

Engineering optical and mechanical properties of radiation cured inorganic-organic nanocomposites

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Abstract

Radiation curable monomers offer a range of physical and optical properties while exhibiting high visible transparency. When their rapid polymerization potential is also considered, it becomes clear that these materials are ideal candidates for use in inorganic-organic nanocomposites. Our group has had considerable success incorporating up to 60 volume percent metal oxide nanoparticles in UV-cured polymers. The resulting materials exhibit a broad range of engineered mechanical and optical properties, while maintaining the polymers' flexibility.

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 radiation cured polymers are generally more flexible than glass materials and exhibit a moderate range of optical, 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 nano-composites on polymer substrates in which strain domains are well matched.¹

The primary optical property of a material is its complex index of refraction, which is an engineering constant that explains the propagation and absorption of electromagnetic waves through materials and at interfaces. The design and production of optical filters is mainly accomplished through the combination of thin films with unique refractive indices. These are typically dielectric and metal films that are almost exclusively deposited using vacuum deposition. Although these materials have been studied extensively, they have significant disadvantages related to the required processing steps and limited mechanical properties of the resultant films.

Nanocomposites composed of inorganic nanoparticles embedded in an organic polymer matrix directly address these issues.² The primary challenge for nanocomposites is to alter the optical properties

of a material without affecting the visible transparency of the final article. When an electromagnetic wave encounters a boundary between two materials of discrete refractive index, the direction of the wave is altered both through reflection and refraction. This holds true with sub-micron particles, where the optical dimension (refractive index and diameter) must be engineered so as to not scatter light waves (scattering decreases transparency). Thus, a homogenous distribution of discrete, mono-disperse nanoparticles with dimensions less than 1/10 the wavelength of the encountered light must occur within these nanocomposites to ensure high visible transparency.

The focus of our research for the past several years has been spin coating inorganic-organic nanocomposite films that are used on visibly transparent, flexible substrates. Radiation curable monomers have a very good set of optical and mechanical properties and the speed of cure have made these ideal for the deposition of commercial thin films. Dispersions of radiation curable monomers are soluble in some of the same solvents that produce stable dispersions of nanoparticles. The engineering limits of polymers have been extended through incorporation of nanoparticles that make up over half the volume of the composite.

Nanocomposites

There are several polymers that have very high visible transparency, but unlike glass have much lower hardness. This can be an advantage for systems that require very high flexibility such as polyethylene terephthalate (PET) or high impact resistance such as polycarbonate. In addition these materials can be easier to process and are less expensive than glass. The low hardness does require surface coatings to protect these materials from excessive scratching. These materials also have significantly lower glass transition temperatures than glass, which limits their use to a smaller temperature operating window. However, this also makes it easier for these materials to form into complex 3-d geometries using thermoforming techniques.

The vast majority of transparent polymers have a refractive index between 1.45 and 1.60 (see Figure 1), with fluoro-polymers dominating the range below 1.45.³ High refractive index polymers include sulfur containing compounds such as polysulfones, halogenated species such as brominated and chlorinated styrenes, and polymers exhibiting conjugated heterocyclics and aromatics such as vinylcarbazole and styrene. UV cured polymers tend to have refractive indices that are similarly bounded. While this range suits many engineering systems requiring high transparency, newer materials are needed as systems move toward simpler manufacturing processes and applications involving highly flexible substrates.

Nanoparticles can be made using chemical vapor deposition and sol-gel synthesis techniques. In both cases, high heats are required to cause the nanoparticles to crystallize and fuse together. Metal oxide powders can be made by vapor techniques such as flame spray pyrolysis, electrospray, and vapor phase processes. The sol-gel synthesis route requires high temperatures to produce a crystalline powder. Powders also create a health hazard, since they can become airborne relatively easily. Solution-based synthesis of nanoparticles was first reported by Stober in 1968.⁴ Many researchers have improved on the

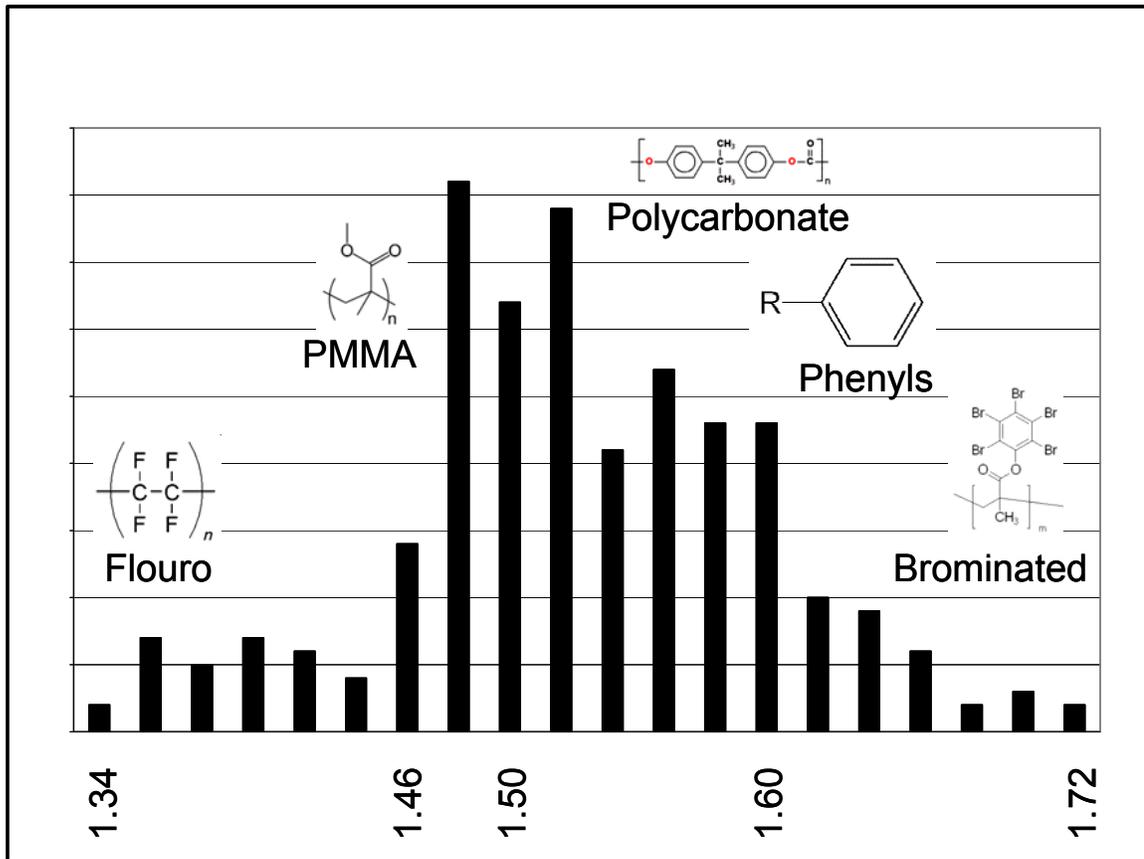


Figure 1. Histogram of refractive indices of polymers showing that the range of refractive index is centered at about 1.5.³

original methods, with a key enhancement being modification of particle surfaces with functional organic groups, designated as an ORMOSIL (Organically Modified Silica).⁵

In optical applications, it is crucial to obtain ultrafine and stable nanodispersions in order to produce thin films with low surface roughness and haze. Although the primary size of most commercial nanoparticles is quite small (5-50 nm), the high nanoparticle surface energies cause agglomeration in the synthesis and post-synthesis processes. This leads to dispersions with primary particles in the nanometer range, but with a significant number of large particle groups exhibiting complex shapes and morphologies due to agglomerated and aggregated networks. These conditions negatively impact haze and transparency. The term agglomerates relates to groups with weak interparticle bonds that allow them to be re-dispersed in a solvent. Ball milling and ultrasonication are typically used to break up agglomerates. The term aggregates (or hard agglomerates) describes groups with primary particles held together by strong attractive forces. Aggregates formed during high-temperature synthesis often persist after ultrasonication or milling and must often be removed through centrifugation or filtration.

As discussed previously, the functionalization of the nanoparticles is extremely important for dispersing nanoparticles randomly throughout a polymer matrix. Maintaining the discrete separation between the nanoparticles is of utmost importance for high visible transparency. Dispersion of nanoparticles in a liquid and a solid can be aided by functionalization of the surface. There are several functionalization schemes such as the use of ions, surfactants, ligands, polymers, coupling agents and shells such as silica or polymer.

The nanoparticles discussed here are metal oxides, which are subject to simple functionalization using organosilanes as is typically used with ORMOSILS. The nanoparticles can be functionalized with different groups that can include single groups that may or may not be polymerizable (see Figure 2). The functionalization including a polymerizable group will aid in making the nanoparticles an integral part of the matrix. This creates a route to produce a homogeneous dispersion of nanoparticles in a polymer matrix which is the key to producing nanocomposites that have high visible transparency while maintaining the elastic properties of the polymer.

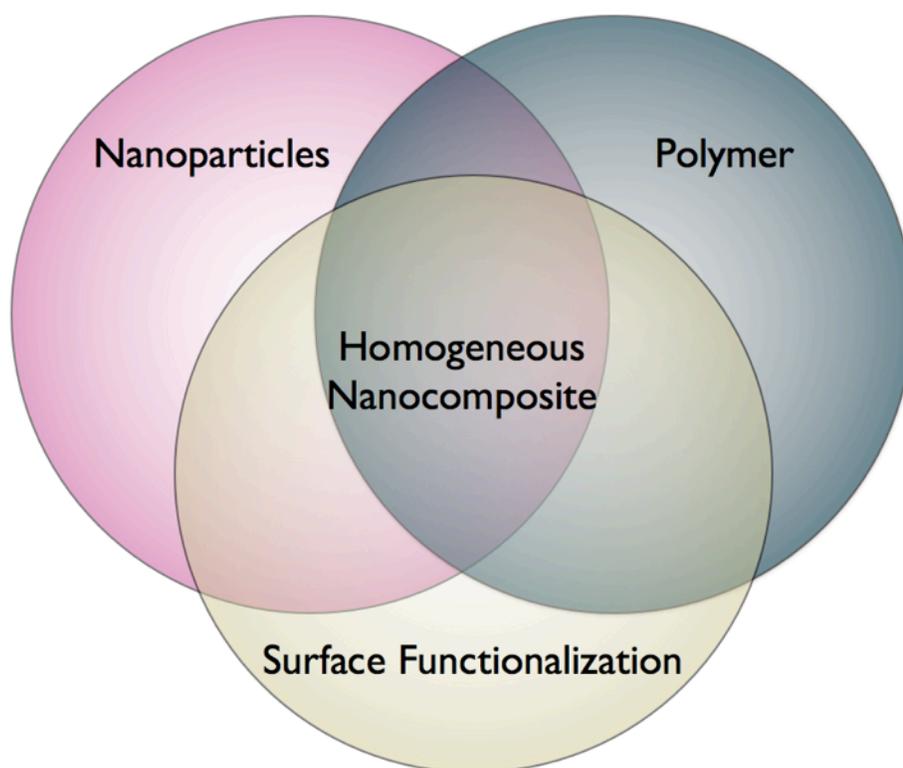


Figure 2. Methods to making nanocomposite films utilizing three basic building blocks: crystalline nanoparticles, polymers and surface functionalization.

Optical and Mechanical Properties

The optical and mechanical properties of a nanocomposite are engineered by varying monomers, initiators, curing conditions, and the concentration of nanoparticles used in the matrix. With spin coating techniques, up to 65 volume percent nanoparticle loading is possible, which is near the theoretical limit of close packing with spheres. Between the properties of the base polymer and the fully loaded nanocomposite, a continuous realm of possible combinations exists.

Models predicting light scatter intensity in a nanocomposite show a linear relationship with path length, packing density, and refractive index ratio, but scattering varies with the cube of particle diameter.⁶

$$\frac{I}{I_0} = \exp \left[\frac{-3V_p l \phi^3}{4\lambda^4} (m - 1) \right] \quad (1)$$

where I/I_0 is the ratio of transmitted intensity to the initial intensity, V_p is the volume packing density of the nanoparticles, l is the path length, ϕ is the diameter of the nanoparticle, λ is the wavelength of light, and m is the ratio of the refractive indices at the inorganic to organic boundary.

The refractive index of a nanocomposite is the combination of the volume fraction of the inorganic and organic components. The composite refractive index can be modeled as:

$$n^2 = \sum_i v_i n_i^2 \quad (2)$$

where n_i and v_i are the refractive index and volume fractions of the components.³ The inorganic nanoparticles have a non-uniform refractive index across the visible spectrum, whereas the organic polymer is nearly constant. To demonstrate this effect, measurements were made using nanocomposite films approximately 500 nm thick with refractive indices between 1.5 and 1.75 (measured at 480 nm). The range of refractive indices was achieved with 5-50% loading of ZnO nanoparticles in the UV-curable monomer TMPTA. Results are shown in figure 3. The films were applied to a substrate using an Optical Dynamics spin coater. The source of the ZnO is a nanoparticle dispersion in methyl ethyl ketone (MEK) produced by Umicore (Zano MEK 067). It is reported as containing 30 nm ZnO nanoparticles at 45 weight percent and uses a surfactant to maintain nanoparticle separation. Reflectance was measured with a contact spectrophotometer (F20 by Filmetrics), with thickness and roughness determined using a contact profilometer (XP-1 by Ambios corporation). This data was then used to determine refractive index using a Cauchy model. It should be noted that the refractive index of the fully loaded ZnO film has been determined to be approximately 1.75, which is slightly lower than the expected 1.82. This is most likely due to the added surfactant reducing the effective refractive index of the ZnO nanoparticles. A similar study of TiO₂ nanocomposite films was undertaken and resulted in a maximum refractive index of 1.88 with volume packing of 65 percent. In this case surface modification was responsible for the reduced refractive index. These films were used to produce thin-film reflective filters with up to 38 layers, with the resultant stack surviving strains up to 25 percent.²

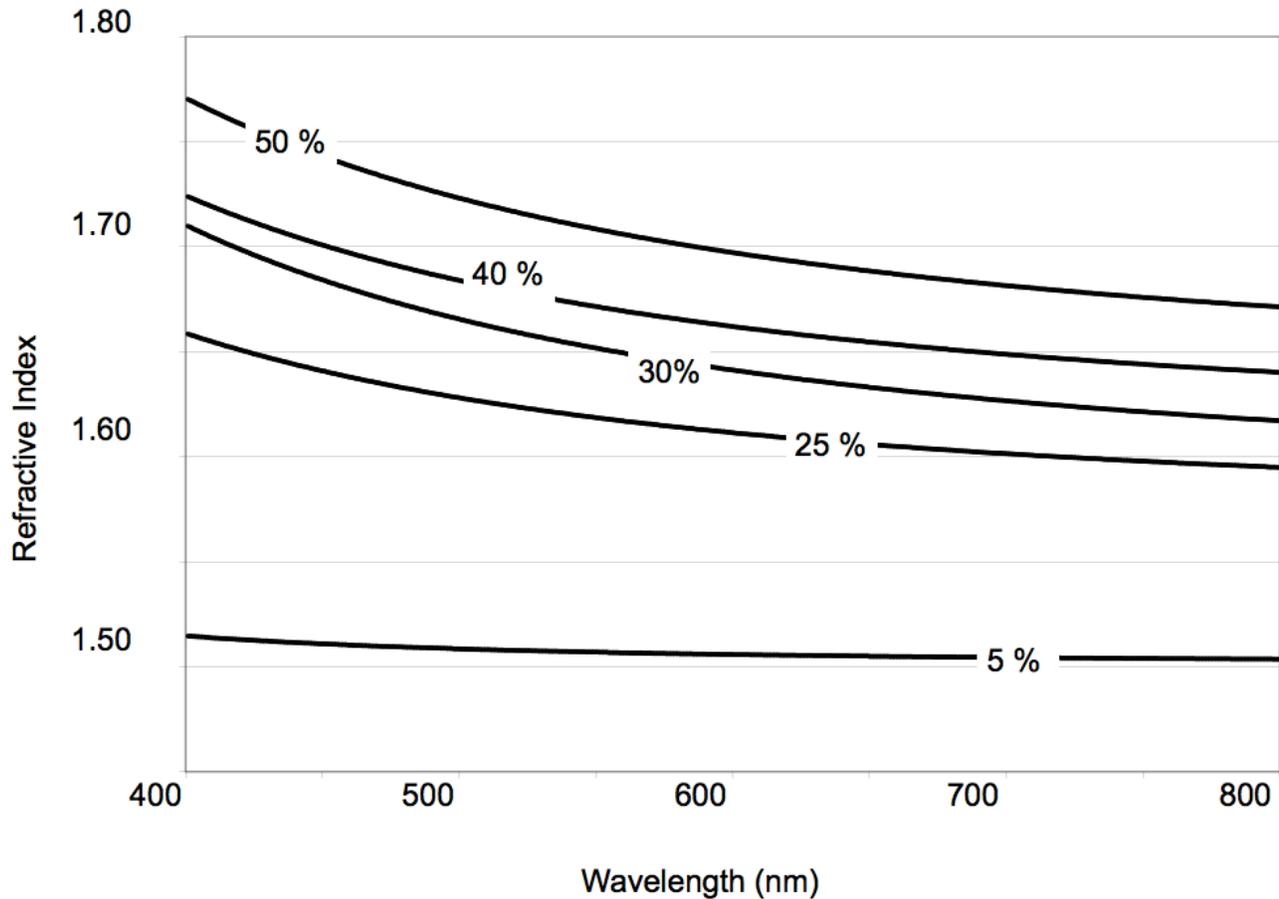


Figure 3: Refractive index dispersion of nanocomposites featuring varying volume fractions of ZnO dispersed in a UV-cured polyurethane acrylate.

As previously discussed, the polymer/inorganic nano- particle composite is used because it allows the material properties envelope to be extended beyond that of the host polymer. The most commonly engineered property is the abrasion resistance of a film. A multitude of commercialized examples exist in scratch resistant clear coatings for automobiles, floors and eyeglass lenses. A similar study of the impact of volumetric loading of nanoparticles on the modulus of a thin film resulted in a maximum modulus near 60 percent loading.⁷ In this study silica nanoparticles were used at volumes ranging from 30 to 75 percent and the modulus was measured using nanoindentation.

These systems have been shown to be more flexible than the traditional vacuum deposition coatings which when deposited onto a polymer will fare much better to point loads. A demonstration of this is shown in Figure 4, which is a comparison of the mechanical response of the coating to a point load using nanoindentation techniques.² The Stiffness measurement of the ceramic coating as the

indentation depth increases shows discontinuities at the points when the brittle coating cracks (figure 4a) and the SEM image of the film shows these brittle fractures (figure 4b). The Stiffness response of the nanocomposite shows no discontinuities indicating that the failure is ductile (figure 4c) and the SEM image of the indentation affirms that the film does behave in a ductile manner. The results show that the nanocomposite does not exhibit the brittle failures and should therefore perform better in systems where high visible transparenence is important.

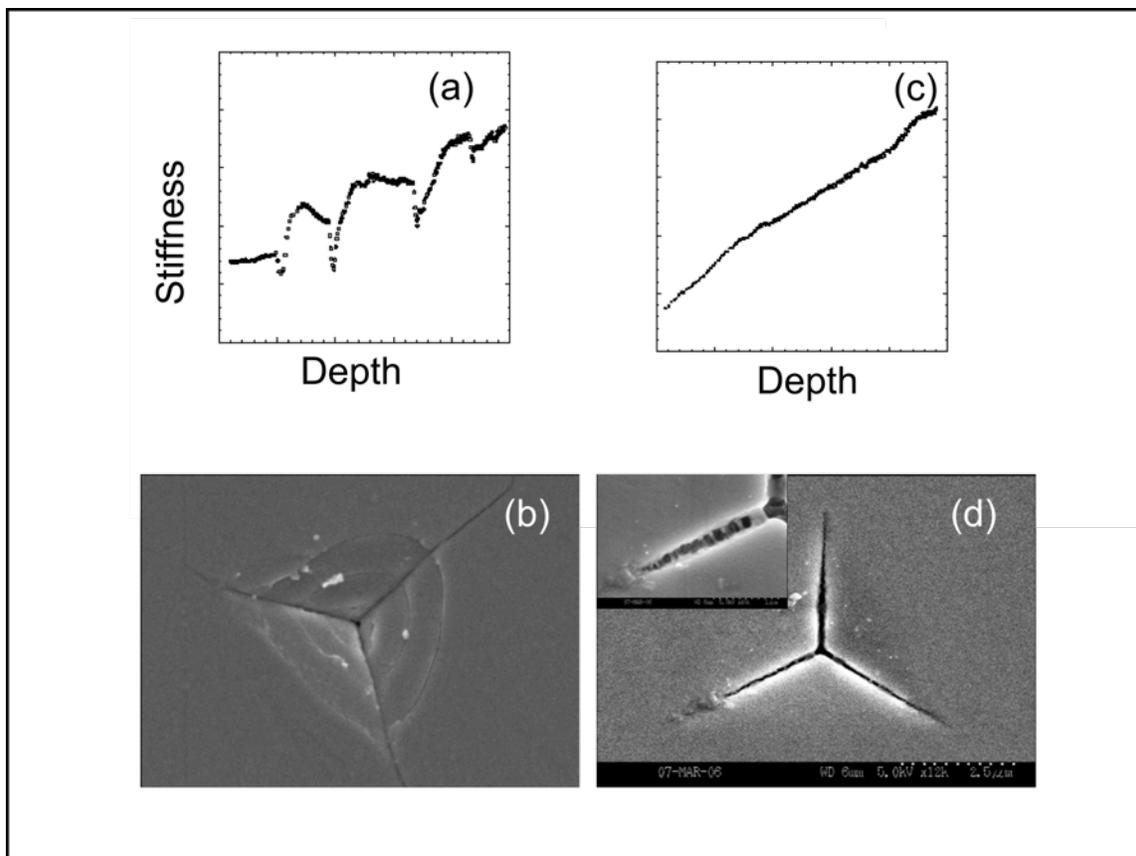


Figure 4. Comparison of a traditional vacuum deposition thin film filter to a nanocomposite coating under a point load induced by nanoindentation.

Conclusion

In this paper we reviewed the engineering of nanocomposite thin films by adjusting inorganic nanoparticle loadings in a polymer matrix. The nanocomposite films were engineered for refractive index and modulus. The polymer matrix was composed of radiation curable monomers and the resulting films exhibited very high visible transparenence and flexibility. The deposition processes was spin coating

techniques in which optical and mechanical properties were engineered with nanoparticles composing nearly 65 percent of the volume.

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