Total Flexibility in Thin Film Design Using Polymer Nanocomposites

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ABSTRACT

Optically clear, mechanically flexible nanocomposites are created by doping host polymers with nanoparticles having higher or lower refractive indices. The composite materials preserve the viscoelastic properties of the binding polymers and exhibit infinite tunability between the refractive index limits of the system. These properties provide unique benefits for multi-layer thin film optical filters. Additionally, the nanoparticles are dispersed in a fluid or bound in a polymer matrix in use, thus reducing toxic risks that may be associated with raw particles. A simple and safe method of producing highly engineerable optical filters is presented.

Keywords: nanocomposite, multilayer filter, refractive index, nanoparticle

1 INTRODUCTION

Metal oxide coatings of varying refractive index have been employed in electromagnetic filters ranging from the UV through to the IR regions and have applications as broad band and narrow band pass filters. Filters in the visible region are generally used both to reduce the reflections from the surface of a lens to aid sight and as reflective filters for fashion eyewear. Reflective filters in the IR region serve as heat rejecters in broad band applications and as sensors in narrow band applications.

Thin-film optical filters have been around for over a century and chemical vapor deposition techniques have been predominately the manufacturing choice. The technique generally includes the deposition of metal-oxide ¼ wavelength thin film layers of varying refractive index to get a change in the optical response from the surface of a substrate. These can include broad band antireflective and reflective coatings as well as edge and band gap filters.

Traditional vacuum deposited anti-reflective coatings have been around since the 1930's and actually performed well when coated on a glass ophthalmic lens since the coatings themselves were ceramic. During the 1970's, manufacturing improvements allowed for polymer lenses to gain general acceptance as an alternative for glass; however, anti-reflective coatings did not fair well on the plastic substrates due to the major differences in the strain behavior of the coating and the lens. Significant progress has been made in this technology, but the disparity in the strain domains continues to be an issue.

Deposition of these layers onto a polymer substrate have typically been accomplished using vapor deposition techniques such as CVD, and sol-gel methods. In these cases the deposited metal oxides (ceramics) have mechanical properties that have strain domains that differ significantly from the polymer substrate. (figure 1) This has caused problems with crazing and cracking of the thin film filters during high strain phenomena such as thermal cycling and mechanical deformations.[1, 2]

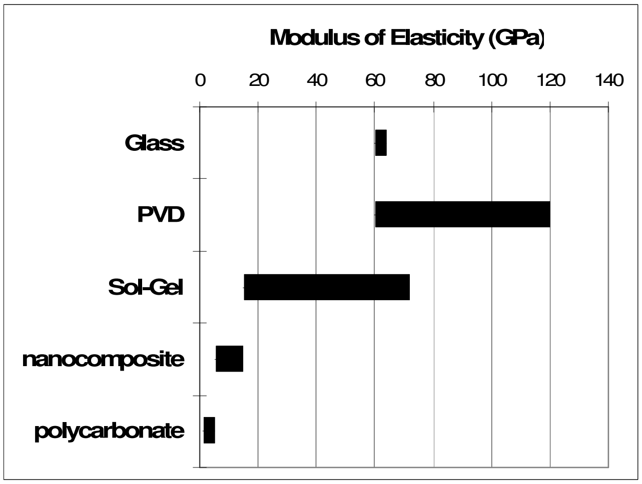

Figure 1: Comparison of the modulus of elasticity of coating materials and a polymer substrate.

More recently researchers have proposed and successfully employed nanoparticles in polymers to build a nanocomposite having an engineered refractive index. These films typically employ spherical particles that have dimensions that are under 100 nm in a polymer. Similar to the artisans of cathedral glass, some have turned to metal chlorides.[3] Yu et. al. produced thin films on the order of several microns using a colloidal silica and acrylic monomer cured in the presence of heat.[4] Others have developed flexible polymer and nanoparticle multilayers into an antireflective coating.[5]

A multilayer nanocomposite coating can be used as a narrow-band reflector whose peak wavelength, bandwidth, and reflectance are determined by the thicknesses and refractive indices of the layers.[6] Traditional deposition techniques using pure dielectric layers are limited to discrete refractive indices and the resulting coatings are extremely brittle.[7]

We have developed a method to deposit a nanocomposite thin film in which the refractive index of the film is tunable over a large range.[8] The method relies on evaporative spin coating in which a solvent born, liquid dispersion of nanoparticles and UV curable monomers is deposited onto a spinning substrate and is subsequently cured. Dispersions of nanoparticles in a carrier solvent are readily available; however, we have synthesized the titanium dioxide dispersion. and in this case titanium dioxide was produced in a solvent.[9] Nanocomposite coatings of up to 15 layers have been prepared for the visible and NIR regions with very discrete layers (as shown by transmission electron microscopy).[10] The resulting stacks exhibit very good mechanical flexibility on polymer substrates as shown using nanoindentation techniques.[11]

Here we demonstrate the abilities of nanocomposites to control filter response through their engineerable refractive indices. With layer counts exceeding 30 (more than twice the layer count of our previous efforts), very little haze is observed. Three formulations of titanium dioxide and UV curable monomers were prepared to produce the following characteristics in the finished films: (1) 1.65 refractive index with a thickness of 73 nm (2) 1.75 refractive index with a thickness of 69 nm (3) 1.85 refractive index with a thickness of 65 nm.

2 BACKGROUND

Our group has been investigating the use of nanoparticles in a UV curable monomer. This requires stabilization methods of nanoparticles favoring the use of solvents that are compatible with the monomers and work well for the spin on process. The spin coating method has been widely studied and allows for a simple low cost deposition of thin films. This simple technique deposits nanocomposite films with high visible light transparence while maintaining the modified refractive index and mechanical strength.

The nanocomposite thin films consist of metal-oxide nanoparticles and a UV-cured acrylate polymer which acts as a binder. The nanoparticles are used to both engineer the refractive index of the individual layers and to improve the mechanical properties of the film. The nanoparticles are initially suspended in a solvent along with an acrylate monomer and a photoinitiator. To insure transparency and avoid light scattering, it is very important that the nanoparticles are not agglomerated and that the primary particle size be much less than 100 nm .

The refractive index of the layers is controlled by adjusting the volume ratio of nanoparticles and monomer, with the refractive index bounded by the pure monomer at the minimum and at approximately 60 volume percent nanoparticles at the maximum. This corresponds well with the theoretical close packing of spheres, and we have noted that the refractive index and modulus of the films reaches a maximum at this point.

The thin film filter design utilizes a simple stack of ¼ wave thickness layers of alternating high and low refractive index materials. The reflectivity off a planer surface from a wave perpendicular to it is

$$R = \left(\frac{n_0 - n_{sub}}{n_0 + n_{sub}} \right)^2 \tag{1}$$

where

R = reflection
n_o = index of refraction of air (1.00)
n_{sub} = index of refraction of the substrate

If polycarbonate is the substrate (n=1.586 at 550 nm) then the reflection of an incident light wave perpendicular to a surface is 5.1 percent. In this case the reflectance is a function of the refractive index which varies with the wavelength. A coating of multiple thin films of different refractive indices on the substrate can be used to interfere with the reflected waves and for a film having a ¼ wave thickness the reflectance can be computed as

$$R = \left(\frac{(n_0 - Y)}{(n_0 + Y)} \right)^2 \tag{2}$$

In this case the refractive index of the substrate has been replaced by the admittance of the surface (Y) and is a ratio of the total tangential magnetic and electric fields as described by Macleod.[6] The admittance for a system of i alternating high and low index films is

$$Y = \left(\frac{n_{high}^{(i+1)}}{n_{sub} n_{low}^{(i-1)}} \right) \tag{3}$$

The first three equations can be used to model the magnitude of reflectance for a multi-layered filter. Continuing with the case of a dual refractive index system, the width of the notch filter is a function of the ratio of refractive indices of the layers

$$\Delta g = \frac{2}{\pi} \sin^{-1} \left(\frac{n_{high} - n_{low}}{n_{high} + n_{low}} \right) \lambda \tag{4}$$

where

Δg is the half width of the notch

From this equation it can be seen that as the ratio of refractive indices increases, the width of the notch filter will do the same.

This simple relationship allows for the determination of the filter response at a specified wavelength (λ) for which the layers thickness is equal to $\lambda/4d$, where d is the optical thickness of the film. The optical distance is the product of the physical distance and the refractive index of the medium which relates to the phase shift of light traveling through a vacuum at this physical distance. In the case that the layer thickness is not a quarter wave thickness, then the computation of the reflectance is more rigorous and generally requires the use of a computer

3 EXPERIMENTAL

The individual layers in the stack were spin-coated onto a substrate using a machine by Optical Dynamics. This well understood technique controls the layer thickness by balancing the centrifugal forces of a developing thin film to the viscous forces that increase as evaporation takes place. The repeatability of this method is extremely high as long as the coating environment is controlled such that the evaporation rate stays constant. This method can also be extended to coat surfaces with roughness on the order of several microns.

After the solvent is evaporated 50-150 nm film of a UV-curable monomer and nanoparticles remain. In this case the monomer is a trimethylolpropane triacrylate (TMPTA). The film is then cured using a pulse xenon UV source lamp, leaving a polymer nanoparticle composite. Subsequent layers are then added on top of the previous layer to build the filter.

The thickness of the layers was determined by applying and curing the individual film onto a hard substrate such as glass. Part of the film was scratched from the surface of the glass and the step height determined using a profilometer (model number XP-1) by Ambios Corporation. The accuracy of the method was confirmed by measuring thickness in several locations and on multiple layers.

The optical response of the final article is measured using a contact probe spectrophotometer model F20 by Filmetrics. The refractive index of the two layers was determined using equations (2) and (3) and the physical thickness as measured by profilometry. The software package TFCalc by Software Spectra, Inc. was used to confirm the calculations of the equations.

The titanium dioxide dispersion was synthesized in our laboratory using a hydrothermal process. The titania nanoparticles have a mean particle size diameter of approximately 20 nm and are functionalized to improve the stability in an alcohol. The functional groups on the particles also aid in the adhesion to the polymer matrix, which keeps the films from cracking under the large strains.

4 RESULTS

To confirm the infinite refractive index control of these nanocomposites we choose to build optically reflective filters centered at 480 nm. The refractive idecis of each of the layers was controlled by varying the ratio of nanoparticles to polymer. The intent was to show that the increase in layers produced the correct response in reflectance and that the width of the notches followed the ratio of nanoparticle loadings.

In this study we have used an anatase form of titanium dioxide nanoparticle to engineer the refractive index. The refractive index of the cured TMPTA is approximately 1.48 and the anatase titanium dioxide is approximately 2.2. At a volume percentage of 60 percent the theoretical refractive index would be 1.91, however the surface modifications to the nanoparticles has dropped the refractive index.

Three refractive indices of 1.65, 1.75 and 1.85 were chosen to demonstrate the refractive index engineering capabilities. Figures (2) and (3) show the response of multi-layer of two refractive indices and indicate that the reflectance magnitude increases as the layers are added as expected. In addition the width of the filter is also directly controlled by varying the ratio of nanoparticles in each film which is directly related to the refractive index. The calculated reflectance magnitude is reported in table 1.

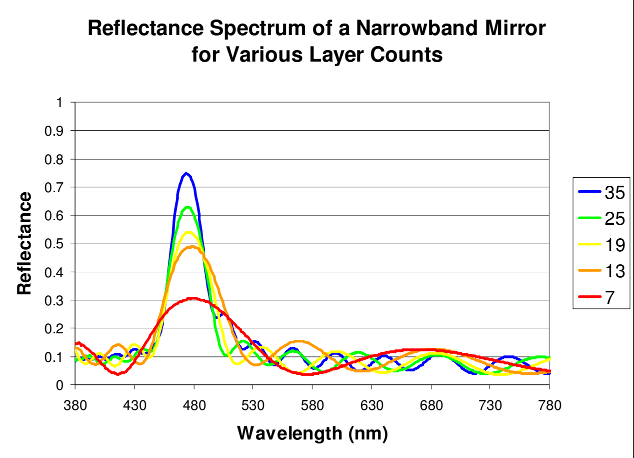

Figure 2: Narrow reflectance filter using refractive indices of 1.75 and 1.85 with layer counts of 7, 13, 19, 25 and 35.

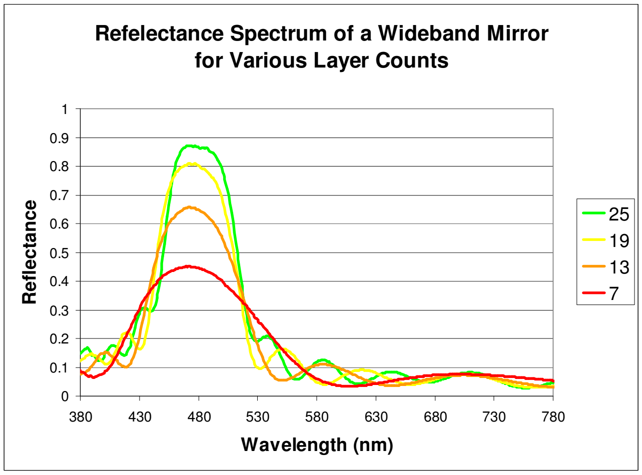

Figure 3: Wide reflectance filter using refractive indices of 1.65 and 1.85 with layer counts of 7, 13, 19 and 25 layers.

Layers	Narrow	Broad
7	27.3	40.8
13	40.0	64.0
19	52.2	79.9
25	62.9	89.4
35	76.7	

Table 1: Calculated reflectance magnitudes of the narrow and broad filters.

Finally to test the mechanical flexibility of the system we simply applied the films to a very thin substrate and bent it around an extremely small radius as shown in figure 4. The results is that there was no damage to the films.

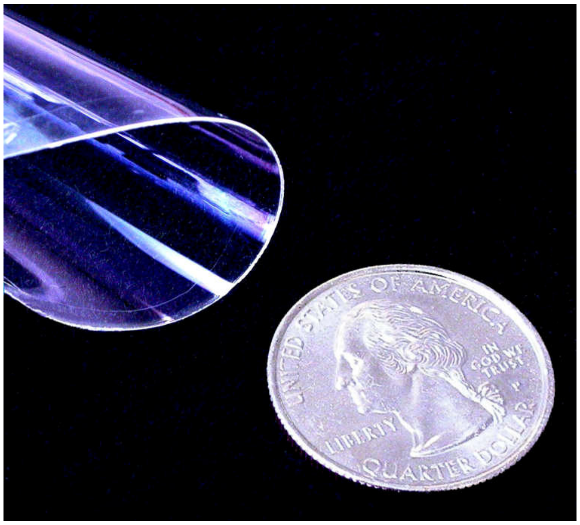

Figure 4: Cast, flexible substrate having a nanocomposite anti-reflective coating demonstrating the mechanical flexibility of the finished coating

5 CONCLUSION

The results clearly show that mechanically flexible thin film filters can be assembled using nanocomposites of inorganic nanoparticles embedded in an organic polymer. Furthermore, the use of a composite allows for an infinite tunability of refractive index between the boundaries of the materials used. The measured results of the final films closely resemble their theoretical models. The goal of this work was to show the capabilities of this simple process in building multilayer thin films that are both optically and mechanically flexible.

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