



AFRL-ML-WP-TP-2007-483

**POLYMER NANOCOMPOSITE THIN FILM MIRROR FOR
THE INFRARED REGION (PREPRINT)**

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MAY 2007

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REPORT DOCUMENTATION PAGE				<i>Form Approved</i> OMB No. 0704-0188	
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1. REPORT DATE (DD-MM-YY) May 2007		2. REPORT TYPE Journal Article Preprint		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE POLYMER NANOCOMPOSITE THIN FILM MIRROR FOR THE INFRARED REGION (PREPRINT)				5a. CONTRACT NUMBER FA8650-05-C-5053	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER 62102F	
6. AUTHOR(S) N. Mandzy and E. Grulke (University of Kentucky) T. Druffel (Optical Dynamics Corporation) Mahendra Sunkara (University of Louisville)				5d. PROJECT NUMBER 4347	
				5e. TASK NUMBER 64	
				5f. WORK UNIT NUMBER 64600002	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Kentucky Chemical & Materials Engineering Dept. 359 R.G. Anderson Building Lexington, KY 40506 ----- Optical Dynamics Corporation 10100 Bluegrass Parkway Louisville, KY 40299 University of Louisville Chemical Engineering Dept. J.B. Speed School of Engineering Louisville, KY 40292				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory Materials and Manufacturing Directorate Wright-Patterson Air Force Base, OH 45433-7750 Air Force Materiel Command United States Air Force				10. SPONSORING/MONITORING AGENCY ACRONYM(S) AFRL/MLBT	
				11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S) AFRL-ML-WP-TP-2007-483	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES Journal article submitted to the Nature Photonics Journal. This work was funded in whole or in part by Department of the Air Force contract FA8650-05-C-5053. The U.S. Government has for itself and others acting on its behalf an unlimited, paid-up, nonexclusive, irrevocable worldwide license to use, modify, reproduce, release, perform, display, or disclose the work by or on behalf of the U.S. Government. PAO Case Number: AFRL/WS 07-0996, 23 Apr 2007. Paper contains color.					
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15. SUBJECT TERMS Coatings, electromagnetic filters, infra red, vapor deposition, sol-gel, optical performance, anti-reflective					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT: SAR	18. NUMBER OF PAGES 20	19a. NAME OF RESPONSIBLE PERSON (Monitor) Lisa Farrier 19b. TELEPHONE NUMBER (Include Area Code) N/A
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			

Polymer Nanocomposite Thin Film Mirror for the Infrared Region

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Thin film metal oxide coatings have been used commercially for electromagnetic filters from the UV to the infra red regions for over half a century. Deposition onto a substrate has typically been accomplished using vapor deposition techniques[1-3] and more recently sol-gel methods [4-7]. These coatings provide very good optical performance under abrasion, thermal cycles and variable humidity when applied on substrates with similar thermal and mechanical properties. When conventional metal oxide coatings are applied to flexible, relatively soft substrates such as polymers, mismatches in mechanical properties can reduce interfacial adhesion or accelerate mechanical failures [8, 9]. The authors recently developed anti-reflective optical filters utilizing self-assembled thin film polymer nanocomposites on polymer substrates using less than five discrete layers. This paper describes the first time demonstration of an IR mirror using fifteen discrete layers with an IR-reflectance that exceeds 90 percent at 1064 nm and transparent in the visible spectrum.

Ultrathin layers of polymer nanocomposites can be used to develop electromagnetic filters with improved mechanical performance on compliant substrates such as polymers. Self-assembled polymer nanocomposite thin film layers composed of UV-cured acrylates and metal oxide nanoparticles were developed as antireflective coatings for ophthalmic lenses [10, 11]. The primary failure mode in this application is associated with intrinsic stresses introduced during processing and the thermal cycling of the plastic. Nanocomposite coatings on plastic substrates exhibit ductile failures, limiting secondary cracks propagating from abrasions and thereby reducing haze [12]. Ceramic thin films in similar studies exhibited brittle fracture, which led to secondary cracks and higher haze measurements [8, 9].

Anti-reflective coatings for the visible range are relatively simple designs of several dielectric layers and are used in many consumer products. These same materials can also be used to create mirrors in the IR region, but the layer counts increase to tens of layers resulting in more complexity in the process. For processes involving dielectric materials, these increased interfaces increase the vulnerability of the coatings to cracking on a flexible substrate. A simple thin film filter design utilizes a stack of $\frac{1}{4}$ wave thickness layers of alternating high and low refractive index materials for which the reflection off a surface is:

$$R = \left(\frac{(n_0 - Y)}{(n_0 + Y)} \right)^2 \quad (1)$$

Where R is reflection, n_o is index of refraction of air and Y is admittance of the surface [13]. The admittance of a reflective stack of i alternating $\frac{1}{4}$ wave high and low refractive index layers is represented as

$$Y = \frac{n_{high}^{(i+1)}}{n_{sub} n_{low}^{(i-1)}} \quad (2)$$

This simple relationship allows for the determination of the filter response at a specified wavelength (λ) having layer thicknesses equal to $0.25\lambda/d$ (λ is the wavelength, and d is the optical thickness which is the product of the refractive index and thickness of the film). The nanocomposite thin films will require more layers than those produced by vacuum deposition since the ratio of refractive indices is less due to the organic binder used in this system.

Reproducible optical response of multilayer filters is accomplished only through precise control of the refractive index and thickness of each layer. In general, preferred layer characteristics include: uniform thickness over surface contours, low surface roughness relative to its thickness for sharp differences in refractive index across the layer interfaces, and the highest possible difference in refractive index between adjacent layers maximizing the admittance of the surface. The nanocomposite thin films consist of essentially spherical metal oxide nanoparticles with narrow size distributions dispersed in a continuous matrix of UV-cured acrylate polymer. High transparency and low scattering for each layer require that the nanoparticles are not agglomerated and are significantly smaller in diameter than the waves to be altered.

Ultrathin nanocomposite films were manufactured by spin coating a dispersion containing nanoparticles, monomer, initiator, and solvent on a plastic substrate. Spin coating controls the layer thickness by balancing the centrifugal forces on a spreading thin film to the viscous forces that increase as evaporation takes place, yielding very good repeatability [14, 15]. The layer is then partially cured using a pulse Xenon UV source lamp, creating a polymer nanoparticle composite. Monomer conversion in the uppermost layer is controlled to be less than 100%, so that monomer in the following layer will crosslink across the interfacial zone, improving interlayer adhesion. Good interfacial adhesion between layers formed by such processing has been shown by nanoindentation studies [12].

The packing of the nanoparticles was pushed toward to the theoretical limit of 73% for hexagonal close packing of spheres in order to generate the largest possible refractive index difference between layers. For our set of processing conditions and materials, volume packing of 60 percent yielded highly reproducible mechanical performance (Figure 1), which is confirmed elsewhere [16]. At this ratio we would expect the refractive index of the layers to follow the rule of mixtures between the nanoparticles and the polymer.

The low index film is composed of an acrylate monomer nanoparticle silica dispersion received from Hansie-Chemie Industries (XP270) and combined with a silica colloid as supplied by Nissan Chemicals (IPA-ST). The colloid improves the bonding between the silica nanoparticles and the acrylate, increases the packing density of nanoparticles, and

improves the mechanical performance of the final film. The monomer is a trimethylol propane triacrylate (TMPTA). The photoinitiator is a benzoyl cyclohexanol supplied by Ciba as Irgacure 184. N-propanol (Sigma-Aldrich) was used for its compatibility with the colloid and to minimize defects caused during the spin process. The high index film was a nanocomposite composed of anatase titania, TMPTA (Sartomer 351), a photoinitiator (Ciba Irgacure 184) and solvent (n-propanol Sigma Aldrich). The titania was made in our laboratory using a hydrothermal process.[17] The titania nanoparticles ($D \sim 20$ nm) were functionalized to improve their dispersion in the coating solution, and to improve their adhesion to the polymer matrix. The spectral response of the films was characterized using a Beckman Coulter Model 800 spectrophotometer in the range of 800 to 2000 nm. The refractive index of each of the two layers was determined to be 1.48 for the low and 1.88 for the high, which for the high index is lower than expected and could be due to impurities or insufficient packing.

A thin film stack was designed to have a reflectance of greater than 90% at a wavelength of 1060 nm; the stack based on the two nanocomposite materials required fifteen layers. (A conventional $\text{TiO}_2/\text{SiO}_2$ CVD stack would require 9 layers) The corresponding $\frac{1}{4}$ wave thicknesses of these films are 180 nm and 140 nm for the low and high refractive index layers. The spin speeds of the machine were adjusted to fine tune the final thickness of the films. The resulting reflectance from the surface is shown in Figure 2 and compares very well with the predicted response.

Thin cross-sections of the stack on polycarbonate were used to verify layer thickness and interlayer adhesion. The coated polycarbonate substrates were shaved with a microtome to produce 50-150 nm thin cross-sections, which were analyzed by transmission electron microscope TEM (JEOL 2010F TEM). Figure 3 shows that the total thickness is approximately 2.4 microns, which agrees with the stack design of 8 layers at 140 nm and 7 layers at 180 nm. The insert image of Figure 3 shows the individual nanoparticles.

The micrograph also shows that the coating performs well at points of high stress concentrations as evidenced by the nature of the tearing of the sample during the microtome process. In the torn areas, there is no evidence of failure along the interlayer surfaces, confirming good interfacial adhesion within the stack. In addition, there is one tear that terminates at the substrate, where it is likely that the propagation is along the substrate/nanocomposite interface.

Elemental mapping (electron energy loss spectroscopy (EELS); JEOL 2010F TEM) was conducted on a two layer nanocomposite of the low and high index nanocomposites. Figure 4 shows that the separation between the high and low index layers is well defined.

The modulus of PVD and sol-gel coatings is well matched to glass, but significantly larger than a polymer substrate such as polycarbonate and PMMA [3, 18, 19], whereas the polymer nanocomposite is well matched mechanically. The metal oxide nanoparticles embedded in the film increase the elastic modulus providing a thin “hard” coat over the softer material, while maintaining the ratio of mechanical properties to the polymer

substrate close to unity. This closely matched strain domain limits the stress induced cracks that occur under large deformations. This multilayered nanocomposite approach has been integrated into a commercial lens manufacturing system requiring less than 5 layers and represents a substantial costs savings compared to conventional coatings.

We have shown that polymer/nanoparticle composite thin films can be used effectively to produce IR mirrors using a simple, scalable and inexpensive process. Additionally these films have better strain capabilities making them suitable for plastic and flexible substrates and for systems that undergo thermal cycling. The nanocomposites coatings have been successfully demonstrated for the UV through the NIR range using nanoparticles of metal oxides. This method could also be used with other nanoparticles which would have better properties in the IR spectrum such as metals and nitrides of metals.

Acknowledgement

This work was supported by the United States Air Force Research Laboratory under contract number FA8650-05-C-5053 (L. Farrier and S. Szaruga).

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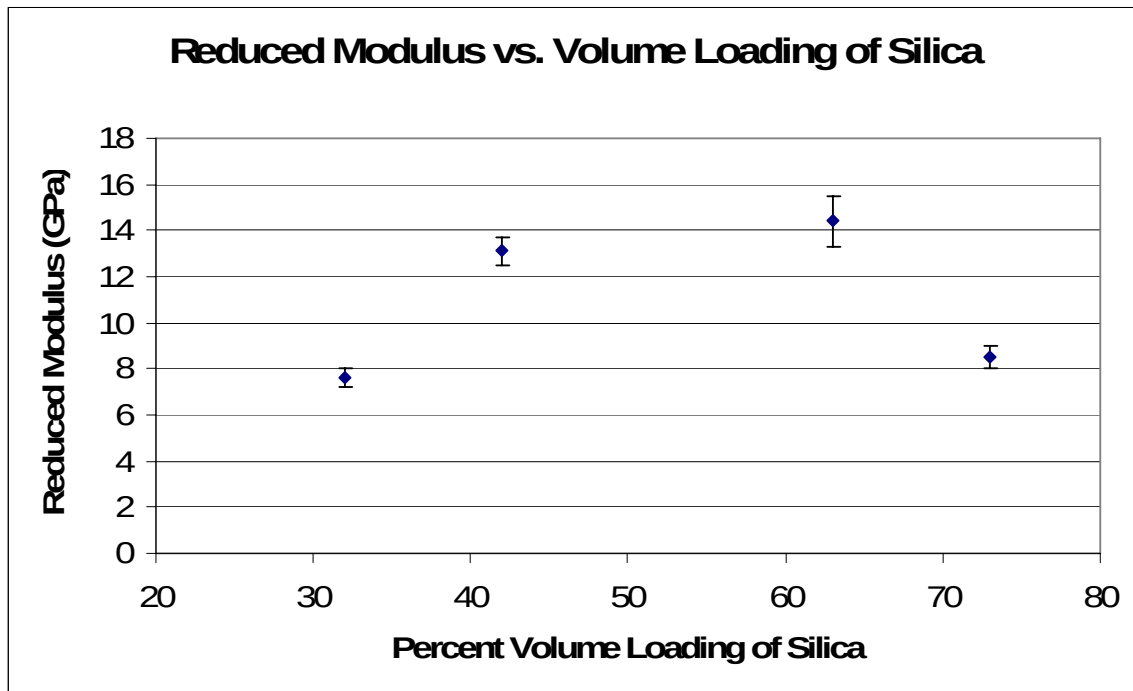


Figure 1

Refelectance Spectrum of Predicted and Measured IR Filter

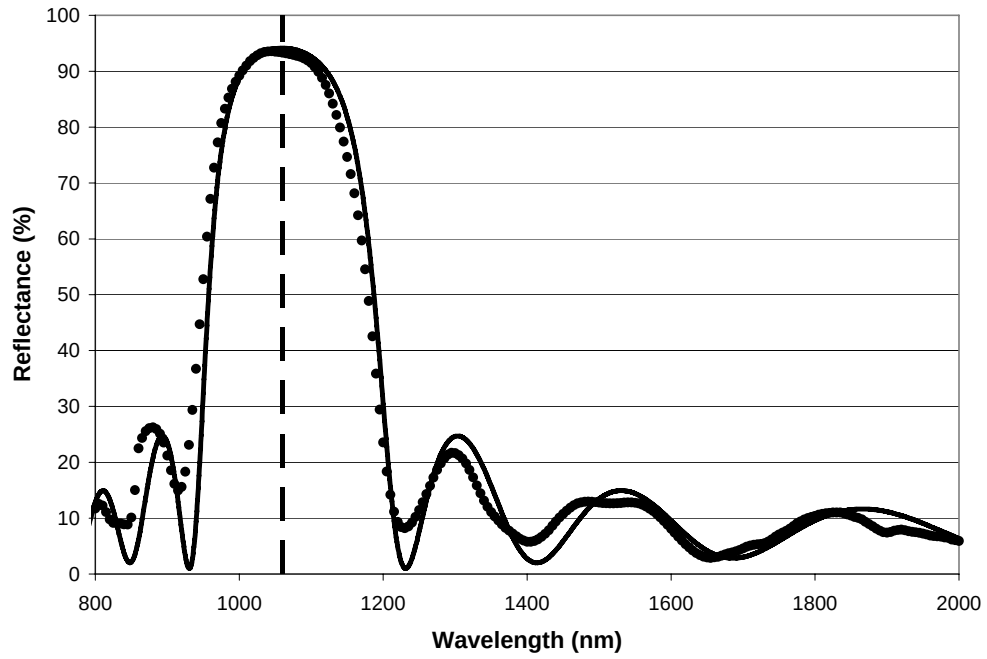


Figure 2

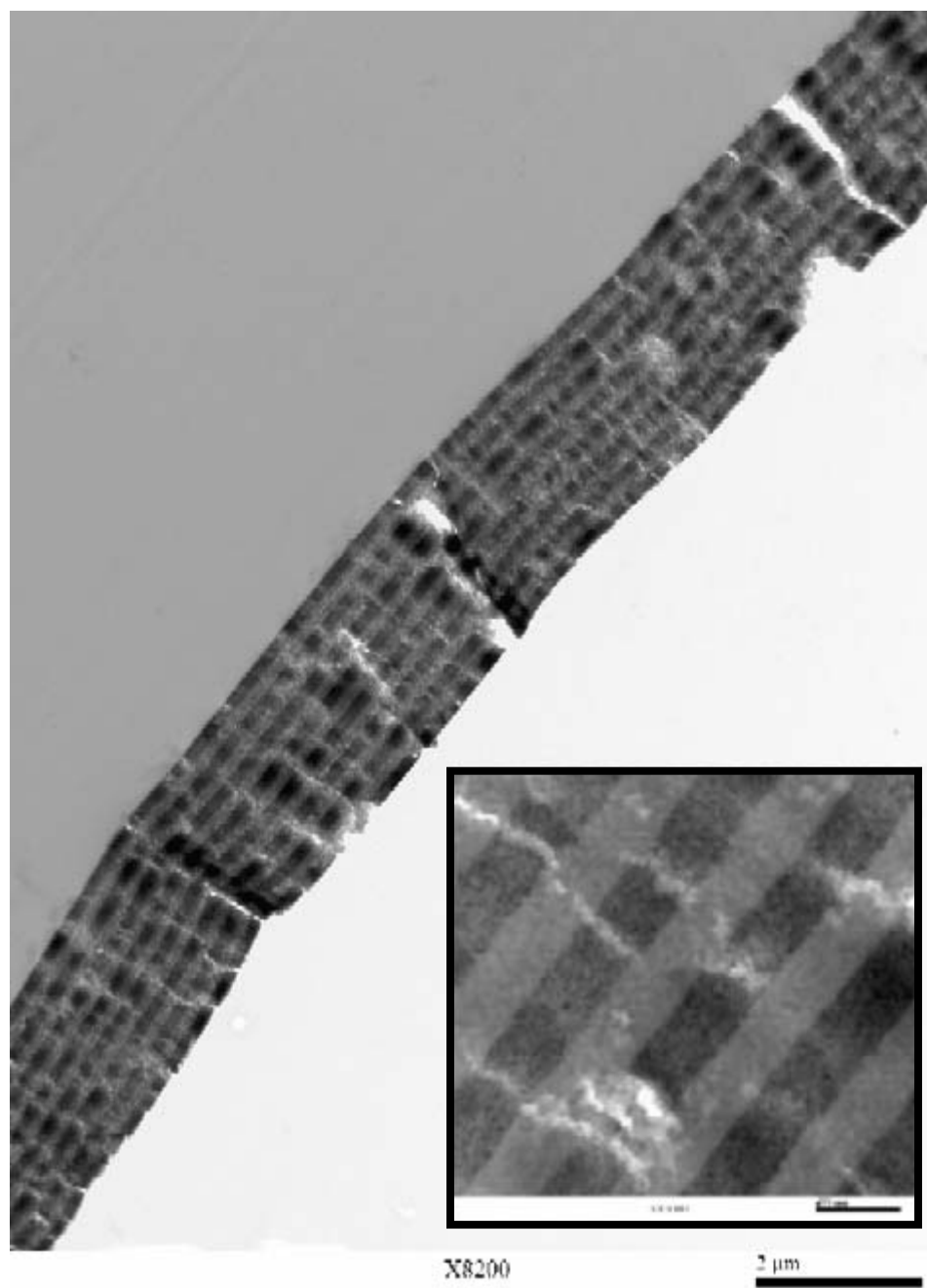


Figure 3

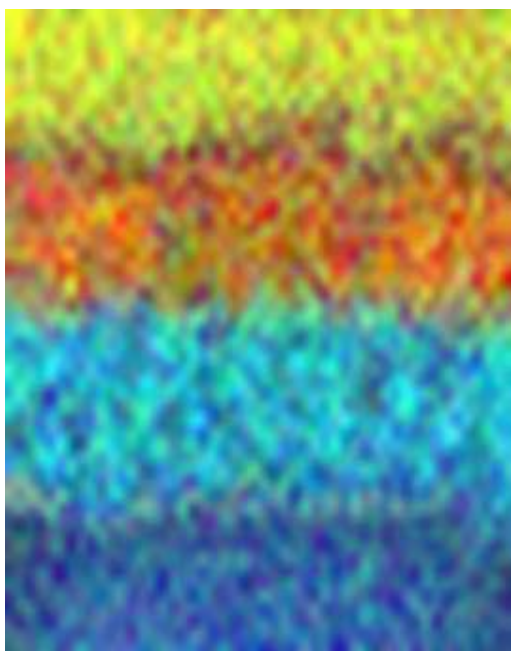


Figure 4

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Figure 1: Reduced modulus of elasticity of a nanocomposite TMPTA film at different packing density of SiO_2 exhibiting a maximum at about 60 volume percent nanoparticles loading.

Figure 2: Measured and predicted reflectance spectrum of the 15 layer stack.

Figure 3: Cross section TEM image of the nanocomposites infrared filter, where the dark section is the TiO_2 and the lighter section is SiO_2 . Inset is a closer view showing the nanoparticles embedded in the polymer matrix.

Figure 4: Elemental mapping of a two layer stack conducted using four elements: carbon (yellow), titanium (red) and oxygen (green).