued in future studies.

Another requirement for a polymer material to be useful for optical replication is for it to be able to be released cleanly from the master mold used to generate the patterned optic. Preliminary experiments conducted with the Sol Epoxy and Resin Designs material showed that these two polymers release cleanly from a Teflon® mold. Because the surface of the available Teflon® mold used was not intended for optical replication and did not have a smooth finish, the surfaces of the polymer replicates in contact with the mold were rough and produced significant scattering when illuminated with visible laser light.

7. Conclusions

This study has identified two commercially available polymers, Sol Epoxy NB2908-51C and Resin Design urethane 071607-D2, which by virtue of their physical and optical properties are excellent candidates for polymer replicated optics for high-peak-power lasers operating at 351 nm. Both materials have linear absorption coefficients corresponding to an optical transmission of > 98% at 351 nm for a 20 μm thick polymer layer, and the Resin Designs material has a damage threshold at 351 nm that is 40% above the minimum required damage threshold of 2 J/cm^2 at the same wavelength and pulse width. Both materials were also shown to release cleanly from a Teflon® mold, which is an important requirement for optical replication.

Considerable additional research needs to be conducted before the generation of replicated polymer optics can be fully realized using these materials. More work needs to be done in developing accurate curing protocols using thermal analysis techniques such as differential scanning calorimetry (DSC). This instrument can determine the glass transition temperature (T_g) of the polymer at different cure times. For polymers, T_g is the temperature at which the polymer backbone begins to become flexible, and can be used as a measure of how well-cured the material is. As the polymer cures, the T_g increases as a function of cure time and cure temperature until it reaches a constant value, at which point it is considered fully cured. Using the DSC allows quantitative determination of the optimum cure temperature and time to ensure that there are no residual monomers left behind that can adversely affect the polymer's optical and mechanical properties.

Although the coatings for laser damage testing were prepared in a Class 10,000 clean room, due to the high viscosity of the polymer materials no efforts were made to filter the polymer materials to remove suspended solids that might act as sites for promoting laser damage. Higher laser damage thresholds may be possible if the polymer materials could be dissolved in a suitable carrier solvent to reduce their viscosity sufficiently to allow filtration through a submicron particle filter, followed by evaporation of the carrier solvent. Further investigation into pattern replication from molds with optical-quality surfaces also needs to be conducted. This activity may require the use of different mold materials such as polished metals or, alternatively, a flexible mold material like polydimethylsiloxane (PDMS), along with mold release agents to produce optical-quality replicated polymer optics for 351 nm applications in OMEGA or OMEGA EP.

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References

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2. T. Kessler, private communication.
3. K. Marshall, private communication.