Microlens Arrays for Optoelectronic Devices

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This paper reports on an improved method of fabricating microlens arrays using a low cost replication process. An accurate negative reproduction (“mold”) of an existing high quality lens surface (master) is made in a soft silicone elastomer. This mold is formed by thermally curing Sylgard® 182 silicone elastomer (made by Dow Corning®) on the lens surface. To prevent distortion of the replica surface, the mold is made on a rigid backing plate. Dispensing a commercial epoxy ‘Polyset’ PCX 28-91B into the mold and curing it under UV radiation generates a replica lens array. The epoxy material is chosen to have minimal shrinkage upon curing. The epoxy material is also chosen to have lower intrinsic loss and have a refractive index tailored to the application. In addition, we have developed a procedure to enable the incorporation of commercially available SiO₂ nanoparticles (Nissan IPA-ST-S, 9-11 nm) into this epoxy material. The incorporation of nanoparticles allows the epoxide to be harder, have a refractive index closer to SiO₂, have even smaller shrinkage while maintaining low intrinsic loss because of the small size of the SiO₂ particles.

Keywords: MEM, microlens array, telecommunication.

1. Introduction

1.1 The use of microlenses

Microlens arrays have many applications [1]. For instance, they are used for laser array wavefront correction where such arrays provide for collimation and astigmatic correction of light emitted from a diode laser arrays. Such correction of light is useful, for instance, in optical interconnection employing vertical cavity source emitting lasers (VCSEL), in the design of pump sources having the optimum light distribution for pumping a solid state laser or an array of these. Another application of lens arrays is found in light emitting diode (LED) array displays where they enhance brightness and collimate the light from each LED. In addition, another application is for liquid crystal displays, where a brightness enhancement film consists of an array of half-microlenses. This array focuses a diffuse oblique

ceiling light source and turns it into light coming at a normal angle from the display to the viewer. In integral photography, lens arrays are used to produce three dimensional, full parallax, full color reproductions of an object. Lens arrays can also be used for detector enhancement where they focus incoming light onto small detector pads. Finally, for optical switching, lens arrays can be employed to collimate light to and from a fiber array and focus it to and from a microelectronic machine (MEM) mirror array. The work that will be discussed here is concerned with this latter application. Specifically, we will discuss materials and processing considerations for the fabrication of such arrays starting from an organic photocurable resin.

1.2 Fabrication of microlenses arrays

There have been many approaches to manufacturing lens arrays: using an ink-jet process to

deposit UV curable lens material on a substrate [2], using hot embossing to manufacture polycarbonate lenses [3], or using resist reflow to pattern a spherical surface [4].

The first approach has the difficulty of tailoring the surface shape of the lens element. It might be easy to make a spherical lens element, but for applications that require aspherical surfaces, the process is difficult to control. The second method has the disadvantage of significant material shrinkage after embossing. This would lead to a distorted reproduction. However, as will be discussed shortly other micromolding techniques may be more suitable. The third approach, resist reflow, is more expensive, requiring use of cleanroom facilities.

Micro-optical structures can be readily produced a number of different micromolding [5] techniques. The choice of technique depends on the exact requirements, not only on the optical performance required, but also on the economics of the situation [5]. Basically, here are three principle micromolding methods: 1) Hot embossing (which we briefly have already discussed), 2) Injection molding and 3) Casting.

Hot embossing is typically a high-throughput process capable of producing high-resolution, low aspect ratio features of the type used in diffractive holograms. It can be employed in either roll-to-roll or stamping modes, using a thin polymer foil substrate.

Injection molding is more expensive than hot embossing, but can produce higher quality features with larger aspect ratios in much thicker ($> 1\text{mm}$) substrates.

Casting has been used for many years in the production of replica diffraction gratings for spectroscopy – a demanding application. Unlike hot embossing and injection molding, casting does not necessarily require an electroformed mold, since high pressures and temperatures are not required. In particular, if the cast material can be cured using UV light rather than elevated temperatures, the entire process can be carried out at room temperature.

There have been previous approaches using micromolding [6] for microlens manufacture. These did not address crucial issues that need to be solved before the replica can be used in a commercial product. These include, the control of distortion of the mold, material loss, environmental stability and

refractive index tailoring of the optical elements. Our procedure addresses the processing shortcomings of [6] and in one embodiment uses the incorporation of SiO_2 nanoparticles into the molded lens array to improve hardness, better match the refractive index to a MEM switch application. This is accomplished while maintaining a low intrinsic loss because the nanoparticles are too small to cause scattering of light.

The following section will give further background on the use of micro lens arrays in MEMS switch applications. This will be followed by sections giving some background on the filling of polymers with small particles and the use of optical adhesives. Elements of the two technologies described in the latter sections were crucial in designing our concept of a nano-filled material for micromolding applications.

1.3 Nanoparticles and their use in polymer nanocomposites

The mixing of finely divided solids such as carbon black, silica (SiO_2), silicate clays, or calcium carbonate into Elastomers has long been used to either reinforce such materials, reduce their cost or both. It has also been known that the reinforcement increases with decreasing particle size [7].

However, there has been a long debate of the merit compounding of fillers to a lesser or greater degree [8]. The first systematic investigation of the physical properties of composites of polymers and SiO_2 particles were first done by Mark et al [9] in which they found that regularly and randomly dispersed particles in poly(methylacrylate) (PMA) impart a much greater strength to PMA, but that the use aggregated nanoparticles improved both strength and toughness. They explained this using a model in which aggregation of nanoparticles acts in a manner analogously to the effect of a having bimodal distributions of polymer molecular weight during buildup of a polymeric network. In such polymer networks buildup the presence of both short and very long polymer chains leads to improvements in elastomeric properties [9].

Many recent applications employ polymer SiO_2 composite structures to manipulate light by Bragg diffraction [9,10]. In such application the particles size are rather large i.e. $\sim 150\text{ nm}$.

In other recent applications such as microlithography it is preferred that light not interact

with the SiO₂ particle- polymer composite and very small nanoparticles particles are used (i.e. size < 1/10λ). Specifically, novel 157 nm resists have been designed with which polymer encapsulated nanoparticles are used to gain a higher transparency at 157 nm along with maintaining lithographic processing conditions similar to those already implemented in IC manufacturing [11].

1.4 Optical adhesives

There are three methods for making permanent optical connections in silica based planar waveguides and other similar photonics components: fiber laser splice, laser welding and adhesive connection. Of these, the use of optical adhesives is the simplest and most cost-effective [12]. There are two types of optical adhesives: chalcogenide glasses and infrared (IR) transparent organic adhesives. Chalcogenide glasses have very high refractive indexes and the consequent poor match to most silica optical components causes high Fresnel losses[13]. The most advantageous of the organic IR optical adhesives are the ones that can be photo-cured. This said, it is also important to consider the weaknesses of such materials namely the need to carefully consider degradation due to structural deformation of material chemistry failure of the optical component adhesive during use. The study of such topics is an active area of research [13,14] Consequently, optical adhesives should be engineered to obtain a good compromise between optical properties and the need for a robust adhesive that can survive in the field. Two examples of such robust adhesives are fluorinated and silicone epoxy adhesives which are available respectively from Daikin Industries Ltd and 'Polyset' Company Inc. We decided to evaluate one of these, a silicone epoxy from the 'Polyset' Company, as a molding material for microlenses. This resin was particularly interesting because it had a small shrinkage upon cure (~0.2%). This resin PCX 28-91B (henceforth referred to simply as 'Polyset') consists of a multifunctional epoxy terminated siloxane resin into which a triarylsulfonium hexafluoroantimonate photoacid generator has been added. Exposure to UV light photogenerates acid which cures the epoxy resin. As was discussed previously, nanocomposites of SiO₂ and polymer are known to have advantageous material properties because of their hybrid nature. If commercially available nanoparticles which have very small sizes (Nissan ST-S, 9-11 nm) are

employed and aggregation is avoided then it would be expected that these material properties could be gained without any undue optical losses engendered by light scattering. This is indeed, what we have found.

2. Results and Discussion

2.1 Background on micro lens arrays in MEMS switch

Free-space optical MEMS devices for use in telecom applications typically require optics to focus or collimate the light to and from optical fibers. The relevant Gaussian beam equations are:

$$z_0 = \frac{\pi W_0^2}{\lambda}, \quad W(z) = W_0 \left[1 + \left(\frac{z}{z_0} \right)^2 \right]^{\frac{1}{2}}, \quad \theta = \frac{\lambda}{\pi W_0}$$

Where λ is the wavelength, W is the beam diameter, z is the distance along the beam axis, θ is the half-angle beam divergence and z₀ is the Rayleigh range and W₀ is the beam waist diameter. For a typical fiber with a mode diameter of 10 μm at a wavelength of 1.55 μm, the beam divergence is 50 mrad and the Rayleigh range is 20 μm. These parameters set the scale for the optics required and, even in the case of systems with focal lengths of a few millimeters, the maximum lens aperture is usually less than one millimeter.

In optical communication systems, reducing insertion loss is the paramount concern. In the case of free-space devices, where light leaves one fiber and couples back into another, maintaining the quality of the fiber mode is essential in minimizing coupling losses. This can only be achieved if the lenses are essentially diffraction limited, which means that the surface figure of the lens needs to be held to within λ/4, or about 400 nm for telecom wavelengths.

In addition to maintaining an accurate surface figure, it is also necessary to ensure that the positions of the lenses in array are well controlled (Figure 1). Typically, after constructing an appropriate error budget, we find that the positions of the lenses in the array must be accurate to a micron.

In devices such as optical cross-connects (OXC)- which may have as many as 1296 input and output fibers-the lens array can be as large as 50 mm x 50 mm, which means the dimensional control over the array must be better than 0.002%. This is an extremely challenging requirement for typical polymer systems

for two reasons: Shrinkage during curing and thermal expansion mismatches between the lens and fiber arrays.

Figure 1. Illustration of a fiber and lens array. The inset shows how small deviations in aligning the fiber and lens axes can lead to large deviations in the direction of the output light. The lens positions in the array must therefore be controlled accurately to match those of the fibers in the fiber array.

2.2 Reasons for use of a backplate

As discussed above, casting with UV curing enables us to carry out the replication process at a fixed temperature. This means that the thermal expansion effects that would arise during hot embossing or injection molding are essentially eliminated. However, thermal expansion mismatch between the lens and fiber array during use is still an issue. In addition, all polymers exhibit shrinkage on curing, and there are limits to what materials can be used, since they must satisfy optical and environmental stability constraints.

A simple solution to these issues is to employ a rigid backing plate, such as glass, both for the lenses and for the mold (Figure 2). Ideally, the backing plate for the lens array will have the same thermal expansion coefficient as the fiber array. The backing plate for the mold is not under the same constraint since it will be employed in the formation and use of the mold at a single temperature. The backing plates improve the dimensional stability of the polymer structures in-plane by constraining lateral contraction/expansion due to thermal expansion or shrinkage effects.

Finite element (FEM) studies have shown, that plates can also be effective in controlling vertical distortion if the thickness of the structures is much smaller than the width of the plates. If the film is very thick, the plate has no effect. Specifically since the plate is about 1.5 inches (38mm) in its width it does not exhibit significant vertical distortion even for

film thickness' up to 1.5 mm. The appropriate thickness' for the backing plates and polymer films can be chosen using FEM analysis. As Figure 3 shows, there is minimal in-plane displacement at a distance approximately equal to the layer thickness away from the mold edge. Displacements normal to the plane can be larger, but as shown in Figure 4 are extremely uniform.

Figure 2. Replica lens formation process. Backing plates are used to constrain the displacements both in the mold and in the replica polymer layers.

We note that the use of a room temperature cured elastomeric mold means that complex geometries can be replicated from almost any type of master. This increases considerably the choice of materials that can be used as a master, including ordinary photoresist features.

The displacements in the thin polymer film used for the actual lenses are typically very small. The only effect that can occur is a change in radius of curvature, as a function of shrinkage, during curing. To first order, this results in a shift in focal length, but this is not usually of concern, as long as it is uniform across the array. If an accurate focal length is required, then the effect of shrinkage can be taken into account and compensated for when the master is fabricated.

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uniform across the array. If an accurate focal length is required, then the effect of shrinkage can be taken into account and compensated for when the master is fabricated.

Finally, this scheme would allow alignment of the fiber array to the lens array by the use of visible light since both the backing and lenses are transparent. This is much simpler than the infrared alignment needed for silicon lens arrays which are opaque to visible light.

Figure 3. Illustration of how, as the mold aspect ratio decreases, the in-plane displacements are confined to within a distance approximately equal to the layer thickness from the edge of the mold. The model assumes a sample 1 mm thick that undergoes 0.5% volume shrinkage on curing.

2.3 Master lens surface treatment

A known, good lens array ("Master") is first coated with a mold release agent to enable it to be separated from the mold. This coating is done by placing the lens array in a dessicator along with a slide coated with (Tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane{ $C_6F_{13}CH_2CH_2SiCl_3$ }, referred to as "trichlorosilane" from now. This agent is available in liquid form from United Chemical Technologies®. These class of chemicals are known as organosilanes.

They have a general formula of $R_nSiX_{(4-n)}$, where X is a hydrolyzable group typically halogen, alkoxy, acyloxy or amine group. Upon contact with surface moisture, they undergo hydrolysis and form a siloxane linkage (Si-O-Si) with the surface of the lens array. The R group is an organic radical that has the anti-stiction property. Here it is a fluorinated organic

group, which is inert and does not form any bonds with other surfaces. When the dessicator is pumped down, trichlorosilane vaporizes and coats the surface of the lens array. This coating is typically one molecular layer thick. Further details can be found in [15].

Figure 4. In-plane (X & Y) and out-of-plane displacements within the 12.5 mm x 15 mm lens array area for a 1 mm thick mold undergoing 0.5% volume shrinkage upon curing. Note that although the out-of-plane displacement is larger than the in-plane it is very uniform

2.4 Elastomer mold formation

As discussed previously, Figure 2 shows schematically the procedure for fabrication of the elastomer mold. Specifically, the master lens array is placed on a glass slide coated with the anti-stiction agent (Figure 5a,b). A rigid glass backing plate with low coefficient of thermal expansion (preferably quartz), not coated with the mold release agent is placed on spacers above the lens array. These spacers are about 1mm larger in thickness than the lens array and are made of either glass or teflon®. This would ensure that the elastomer mold that

adheres to the backing plate would be approximately 1mm in thickness.

Figure 5. a) Mold fabrication setup b) Cross-section of the mold fabrication setup $\delta \sim 1\text{mm}$.

This setup is placed in a petri dish or similar enclosure. Dimethylsiloxane monomer along with a polymerizing catalyst (both available as Sylgard® 182 kit from Dow Corning) is dispensed into the petri-dish to completely cover the setup. The dish is placed in an oven at 65°C for about 5 hours. Polymerization reaction takes place and Polydimethylsiloxane (PDMS) is formed. PDMS takes the shape of the surface over which it polymerizes. In this case, the surface of the lens is of interest. PDMS adheres to the surface of the glass backing plate since it is uncoated with the anti-stiction layer and does not do so on the lens surface or the glass plate it is placed on. This allows us to peel off the glass plate and the lens array after cure. A negative replica of the lens surface is then available on the rigid backing plate.

Care should be taken not to introduce any material that can contain bases into the elastomer during the cure process. Presence of a base poisons the catalyst and prevents the polymerization reaction.

Initially we had used Buna-Nitrile spacers (commonly used for O-rings). These contain amines and prevent mold formation.

Usually the polymer exhibits large shrinkage upon curing. This would cause a freestanding mold to contract and distort. A replica made from such a mold would not reproduce the surface of the master accurately. As discussed before, by attaching the backing plate, the elastomer is now forced to follow the dimension changes of the plate, which is much smaller than that of the elastomer. For mold thickness of about a mm, the region of distortion around the edge is about a couple of mm. By having a buffer space (about a few mm, without any features) around the edges of the master, an accurate negative replica of the surface features away from the edges can be made.

2.5 Treatment of rigid surface plate

2.5.1 Surface energy and contamination control

Obtaining a contamination free lens backing plate is essential to obtain good adhesion of the epoxy material to its surface. The backing plate frequently has organic contamination on its surface. This is removed by soaking the plate in chromic acid. Chromic acid is a very powerful oxidant and removes most of the organic contaminants. Since the epoxy is hydrophobic, it's necessary to tailor the surface of the backing plate to have comparable surface energy. Subjecting the plate to HMDS vapor prime achieves this. Contact angle measurements are made to ensure that repeatable surface conditions are obtained at the beginning of the process. Table 1 demonstrates the effect of the prime process.

Apart from contact angle measurements, two other techniques may be useful for ascertaining how clean is the rigid substrate.

These are X-ray photoemission spectroscopy (XPS) and Fourier transform spectroscopy (FT-IR). Hydrocarbon surface contamination in XPS shows a very large peak at ~300 eV due to carbon. This contamination can also be seen by FT-IR spectroscopy from the presence of IR bands between 3000 and 2800 cm^{-1} which are attributable to the stretching of C-H bonds.

Hydrocarbon contaminated surfaces were a problem because these gave cured microlenses with extremely poor adhesion.

Table 1: Effect of prime process. All the surfaces are restored to a known energy state as evidenced by contact angle.

Step	Glass	Quartz in house	Quartz-vendor
Pre-treatment	5°	24°	35°
Chromic acid ^a	6°	17°	15°
HMDS prime ^b	58°	59°	59°

a) Cleaning done by soaking substrates in chromic acid (chromerge, Fisher Scientific) for 1 hour followed by rinse with distilled water and drying in a convection oven at 150°C for 1 hour. b) See experimental.

2.5.2 Adhesion promotion

Apart from conditioning the surface energy to better match the epoxide, another method to achieve better adhesion is to employ trialkoxysilylalkane/epoxy adhesion promoters. In such adhesion promoters the trialkoxysilyl moiety react both with SiOH moieties at the surface of SiO₂ and water to form a thin film of polymer matrix on the treated surface. This film consists of trialkoxysilyl moieties that have reacted with the surface SiOH and with each other through hydrolysis (formation of SiOH) followed by condensation to form Si-O-Si bonds. Apart from the trialkoxysilyl moiety, these materials also contain an epoxy moiety that is designed to react with the epoxide resin when it is applied to the treated rigid substrate. The structures of two adhesion promoters that we have employed on the rigid substrate are shown in Figure 6.

Upon aging at 85°C and 85% relative humidity (85/85) for 72 hours both using HMDS or the trialkoxysilylalkane/epoxy proved effective and gave lens arrays retaining adhesion to the rigid substrate. Also, there was no statistically significant shift in focal length distribution for the array. However, samples with 'Polyset' resin alone became slightly hazy. This increase in haziness did not occur when the material consisted of 'Polyset' resin filled with nanoparticles (see below). This may indicate that the filled material is more resistant to water penetration possibly because of a higher degree of crosslinking (see below).

Figure 6 Trialkoxysilane/alkyloxirane (i.e. epoxy) derivatives available commercially from Aldrich Chemicals.

2.6 Replica fabrication

An UV curable epoxy, with low shrinkage and low hydroxyl group content (PCX 28-91B) is dispensed on the negative just enough to fill the lens cavities. A quartz or BK-7 backing plate (referred to a lens backing plate) is gently placed to cover the epoxy and is exposed to UV radiation. The epoxy cures and yields lens arrays adhering to the quartz plate. The lens array is peeled off from the mold by gently lifting one edge of the backing plate. To fully cure the epoxy, the lens array is heated at ~140°C for about one hour. The heat is slowly ramped up to avoid thermal shocks. Normally an epoxy would shrink significantly after thermal curing. The epoxy PCX 28-91B ('Polyset') (supplied by vendor 'Polyset' Inc., Troy, NY under a non-disclosure agreement) exhibits minimal shrinkage of about 0.2% (volumetric).

Also, we have found that using conditions that we have developed 'Polyset' can be filled with commercially available SiO₂ nanoparticles (e.g. Nissan IPA-ST-S, 9-11 nm) to further reduce shrinkage and improve other properties. It is estimated that fraction reduction in shrinkage to be the same as the loading of nanoparticles. Consequently, a sample with 19 wt % loading of nanoparticles would have a shrinkage ~81 % of the value for 'Polyset' (i.e. ~ 0.16 %). Changes of shrinkage of such low magnitude were however, too low to be detectable by profilometer or by changes in insertion loss.

The refractive index of the cured epoxy can be tailored to match the backing plate index. This would reduce any reflection losses that would otherwise occur at the interface between the lens film and the

glass backing plate. Finally, the lens surface is AR coated to reduce loss at lens-air interface.

Figure 7(a) compares the surface profiles of the master and the replicated lens. Figure 7(b) compares the focal length distribution of the master and the replica about the mean focal length. The surface profile of the replica is very close to that of the master. This translates into comparable focal length profiles. Table 2 details the loss measurements made on the master and the replica. Comparable loss results indicate that the lens behavior has also been closely replicated.

Figure 7 Surface profiles of the a) master and the b) replica.

The cured 'Polysset' resin which makes up the microlenses has a relatively small absorbance loss of about 0.2 dB for a layer of about 75 μm thick ($\sim 0.003\text{dB}/\mu\text{m}$). Since the lens material is only tens of microns thick, the absorption due to 'Polysset' would not impose a significant power penalty. Replicas made with silica filled 'Polysset' resin did not show any significant difference in insertion loss.

Table 2: Loss and focal length range measurements on master and replica lens arrays

Property	Master	Replica
Focal length range	61 μm	82 μm
Average loss	1.89dB	1.83dB
Insertion loss spread	0.79dB	1.47dB

2.6.1 Preparation of epoxy resin filled with SiO_2 nanoparticles

As previously discussed, we were interested in incorporating nanoparticles into 'Polysset' resin, in order to gain advantageous material properties without causing undue scattering of light. We incorporated SiO_2 nanoparticles into the 'Polysset' epoxy resin either by using bare nanoparticles or ones which had been surface coated with a trialkoxysilyl

reagent. To modify the nanoparticles we adapted procedures found in the literature [11].

Specifically, to surface coat the nanoparticles we started with a colloidal solution of them in isopropyl alcohol (IPA) and reacted this with 3-glycidyloxypropyl trimethoxysilane (GLYMO). This reagent was chosen because it was expected to form an epoxy resin like coating encapsulating the nanoparticles in a matrix closely resembling the cured 'Polysset' resin. Indeed, after isolation of the coated nanoparticles, solid state NMR spectroscopies (carbon and silicon) revealed that GLYMO forms a coating on the nanoparticles by reaction of its trimethoxysilyl moieties and by ring opening of its epoxide group. If the acidic solution of nanoparticles is neutralized prior to mixing with the resin; the nanoparticle filled 'Polysset' resin is stable for an extended periods (>3 months) prior to UV exposure. Additionally, the resin filled with GLYMO coated nanoparticles cures well upon UV exposure forming a tight cross-linked network in which the movement of silicon atoms is even more restricted than in a sample of the 'Polysset' resin cured by itself (solid state Si NMR).

Another trialkoxysilane reagent 3-(trimethoxysilyl)propylmethacrylate was also used to coat the SiO_2 nanoparticles and gave similar results.

The second method of adding 'bare' nanoparticles to the 'Polysset' resin employs a commercial colloidal solution of SiO_2 nanoparticles in methylethylketone (Nissan MEK-ST). Unfortunately, after solvent removal the blend is unstable, even if the nanoparticle solution is neutralized prior to mixing, and can only be kept for a short time (<1 hour) before solidifying spontaneously. This said, the 'Polysset' resin filled in this manner could still be employed to make microlenses provided the filled resin is applied to the mold and UV cured immediately after its preparation (i.e. <1 hour).

This difference in stability of the blends can be rationalized: The SiOH moieties at the surface of the bare nanoparticles may tend to cause agglomeration of nanoparticles; also, being somewhat acidic these bare nanoparticles may also cause premature curing of the 'Polysset' resin. In contrast, for GLYMO coated nanoparticles the SiOH moieties may be less readily available as they are part of the GLYMO coating and consequently less able to cause deleterious reactions. Similarly, nanoparticles

functionalized with the methacrylate silane reagent also formed stable blend with 'Polyset' resin, which could be easily UV cured.

A detailed accounting of the solid state NMR study done on some of these nanoparticles and resins follows.

2.6.2 Preparation of lenses using nanoparticle/'Polyset' blend composite

Nanoparticle/'Polyset' blends are very viscous and not easy to handle if used at room temperature. Also, dispensing the blends in such a viscous state leads to incorporation of air bubbles into the lenses. Consequently, the blends, before application to the mold, are placed in an open syringe barrel and heated with a hot stream of air to reduce viscosity. These heated mixtures are degassed under vacuum. The degassed blend is then dispensed from the syringe to the lens mold by using an automatic dispenser (EFD 2000x), which applies a controllable pressure to the syringe. In this manner, good control of the volume and rate of the dispensing can be maintained. The dispenser can be made to automatically fill each lens cavity in the mold one at a time. This is achieved by placing the mold on a x-y stage under computer control. Each time a lens cavity is under the syringe, the computer dispenses a known volume of the mixture into the cavity. This procedure greatly improves the quality of lenses obtained yielding bubble free, uniform lenses across the array. After all the lens cavity in the mold have been filled, the quartz backing piece was placed on top of the mold, starting from one edge as shown in Figure 8. This scheme prevents the entrapment of air bubbles as the quartz plate is being placed into position.

Figure 8. Placement of quartz plate on top of filled mold.

2.7 Characterization and testing of replica materials and Processing

A variety of analytical tools were used to evaluate the curing conditions, the final cure state, and the effect of aging on 'Polyset' resin by itself and blended with SiO₂ nanoparticles of various types. These tools include solid state nuclear magnetic resonance spectroscopy (NMR), fourier transform infrared (FT-IR) spectroscopy both in the near and mid spectral region, hardness measurements using a durometer, and refractive index measurements at 1300 and 1500 nm employing a Metricon prism coupler.

2.7.1 Solid state NMR study of SiO₂ nanoparticles and resins

Solid state NMR is a technique, which is able to probe the chemical environment (i.e. chemical bonds to target nuclei) near the target NMR nuclei (e.g. ¹³C or ²⁹Si) of a given solid material. It can also how sterically constrained the target nuclei is in its solid matrix and hence the rigidity of the matrix.

¹³C and ²⁹Si NMR (C, Si) solid state spectroscopy was done for four different samples; a sample of bare SiO₂ nanoparticles obtained from an IPA colloidal solution, SiO₂ nanoparticles coated with GLYMO, a cured sample of 'Polyset' resin and a cured sample of the 'Polyset' resin filled with GLYMO coated SiO₂ nanoparticles.

Silica Nanoparticles

The silicon spectra for the bare nanoparticles was obtained with direct polarization (DP) and shows predominantly Q⁴ silicons (i.e. Si(OSi)₄). The silicon relaxation times can be very long and the relative intensities of the Q³ (i.e. Si(OSi)₃(OH)₁) and Q⁴ peaks may not be correct. The spectra were acquired with a 60 s delay time (Figure 9).

Figure 9. Silicon solid state spectrum of bare SiO₂ nanoparticles.

Silica Nanoparticles coated with Glymo**Si NMR**

The silicon spectra (Figure 10) of the GLYMO coated nanoparticles were obtained with (top) and without cross polarization. The CP spectra shows both Q and T silicon peak (i.e. silicon atoms bond to four oxygens or three oxygens and a carbon respectively). The Q^3 peak (-101 ppm) (i.e. $Si(OSi)_3(OH)_1$) is most intense in the CP spectra. The T^3 (-58 ppm) peak (i.e. $Si(OSi)_3(C)_1$) is the most intense GLYMO peak in the CP spectra. The direct polarization (DP) spectrum was recorded with a 50° pulse and a delay time of 15 s and shows a large Q^4 peak (i.e. $Si(OSi)_4$), as expected for a nanoparticle. The largest GLYMO peak is from the T^2 silicons (i.e. $Si(OH)_1(OSi)_2(C)_1$) at 48 ppm. This peak is very sharp and indicative of very mobile silicon atoms which is expected given that they are attached by only two Si-O-Si bonds. Weak T^3 peaks are also observed at 58 ppm ($Si(OSi)_3(C)_1$) this indicates that upon reaction GLYMO does not typically form three Si-O-Si probably due to steric constraints during formation of the GLYMO derived film on the nanoparticles. A broad unassigned peak is also observed at -15 ppm.

Figure 10. Silicon solid state spectra of GLYMO coated SiO_2 nanoparticles. Top with CP, bottom without CP

C NMR

To help in the assignment of the solid carbon NMR spectrum of the GLYMO coated SiO_2 nanoparticle, the carbon spectra was obtained of a liquid sample of GLYMO itself (Figure 14). The peaks at 5.7 and 23.4 ppm are assigned to carbons a and b (Figure 11). The carbons c and d appear at

73.6 and 72.1 ppm. The epoxy carbons e and f are observed at 43.7 and 50 ppm. The methoxyl carbons overlap with the low field epoxy peak.

Figure 11. Solution carbon NMR spectrum of GLYMO.

The carbon spectrum for the GLYMO coated nanoparticles was obtained with cross polarization (Figure 12). Peaks are observed at 8 and 23 ppm that can be assigned to the GLYMO carbons nearest to the silicon surface. No peaks are observed at 44 and 51 ppm, the chemical shift of the epoxy carbons. This shows that the epoxy has been reacted completely when GLYMO coated the SiO_2 nanoparticles.

Figure 12. Carbon solid NMR spectrum of GLYMO coated SiO_2 nanoparticles.

Cured 'Polyset' resin***C NMR***

'Polyset' is a multifunctional epoxy terminated resin. A solid state carbon spectrum of the cured 'Polyset' resin was obtained with cross polarization (Figure 13). The peaks at ~0 and 10 ppm can be assigned to different types of carbon atoms directly bonded to silicon atoms. The large peak near 30 ppm is most likely assigned to cyclohexyl carbons. The peaks between 70-80 ppm are most likely assigned to a CH carbons next to oxygen in a ring opened epoxide. The non-ring opened CH carbons of the epoxy moiety would be expected show peaks near 44 and 51 ppm. A peak is indeed observed near 51 ppm and the other epoxy resonance could be hidden under the broad peak at 30 ppm. This indicates that even after nominal cure some epoxy moieties remain.

Figure 13. Solid state carbon NMR spectrum of the cured 'Polyset' resin.

Si NMR

The silicon solid state spectrum for the cured 'Polyset' resin was obtained with (top) and without cross polarization (CP). The CP spectrum shows two main peaks at 9 and -67 ppm, with a small peak at 110 ppm. The peak at 9 ppm can be assigned to silicon in 6-membered rings (see Figure 18), and the peak at 67 ppm is assigned to T³ silicon (i.e. Si(OSi)₃(C)₁). The smaller peaks at 50 ppm and 110 ppm are most likely due to T² and Q⁴ silicon (i.e. Si(OSi)₂(OH)₁(C)₁ and Si(OSi)₄ respectively.)

Figure 14. Solid state silicon NMR spectrum of the cured 'Polyset' resin. Top spectrum with cross polarization, bottom spectrum without.

The spectrum without cross polarization was acquired with a 90° pulse followed by a 15 s waiting period, and only a sharp peak at 48 ppm from the T² silicon is observed. This shows that the relaxation times for the peaks at 9 and 67 ppm are very long, since they are difficult to observe with a 15 s delay time indicating that they are in a sterically restrained environment consistent with cured 'Polyset' resin.

Cured mixture of 'Polyset' resin and GLYMO coated SiO₂ nanoparticles.

C NMR

The solid state carbon spectrum for the cured mixture of the 'Polyset' resin and the GLYMO coated SiO₂ nanoparticles (Figure 15) is similar to the spectrum for cured 'Polyset' resin alone. The additional carbon resonances from the GLYMO are expected to overlap with those from the filler. The spectrum shows one main peak (~10 ppm) attributable to a carbon adjacent to silicon, the other peak which was observed at ~0 ppm in the spectrum of the 'Polyset' resin cured by itself. The peak at 51 ppm could arise from unreacted epoxy carbons. The peak at 70-80 ppm is from carbons next to oxygens, presumably from ring opened epoxy groups. The main peak at 30 ppm is noticeable broader than the similar peak in the spectrum of the 'Polyset' resin cured alone.

Figure 15. Solid state carbon NMR spectrum of the cured 'Polyset' resin cured with the GLYMO coated SiO_2 nanoparticles.

Si NMR

The silicon solid state spectrum for the cured mixture of 'Polyset' resin and GLYMO coated SiO_2 nanoparticles was recorded with (top) and without cross polarization shows two main peaks at 11 and -65 ppm (Figure 16). The peak at 11 ppm can be assigned to the silicons in 6-membered rings, and the peak at -65 ppm can be assigned to the T^3 silicons. The T^3 peak contains the signals both from the GLYMO and the filler, and these peaks cannot be resolved. The low signal-to-noise ratio makes it difficult to observe the Q peaks that were observed in the filler alone. It is worth noting that large differences were observed between the direct polarization and cross polarized spectrum for the filler alone, and a large T^2 peak was observed in the DP spectra. This is assigned to very mobile silicons in the filler that do not appear to be present in the composite. This would be consistent with the cured mixture forming a more tightly crosslinked network than that formed for the resin cured by itself.

2.7.2 Hardness comparison of filled versus non-filled 'Polyset' resin.

When 'Polyset' is cured at 120°C after UV irradiation (20 minutes) it gives a hardness of about 70 (on the shore D scale) curing at higher temperatures increases this hardness up to 80 at a cure of 150°C (1 hour at 150°C). In contrast, the SiO_2 filled 'Polyset' resin achieve immediately achieves a hardness of 88 without any thermal cure. This is advantageous because minimizing thermal cure temperature will decrease stress induced in the

cured lens material induced by its difference in coefficient of thermal expansion with the rigid backing.

Figure 16 Solid state silicon NMR spectrum of the 'Polyset' cured with the GLYMO coated nanoparticles. Top spectrum with cross polarization, bottom spectrum without.

The observed increase in hardness is consistent with a filled system with particle sizes of ~ 11 nm showing no aggregation. Larger improvements in hardness are predicated by the use of larger particles or aggregates in the ~ 150 nm size range (vida infra).

2.7.3 Aging comparison of filled versus non-filled 'Polyset' resin.

Aging under 85/85 conditions was done for both the samples made up of Polyset filled with GLYMO coated SiO_2 nanoparticles or consisting of Polyset alone. Under both types of surface priming (vida infra) good adhesion was maintained after aging. However, the samples made up of 'Polyset' alone gave a slight haziness after aging which was not observed for the ones made of filled material. A possible explanation for this observation is that when the 'Polyset' material is filled with SiO_2 nanoparticles it becomes more crosslinked through the rigid nanoparticles (as shown by NMR and hardness measurements) and consequently less prone to water penetration which would cause haziness. Increasing cross-linking to decrease water absorption is strategy commonly employed in polymer waveguide materials [16].

2.7.4 Near FT-IR spectroscopy of Polyset and its blends with nanoparticles

Near IR spectroscopic analysis was used to compare the absorbance the resin without and without different encapsulated nanoparticles. Near IR spectroscopy was chosen because it nicely monitors the region of the electromagnetic spectrum of interest for fiber optic telecommunication (i.e. $\lambda = 0.9\text{--}2.0$ microns). It was a concern that nanoparticles containing SiOH moieties which give a vibrational overtone absorbance at around 1.5 microns might be a problem. Also, it was hoped that the addition of encapsulated SiO₂ nanoparticles might decrease the absorbances due to CH overtones and combination bands due to these groups which also occur in this region [17].

It was found that the use a cured blend of the SiO₂ GLYMO coated nanoparticles and 'Polyset' did indeed show a reduction in the CH overtone bands found at 1.75 and 1.72 microns (Figure 17); however, the decrease in the more interesting higher overtone region between 1 and 1.5 microns is not as noticeable. Fortunately, the addition of these nanoparticles does not cause an increase in absorbance in the 1.5 micron region due to SiOH or absorbed water. Also, there was no shift in either the position or slope of the uncorrected baseline of the near IR spectra background compared to cured 'Polyset' indicating that the scattering losses were the same. Consequently, no significant SiO₂ nanoparticle agglomeration had occurred.

Figure 17 Comparison of FT-IR spectra a) 'Polyset' resin with 19% SiO₂ nanoparticle modified with trisilylglycidylglycidyl moiety. b) 'Polyset' resin alone. AU/micron Y axis.

The cured blend of the bare nanoparticles with the 'Polyset' resin gives similar results (Figure 18). However, the use of these bare nanoparticles in the resin does cause a quite noticeable increase of absorbance in the 1.5 micron region due to the presence of hydroxyl moieties.

Figure 18 Comparison of FT-IR spectra a) 'Polyset' resin with 13 wt % bare SiO₂ nanoparticle b) 'Polyset' resin alone. AU/micron Y axis.

The analysis described above was done on samples having a thickness of at least 0.5 mm. Samples with in this thickness range gave baselines in which interference fringes from internally reflected light contributed little to the baseline and made comparison between near IR bands in different samples relatively unambiguous.

2.7.5 Study of cure conditions and aging for Polyset

Mid IR studies

It was of interest to study how curing conditions and humidity aging affected transparency of a film having a thickness similar to that of our microlenses (i.e. ~ 0.075 mm). Unfortunately, films of 'Polyset' film spun onto silicon having approximately this thickness show pronounced interference fringes in the near IR region (i.e. 0.9–1.6 microns) which makes direct comparisons of overtone bands between different samples ambiguous. Consequently, we chose to monitor the primary band for OH stretching because it is an easily observed band in the mid IR region (~ 2.9 microns) which is very sensitive to change of cure or aging and has an overtone which occurs at around 1.5 microns [17]. It is reasonable to assume that any increase in the band intensity at the

primary band of the OH stretch should be mirrored in its overtone and increase absorbance in the near IR. Before curing 'Polyset' resin has a small band in the mid IR at 2.9 microns consistent with alcoholic OH's.

Figure 19 shows a mid IR spectroscopic comparison of 'Polyset' films cured under different conditions before and after a humidity aging at 85% humidity and 85°C (85/85). If the amount of UV exposure is kept constant it is seen that at ~2.9 microns the OH absorbance due to alcohol increases with decreasing cure temperature. Interestingly, upon aging of the samples at 85/85 much of this absorbance difference is removed (Figure 23). Specifically, aging little affect the samples cured at low temperature while making those cured at high temperature more absorbant (Figure 19).

Furthermore, the OH band cannot be due to simple physical absorption of water because it occurs irreversibly (ie. Attempts to remove water by vacuum with or without applied heat, even in the presence of a strong such as P_2O_5 does not remove the band).

Commensurate with the increasing alcoholic OH band strength there is a shifting of wavelength from 2.88 to 2.96 microns (i.e. 3470 to 3378 cm^{-1}).

The simplest explanation for this shifting is that a higher concentration of alcoholic OH's leads to hydrogen bonding.

Figure 19 Comparison of FT-IR spectra for different cure conditions and aging for 'Polyset'

The formation of the OH moieties themselves may be due to the reaction of remaining protonated epoxide ring in the cured resin matrix undergoing with water present in the matrix. Curing at higher temperatures after UV exposure lowers the amount of water available for reaction. However, during 85/85

aging water can enter the matrix and react with these moieties.

Consistent with the above mechanism, an increase in irradiation with UV causes an increase in the strength of the mid IR alcoholic OH band (Figure 20).

Figure 20 Comparison of FT-IR spectra for different exposure conditions for 'Polyset'

Consequently, PAG content and the amount of irradiation may control the extent of OH formation and also predicate the absorbance (i.e. loss) in the communication near IR region for a microlens. Indeed, by minimizing interference fringes for a given sample [18] it can be seen that absorbance at 1.5 microns increases with irradiation time (Figure 21).

Figure 21 Comparison of near FT-IR spectra 'Polyset' with increasing doses of UV exposure

However, for the loading of PAG we employed even the highest level of absorbance observed for the resin is not problematic as long as it remains constant during its use as a microlens. Consequently, our studies would suggest that a cure with UV alone or followed by a low cure temperature would be preferred as it give immediately the maximum

expected absorbance and prevent it changing over time.

The behavior of 'Polyset' filled with nanoparticles is analogous.

2.7.6 Refractive index studies

The refractive index of cured samples of 'Polyset' resins was examined at three wavelengths 0.633, 1.3 and 1.5 microns before and after aging at 85/85. It was found that 85/85 aging only slightly decreased the refractive index (Figure 22). Specifically, in the communication bandwidth at 1.3 and 1.5 microns only a decrease of about 0.0047 was observed. Focal length changes are directly proportional to the changes in refractive index for small changes in index, in our plano convex lenses; this means that the observed change in refractive index corresponds to a 0.32% change in focal length. The requirements for the optical switch arrays call for less than 1% change in the focal length over time under the all possible cycling conditions (temp, humidity). Consequently, the change we have observed is within the desired specification. Although similar studies were not made on the nanoparticle filled lenses, it is anticipated that even less change upon aging should occur.

Figure 22 Refractive Index as function of wavelength before and after 85/85 aging.

2.7.7 Application of antireflective coating

An air-glass (index 1/1.45) interface reflects about 4% of the light [19]. This loss is not acceptable. To prevent this, the usual practice is to provide an anti-reflective layer coating on the lenses. This is usually a multi-layer stack consisting of alternate layers of TiO_2 (index 2.5)/ SiO_2 (index 1.45) coatings on top of the lenses. The thickness of each layer is one-quarter wavelength. These films are

deposited by evaporation of Ti and Si in an oxygen ambient. This was performed by an outside vendor (Denton vacuum). During the deposition, the temperature could rise up to 125°C and the samples are able to withstand this. After the coating process, the reflection losses drop to less than 0.25%. While the deposition parameters are proprietary to the firms, a broad overview of these schemes is given by MacLeod [20]. In case of silicon lenses, a single layer of silicon nitride one-quarter wavelength thick would be sufficient to reduce reflection losses to less than 0.25% in the 1.5 μm wavelength range.

2.8 Use of Silsesquioxane to increase silicon content of epoxy resin

In order to increase its silicon content we have also blended silsesquioxane materials (Figure 23) with 'Polyset' resin. Silsesquioxanes with and without epoxy functionalization may be used. Silsesquioxane materials may also be blended with 'Polyset'. However, silsesquioxane without pendant epoxide moieties tend to phase-separated upon cure at rather modest loading levels (5 wt %). The use of silsesquioxanes which have pendant epoxide moieties allows for higher levels of loading (up to 10 wt %). This is consistent with the silsesquioxanes becoming covalently bound into the cured 'Polyset' resin matrix. Unfortunately, the use of silsesquioxanes have two drawback; they are expensive and are also prone to hydrolysis unless precautions are taken to exclude water. In infrared studies 'Polyset' loaded with silsesquioxane gave slightly stronger OH primary and overtone bands than those observed for 'Polyset' resin itself or blended with nanoparticles.

Figure 23 Depicting various 1,3,5,7,9,11,13-heptacyclopentyl-pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (POSS) derivatives available commercially from Aldrich.

3. Experimental

3.1 Spectroscopy and analysis

Solid-state carbon and silicon measurements were performed on a Varian Unity NMR spectrometer at 100 MHz using a 7.5 mm magic angle spinning probe. FT-IR spectra were obtained using a Thermo-Nicolet Nexus 670 spectrometer. Near IR were done using this bench equipped with a CaF_2 beamsplitter and white light source. Mid IR experiments were done a KBr beamsplitter and a Ever-Glow source. Thermogravimetric analysis. was done using a Perkin Elmer TGA7 interfaced with a TAC 7/DX Thermal Analyzer controller. Ultraviolet-visible spectroscopy was done with a HP845X UV visible system.

3.2 Chemicals

Unless otherwise specified chemicals were obtained from Aldrich Chemicals and used without purification. Silicon nanoparticles colloidal solutions were obtained from Nissan Chemicals. 'Polyset' PCX 28-91B was supplied by the vendor Polyset Inc., Troy NY.

3.3 Hardness Measurements

Hardness measurements were done with a Shore 282088 Durometer.

3.4 Procedure for 85°C 85% aging.

Samples of 'Polyset' were spun onto silicon using at 3000 rpm for 90 seconds. The samples were cured for 1000 s at 3.3 mW/cm^2 intensity using a broadband oriel 68810 mercury arc lamp giving samples with a thickness of ~28 microns. The samples then were subjected to 85°C at 85% relative humidity for 72 hours. Refractive indexes at 633, 1300, 1500 nm were measured using a Metricon Model 2010 prism coupler. Samples must have be survived the temperature treatment without any cracking or haze before being considered as passed.

3.5 Procedure for HMDS priming

The HMDS deposition was done using a YES oven. Substrates are processed for 10 minutes at 150°C a pressure between 20-30 torr.

3.6 Preparation and use of trialkoxysilane adhesion promoters

A 2 wt % solution of trialkoxysilyl adhesion promoter is prepared in ethanol containing 5 wt% water (i.e. 95% ethanol). The pH of this solution is adjusted to 4.5 using glacial acetic acid. To allow for formation of SiOH moieties though hydrolysis at least 15 minutes should be allowed after mixing before using it to treat a substrate. The substrate is treated by immersing it into the a stirred solution of the adhesion promoter for 5 minutes. After treatment, the substrate is cleaned in an ultrasound bath containing ethanol for 15 minutes and air dried.

3.7 Preparation of samples for Mid IR spectroscopy

Samples for mid IR spectroscopic studies of curing and aging conditions were prepared by spinning the resin at 1000 rpm onto a single polished silicon 4 inch silicon wafer. The exact exposure and thermal cure are specified in the discussion.

3.8 Measurement of surface profiles

The surface profiles were obtained on a Wyko scanning optical profilometer. Focal length profiles were obtained using a beam profiler.

3.9 Experimental methodology for loading epoxy with SiO_2 nanoparticles

3.9.1 Preparations of samples for near IR spectroscopy:

Samples for near IR spectroscopy were prepared by pouring the resin into teflon molds having thicknesses in the 0.25 to 0.5 mm range. The films were cured 20 minutes with a ILC 4001 light curing unit from Electro-lite corporation. Followed by a slow ramp up to a cure temperature of 140°C which is maintained for an hour.

3.9.2 Modification of colloidal SiO_2 nanoparticles in isopropanol with surface epoxy functionlization:

A 30 wt % suspension of 9 nm SiO_2 nanoparticles in isopropyl alcohol (Nissan IPA-ST-S) (100 g) was mixed with 14.4 mL of 3-Glycidyloxypropyl trimethoxysilane (Aldrich Chemicals). This mixture was stirred for 2 days at room temperature. Residual 3-glycidyloxypropyl trimethoxysilane was then remove by diallysis (Fisherbrand regenerated cellulose dialysis tubing

nominal MWCO 12,000-14,000, 25 mm vol/cm:1.98) in IPA. Removal of the excess reagent was monitored by ultraviolet absorbance spectroscopy looking at the decrease in UV absorbance at 210 nm with time. The IPA wash solution was changed daily and removed the excess reagent after 2 weeks. The solution after dialysis and removal from the dialysis tubing was found to contain 19.5 wt % modified nanoparticles.

The presence of the glycidyl groups was confirmed by thermogravimetric analysis and Fourier Transform IR spectroscopy. Thermogravimetric analysis found that the nanoparticles consisted of 92.69 wt% SiO₂. The particles were found to have a coverage of 1.6 micromoles/m² of the trimethoxysilane reagent.

3.9.3 Transfer of modified colloidal SiO₂ nanoparticles into blending solvent compatible a commercial photocurable epoxy/siloxane resin:

Because the IPA did not blend with 'Polyset' PCX 28-91B (a commercially photocurable epoxy/siloxane oligomeric resin from 'Polyset' Company Inc) the suspension of modified SiO₂ nanoparticles could not be blended directly with the resin. Consequently, 15 g of the modified nanoparticles solution (2.93 g modified nanoparticles) was mixed with 15 g of 1-methoxy-2-propanol acetate to give a clear solution with this solvent which compatible with both the modified nanoparticles and miscible with the IPA but has a higher boiling point than IPA. The IPA was then removed by distilling it away at ~80°C giving a clear solution of the nanoparticles in the higher boiling point solvent. The solution thus obtained test positive (red color) for acidity using a "neutral red" test solution (see below for neutral red preparation). The solution is neutralized by placing it over anhydrous potassium carbonate for 1 hour. Failure to neutralize the solution of nanoparticles leads to premature setting of the photocurable epoxy resin a short time after mixing it with the modified nanoparticle 1-methoxy-2-propanol acetate solution. This gives a solution, which consists of 16 wt % modified SiO₂ nanoparticles in 1-methoxy-2-propanol acetate. This solution can be stored at room temperature for several weeks without degradation. Alternatively, MEK can be mixed with the IPA colloidal solution where it acts as a co-solvent to make compatible the 'Polyset' resin and IPA. However, great care must be used when removing the volatile solvent mixture MEK and IPA

under vacuum as undue cooling will result in coagulation of the colloid. Consequently, this procedure only works well with relatively small amounts of material. An example of this type of mixing procedure is given for the mixing of the methacrylate functionalized nanoparticle.

3.9.4 Preparation of solution of the epoxy functionalized SiO₂ nanoparticle in a commercial epoxy/siloxane resin.

A solution of modified SiO₂ nanoparticles in 1-methoxy-2-propanol (15.79 g) prepared as described above was blended with 'Polyset' PCX 28-91B resin (11.05 g). After mixing the two materials on a roller for half an hour to obtain a clear mixture of the two components, the material was put under high vacuum to remove the 1-methoxy-2-propanol. Removal was assisted with slight heating (~40°C) applied after most of the solvent had been removed to ensure a more complete removal of the solvent. In this manner a solution was obtained which consisted of 19 wt % in 'Polyset' PCX 28-91 B. This solution can be stored at room temperature for several weeks without degradation. It readily sets after exposure for 20 minutes with a ILC 4001 light curing unit from Electro-lite corporation.

3.9.5 Blending of non-modified colloidal SiO₂ in methylethylketone with 'Polyset' PCX 28-91B (alternate procedure):

A 30 wt % suspension of SiO₂ nanoparticles in methyl ethyl ketone (Nissan MEK-ST) (1.0 g) which had been placed over anhydrous K₂CO₃ to remove residual acidity (neutral red test) was mixed with 'Polyset' PCX 28-91B resin (2.0 g). The clear solution was stripped of solvent under high vacuum until most of the solvent was removed. Application of gentle heat (40°C) under high vacuum was used to remove any residual solvent. In this manner a 'Polyset' resin is prepared containing 13 wt% unmodified SiO₂ nanoparticles. Failure to treat the SiO₂ nanoparticle suspension with K₂CO₃ results in gelling of solution when mixed with the 'Polyset' resin at room temperature after 30 min. Attempts to remove the solvent prior to the gelling nonetheless results in premature setting of the resin/ SiO₂ nanoparticle mixture. Mixture only is stable for ~1 hour before solidification occurs.

3.9.6 Modification of colloidal SiO₂ nanoparticles in isopropanol with surface methacrylate functionalization:

The procedure was the same as for coating with GLYMO except that the 7.25 mL of 3-(trimethoxysilyl)propylmethacrylate (Aldrich Chemicals) was employed as trialkoxysilane reagent. This mixture was stirred for 2 days at room temperature.

The presence of the acrylate groups was confirmed by thermogravimetric analysis and Fourier Transform IR spectroscopy. Thermogravimetric analysis found that the nanoparticles consisted of 89.77 wt% SiO₂. The particles were found to have coverage of 2.2 micromoles/m² of the trimethoxysilane reagent.

3.9.7 Preparation of solution of the acrylate functionalized SiO₂ nanoparticle in a commercial epoxy/siloxane resin:

A solution of acrylate modified SiO₂ nanoparticles in IPA (1 g) prepared as described above was diluted with 1 mL MEK and then blended with 'Polyset' PCX 28-91B resin (0.8 g). After mixing the two to obtain a clear mixture the material was slowly evaporated under partial vacuum using a slightly warm heat source. This is done in order to avoid cooling the mixture too much and causing coagulation of the colloid. In this manner, a solution was obtained which consisted of 19 wt % in 'Polyset' PCX 28-91 B. This solution can be stored at room temperature for several weeks without degradation. It readily sets after exposure for 20 minutes with a ILC 4001 light curing unit from Electro-lite corporation.

3.9.8 Procedure for the preparation of the solution for acidity testing.

2.312 g of neutral red (Aldrich Chemicals) was suspended in 80 mL of ethanol containing 8.8 mL of 1 N NaOH. After stirring, the suspension was filtered to remove any undissolved material. The collected filtrate was diluted with 800 mL of distilled water stirred and allowed to crystallize. The crystals formed were filtered and washed with distilled water. After drying the crystals, these were dissolved in a heated solution consisting of 80 mL of ethanol diluted with 800 mL of distilled water. After dissolution, the solution was cooled down to 0°C to promote crystal formation. These crystals were filtered washed with water and dried. In this manner, 1.01 g of purified neutral red is obtained. The test solution is prepared

by dissolving 6.2 mg of the reagent in 1L of tetrahydrofuran. For acidity testing typically five drops of this solution are added to 1 mL of a nanoparticle colloidal suspension; if the solution becomes red, the presence of acidity is confirmed.

3.9.9 Example of use of silsesquioxane:

Glycidoxypropyldimethylsilyloxy)heptacyclopent ylpentacyclosiloxane (Aldrich Chemicals) (100 mg) was dissolved in 'Polyset' PCX 28-91B resin (900 mg). A clear solution results which is highly sensitive to curing.

4. Conclusion

We have described how to make replicas of a lens array through a molding process using a rigid substrate and a commercially available photocurable epoxy/silicone resin, 'Polyset'. Clean surfaces treated with either HMDS or a trialkoxysilane adhesion promoter give the best adhesion. For curing UV exposure of the resin followed by a thermal cure at high temperature imparts better hardness to 'Polyset' but makes it susceptible to changes in loss in the telecommunication bandwidth during humidity aging. Also the need for a post exposure thermal cure may cause stress buildup in the lenses due to the difference in coefficient of thermal expansion of the cured resin and the quartz baking (~140 times higher for the resin). In contrast, the use of a SiO₂ nanoparticle filled resin gives a rise to a hard resin system immediately after UV exposure without need for additional thermal treatment. NMR spectroscopic studies confirm the more rigid nature of a cured blend of 'Polyset' with the nanoparticles. Additionally, it was found that the use of a trialkoxysilane reagent (e.g. GLYMO) at the surface of the nanoparticles allowed them to form stable blends when mixed with the 'Polyset' resin. The use of 'bare' SiO₂ nanoparticles in blends with 'Polyset' but these blends must be cured quickly (i.e. <1 hour) otherwise coagulation occurs. Examination by near FT IR spectroscopy of cured resin shows that the blend with the GLYMO coated SiO₂ nanoparticles gives rise to less intense CH overtones bands than the cured resin containing 'Polyset' alone without any increase in the OH overtone band and do not show haziness after 85/85 aging. Bare SiO₂ nanoparticles blends with 'Polyset' also give less CH overtones but unfortunately also give rise to a significantly larger H overtone band at around 1.5 microns. Finally, the use

of SiO₂ nanoparticles does not impart any scattering as would be expected given their small size compared to the wavelength of light.

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