Nanocomposite Optical Filters Under Extreme Strain

Thad Druffel*, Omar Buazza, Matt Lattis, Scott Farmer

Optical Dynamics, 10106 Bluegrass Parkway, Louisville, KY, USA 40299-2202

Abstract

Nanocomposites are created by doping host polymers with nanoparticles that typically have higher or lower refractive indices. The ability to tailor the mechanical and optical performance of these composites has led to their increased use in transparent materials. Nanocomposites maintain the elastic properties of the binding polymers and exhibit infinite refractive index tunability between the limits of the system. These unique properties provide distinct benefits for multilayer thin-film optical filters. Because the nanoparticles are dispersed in a fluid or bound in a polymer matrix in use, toxicity risks that may be associated with raw particles are reduced. Using a stable dispersion of titanium dioxide nanoparticles and a UV-curable monomer, we were able to design and produce several quarter-wave filters that were capable of strains of up to 20 percent.

Introduction

Nanocomposites using organic polymers and inorganic nanoparticles will play an important role in applications requiring high visible transparency and mechanical flexibility. A unique class of materials is created when the elastic properties of polymers are combined with the inherent hardness of crystalline nanoparticles. Transparent polymers are generally more flexible than glass materials and exhibit a moderate range of optical, electrical, and mechanical properties. The incorporation of inorganic nanoparticles in the polymer system significantly increases the physical parameter range beyond that of the host polymer and allows material properties to be engineered for specific applications. Of particular interest to our group are thin-film nanocomposites on polymer substrates in which strain domains are well matched.[1,2]

True nanoparticles are significantly smaller than visible light wavelengths and, therefore, generally do not cause significant optical scattering when incorporated in a polymer. Careful nanoparticle selection can influence refractive index, electrical conductivity, UV absorption, magnetism, and a host of other properties in the finished nanocomposite. The elastic properties of the binding polymers can be maintained while improving abrasion resistance through the inclusion of high-hardness nanoparticles. This provides opportunities to improve transparent materials that require clarity and abrasion resistance.

Thin-film coatings of less than 100 nm to tens of microns in thickness are important in many polymer substrate applications, but the conditions under which these systems are used must often be limited to maintain film and substrate integrity. Since mainstream coatings are often ceramics applied using vacuum deposition, they normally have strain domains that are significantly different from the polymer substrate. Under large strains these coatings tend to crack and induce objectionable optical scattering that is quantifiable as haze. These cracks allow other types of damage to easily propagate from them as well. The processing temperatures used to apply these coatings also leave

behind large intrinsic stresses that further limit their utility due to significant changes in the ultimate strength of the coated substrate.

Here we demonstrate a thin-film optical filter composed of a multilayer nanocomposite undergoing strains in excess of 20 percent. These filters were designed to have a peak reflectance at a chosen wavelength in the visible region. As strain is applied to the system the peak wavelength changes, but the intensity of the reflectance remains constant. This confirms that the films are not failing at large strains and demonstrates a performance unmatched by traditional vacuum deposition techniques.

Background

Our group has been investigating systems that use nanoparticles in UV-curable monomers. For our typical applications, the nanoparticle stabilization methods must be compatible with solvents and monomers that work well in a spin coating process.

Our nanocomposite thin films consist of metal-oxide nanoparticles and a UV-cured acrylate polymer that acts as a binder. The nanoparticles are used to both engineer the refractive indices 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 ensure transparency and avoid excessive light scattering, the primary particle size must be much less than 100 nm and the suspension must be properly stabilized to avoid particle agglomeration.

The refractive index of a layer is controlled by adjusting the volume ratio of nanoparticles and monomer. For a layer using high-index particles in a lower index monomer, the refractive index limits occur at the index of the pure monomer (the index minimum in this case) and at the index achieved with approximately 60 volume percent nanoparticle loading (the index maximum in this case). This corresponds well with the theoretical close packing of spheres, and we have noted that the refractive index and modulus of the film reach their maxima at this loading.

Quarter-Wave Stacks

High-reflectance filters are often created with a stack of alternating high and low refractive index layers, with each layer having an optical thickness of ¼ wave.

The reflectance of an uncoated planar 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 = reflectance
n_o = index of refraction of air (1.00)
n_{sub} = index of refraction of the substrate

If PMMA is the substrate (n=1.5 at 550 nm), then the amount of incident light reflected by the uncoated surface is 4%. In this case the reflectance is purely a function of the refractive index difference between the substrate and air (it should be noted that the refractive index of the substrate varies with wavelength and, therefore, the reflectance does as well).

A coating of multiple thin films of different refractive indices on the substrate can be used to interfere with the reflected waves. For a film having ¼ wave optical 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.[3] 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 the reflectance for a multilayer filter. Continuing with the case of a dual refractive index system, the width of the filter's notch is a function of the ratio of the 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 filter's notch will do the same.

These relationships allow filters to be designed and their simplified response at a specified design wavelength (λ) to be modeled. Each layer's optical thickness (d) is made equal to $\lambda/4$, with optical thickness defined as the product of the physical thickness and the refractive index of the material (refractive index indicating how much the speed of light is reduced in the material compared to the speed of light in a vacuum). In cases where layer thickness is not equal to a quarter wave, computation of the reflectance is more laborious and generally requires the use of a computer.

Stress in Thin Films

The deformation of a system of films is controlled by the stiffness of each of the individual layers. The stiffness of each layer is the product of the modulus of elasticity and its cross-sectional area.

$$K = EA \tag{5}$$

where
K = stiffness
E = modulus of elasticity
A = cross sectional area (thickness x width)

Quarter-wave optical films have thicknesses on the order of 100 nm. To create a viable optical element, these films are generally laid down on a substrate with a thickness of at least a millimeter. This represents a thickness difference of three to five orders of magnitude. While the modulus of elasticity of ceramic films is generally one to two orders of magnitude larger than that of a plastic substrate, the stiffness of the film will still be several orders of magnitude smaller than the substrate because the films are so thin. Additionally, ceramic films are typically limited to strain domains of approximately 1 percent, while many polymers can withstand very large strains. This means the films will not significantly contribute to the overall stiffness of the article and they will be quickly strained beyond failure. Externally applied loads will ultimately be borne almost entirely by the polymer substrate.

What this means in real-world applications is that plastic substrates coated with thin-film filters using vacuum deposited ceramic materials are typically unable to resist large strains induced by thermal and mechanical forces. As a result, the brittle ceramic films will either buckle under compressive loads or crack under tensile loads. These brittle failures on the surface will cause excessive light scattering and will reduce visible transparency. Therefore, engineering applications for thin-film dielectric coatings on polymers tend to be limited. A nanocomposite film, on the other hand, has a strain domain that is closely matched to the polymer; therefore, it can undergo large induced strains without failure.

Experimental

The individual layers in the stack were spin coated onto a substrate using a machine by Optical Dynamics. This well-understood technique controls layer thickness by balancing the centrifugal forces of a developing thin film with 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 evaporates, a 50-150 nm film of a UV-curable monomer and nanoparticles remains. In this case the monomer is a trimethylolpropane triacrylate (TMPTA). The film is then cured using a pulsed xenon UV lamp, leaving a polymer nanoparticle composite. Subsequent layers are then added on top of the previous layer to build the filter.

The physical thickness of the layers was determined by applying and curing the individual films on a hard substrate (glass). Part of the film was scratched from the surface of the glass and the step height was determined using a profilometer (model number XP2 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 was measured using a contact probe spectrophotometer model F20 by Filmetrics. For a given quarter-wave stack design of

alternating index layers the refractive index of the layers is computed 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 results of the equations. A simple method of determining the refractive index of the films is to build a multilayer stack of high and low refractive index materials and model their response using a computer (once the physical thicknesses have been established).

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

Demonstration of multilayer film flexibility was accomplished by casting the film onto a highly flexible, thin substrate and then applying strains to the article. The first method was to simply bend the substrate/film. In order to apply larger strains we clamped the article in an apparatus that allows pressurized water to be introduced into a cavity formed by the thin, flexible substrate and the apparatus. Since the apparatus is much more substantial, the pressurized water inflates the substrate/film. This method introduces an isotropic strain in the plane of the film.

Results

In the case of the high-index layer, the introduction of the inorganic particles creates a non-uniform refractive index across the visible spectrum, complicating analysis of the film. To verify the refractive index of the nanocomposites, we first built a 9-layer reflective filter composed of alternating high and low refractive index films. Because the finished filter provides significant physical thickness and a large, highly responsive peak at its fundamental wavelength, the optical properties of the high-index layer can be accurately determined using thin-film modeling software to match the measured response of the filter.

In this study we used an anatase form of titanium dioxide nanoparticles to engineer the refractive index of the high-index layer. The refractive index of cured TMPTA (the binding polymer of the layer) is approximately 1.48, and the anatase titanium dioxide is approximately 2.2. With 60 volume percent particle loading, the theoretical refractive index is 1.92; however, surface modification of the nanoparticles decreases their refractive index.

The low index utilized silicon dioxide and TMPTA, which have similar refractive indices and very flat refractive index distributions. This makes the finished film relatively easy to characterize. By depositing nine successive layers of this film alone we determined that the thickness of the individual layers is 91.6 nm and the refractive index is 1.475.

The thickness of the 9-layer reflective stack was measured to be 825 nm, which yields a thickness of 92.4 nm for the high-index layer (according to the measurements above). This system was modeled in TFCalc using a flat dispersion of 1.48 for the refractive index of the low and a mixture of 1.48 and anatase TiO_2 for the high. The best fit to the observed reflectance spectrum yields a refractive index for the high of 1.885 (figure 1). As a check, we also ran a sensitivity analysis in which we allowed the

thicknesses of the coatings to vary by +/- 5 nm. The results show that the optical response of the filter fits well using these parameters.

This system was then tested for flexibility by simply bending the substrate/filter at a very short radius. This is shown in figure 2. It can be observed that the optical clarity of the system has not been impacted by the induced strains. No visible damage was noted to the article. In fact, this system was also subjected to very large thermal loads in which the article was moved between a boiling water bath and an ice water bath with no visible signs of coating degradation.
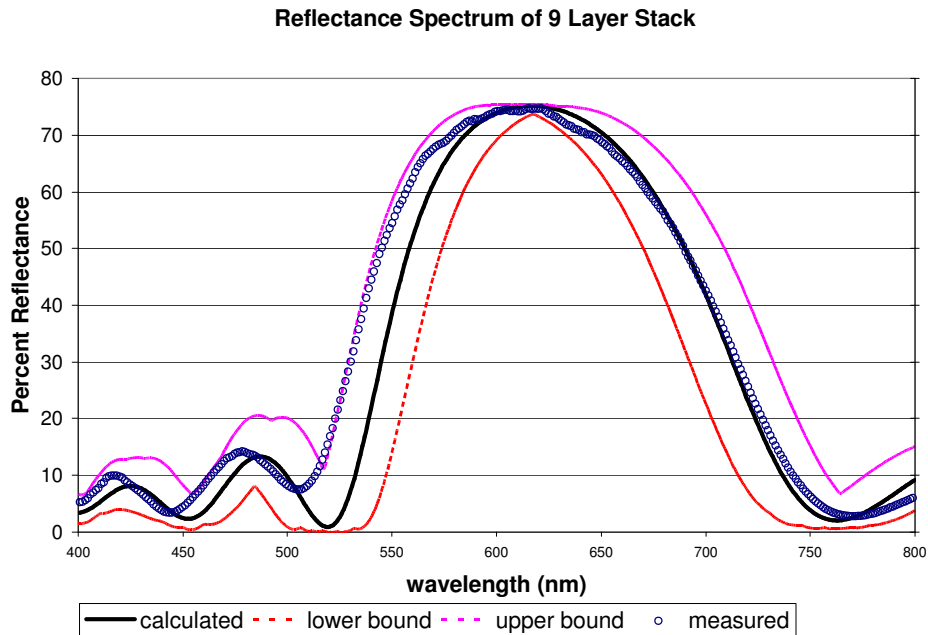
Reflectance Spectrum of 9 Layer Stack

Figure 1: Measured reflectance spectrum of a 9-layer alternating high (TiO2 nanocomposite) and low (SiO2 nanocomposite) index stack compared to a modeled stack bounded by +/- 5nm thickness variations.

Figure 2: A 9-layer nanocomposite thin-film coating on a polymer substrate demonstrating high flexibility and transparency.

To further study these nanocomposite films, we built an apparatus that would allow for the application of an in-plane stress. By applying hydrostatic pressure to one side of the substrate, we cause it to inflate and produce a tensile strain. The coating/substrate was strained up to 20 percent and the reflectance spectrum was measured. As expected, the system did not fail while undergoing these strains, as shown by the response of the reflectance (figure 3). In fact, we observed no significant change to the height of the reflectance response, indicating that the refractive indices of the layers were maintained. This information could be used to determine the Poisson's ratio of the thin films.
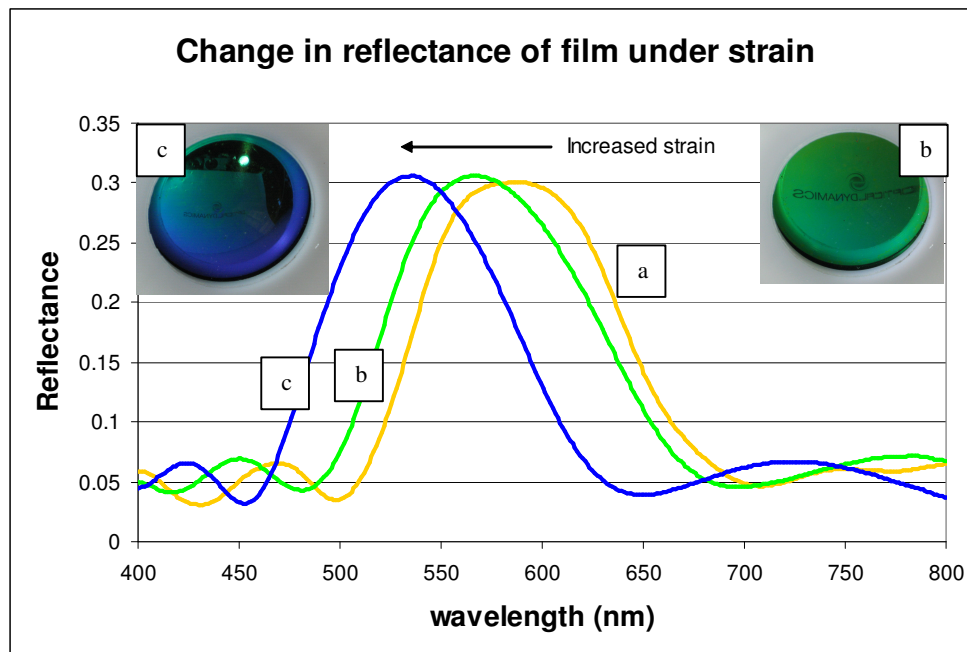

Figure 3: Demonstration of nanocomposite flexibility by stretching a thin film. Pressure was applied on one side of the article inducing a uniaxial strain in the plane of the films. The reflectance response of the films at 0, 10%, and 20% strain are shown graphically. The unstrained film has a peak response at approximately 590 nm and is shown by curve (a). At a 10% strain (b) the spectrum is shifted to about 560 nm and the reflected color is green. At a 20% strain (c) the spectrum's peak is shifted to about 530 nm and the reflected color of the mirror is blue. In each case the peak reflectance of the mirror stays constant at 30%.

Conclusion

Thin-film coatings of less than 100 nm to tens of microns in thickness are important in many polymer substrate applications, but the conditions under which these systems are used must often be limited to maintain film and substrate integrity. Since mainstream coatings are often ceramics applied using vacuum deposition, they normally have strain domains that are significantly different from the polymer substrate. Under large strains these coatings tend to crack and induce objectionable optical scattering that is quantifiable as haze. These cracks allow other types of damage to easily propagate from them as well. The processing temperatures used to apply these coatings also leave

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