

Linear and Nonlinear Optical Properties of Palladium Nanoparticle Reinforced Fluoropolymer Composites

James Spicer^{1,2}, Kevin See¹, Yasushi Katsumi¹, Dajie Zhang², John Brupbacher³, and Terrence Vargo⁴

¹ The Johns Hopkins University, Department of Materials Science and Engineering, Room 103 Maryland Hall, Baltimore, MD 21218, spicer@jhu.edu

² The Johns Hopkins University, Advanced Technology Laboratory, Baltimore, MD 21218

³ The Johns Hopkins University Applied Physics Laboratory, Laurel, MD 20723

⁴ Integument Technologies, Inc., Tonawanda, NY 14150, tvargo@integument.com

ABSTRACT

The linear optical properties of a functionally graded, palladium nanoparticle reinforced fluorinated ethylene polymer matrix nanocomposite (PMNC) were investigated in this work. Synthesized through repeated infusions of a palladium organometallic precursor gas into an insulating, fully fluorinated polymer matrix film, the composite consists of discrete, palladium nanoparticles distributed throughout the polymer matrix. Under controlled processing conditions, preferential near-surface nucleation of nanoparticles can be achieved and, as a result of increases in nanoparticle density near the surface, percolation of the nucleated particles was observed. The presence of this near surface percolated layer significantly alters the optical properties of this materials system. The reflectivity of the nanocomposites was investigated in depth and compared to behavior predicted using the Tourquato-Kreibig-Fresnel (TKF) theory. The nonlinear optical properties of these materials have also been investigated using optical limiting experiments. Under relatively low fluence conditions, the palladium nanoparticles are excited to effectively change the nanocomposite into an efficient reflector as a result of plasma formation at the material surface. With plasma formation, optical transmission through the nanocomposite decreases significantly. Using a 8 ns laser pulse at 1064 nm, the measured transmission characteristics show that pulse fluences of nearly 1.3×10^4 mJ/cm² reduced the transmission coefficient to less than 10% of the linear value.

1. INTRODUCTION

Currently it is possible to synthesize a wide array of nanocomposite materials systems with controllable physical properties [1-3]. Polymer Matrix Nanocomposites (PMNCs) synthesized by uniformly incorporating metal nanoparticles within an insulating polymer matrix are of interest owing to the optical properties they exhibit that are distinct from that of the bulk [4,5]. PMNCs can be synthesized through established thin film processing technologies such as

physical vapor deposition and chemical infusion techniques [6,7].

A chemical infusion synthesis method was used for this study since it presents a wide range of organic precursor and polymer combinations that allow fabrication of a variety of metal-polymer nanocomposite materials systems with desirable properties. The infusion synthesis method is a type of chemical vapor deposition process carried out in the free volume of the polymer matrix material [8]. This process can be repeated to control the volume percentage content of metal nanoparticles in the polymer leading to significant changes in the optical properties of these materials [9].

2. THEORY: OPTICAL PROPERTIES

Torquato-Kreibig-Fresnel theory addresses the scattering characteristics of nanoparticles embedded in a matrix material that includes multipolar interactions between the distributed particles in the matrix [10]. By knowing the bulk properties of the nanoparticles and the matrix, as well as the volume fraction of the nanoparticles, the TKF model represents the effective dielectric constant, ϵ_e , as follows:

$$\epsilon_e(\omega) = \epsilon_m \left[\frac{1 + 2\phi B - 2(1 - \phi)\xi_2 B^2}{1 - 2\phi B - 2(1 - \phi)\xi_2 B^2} \right] \quad (1)$$

where ϕ is the particle volume fraction, ξ_2 is the structure parameter, ϵ_m is the dielectric constant of the polymer matrix, and B is calculated using the equation

$$B = \left[\frac{\epsilon_p - \epsilon_m}{\epsilon_p + 2\epsilon_m} \right] \quad (2)$$

where ϵ_p is the frequency and size dependent dielectric function of the nanoparticles. The structure parameter

accounts for the multipolar interactions between the particles that occur at high volume fractions [11]. As the volume fraction becomes less than 0.1, the structure parameter approaches zero and the above equation becomes the well-known Maxwell-Garnett dielectric function used to model composite systems with small embedded particles [12-14]:

$$\epsilon_e(\omega) = \epsilon_m \left[1 + \frac{1 + 3\phi(\epsilon_p - \epsilon_m)/(\epsilon_p + 2\epsilon_m)}{1 - \phi(\epsilon_p - \epsilon_m)/(\epsilon_p + 2\epsilon_m)} \right]. \quad (3)$$

To apply this model to our system appropriately, baseline structural and physical measurements were performed to establish the size, shape, and distribution of Pd nanoparticles in the polymer matrix.

3. STRUCTURAL AND OPTICAL CHARACTERIZATION

For this study, either semicrystalline hexafluoropropylene-co-tetrafluoroethylene (FEP) or ethylene-co-tetrafluoroethylene (ETFE) was used as the matrix polymer for nanoparticle synthesis. This synthesis was performed through vacuum processing techniques to heterogeneously nucleate and grow nanoparticles within the polymer [8]. Palladium nanoparticles were produced through the repetitive infusion and decomposition of the organometallic precursor Pd Acetylacetonate $[\text{Pd}(\text{C}_5\text{H}_7\text{O}_2)_2]$ in the polymer matrix.

3.1 Structural Characterization Results

High resolution transmission electron microscope (TEM) micrographs showed that the Pd nanoparticles were spherical, ranged between 7-15 nm in diameter with the diameter increasing with successive infusion cycles. Figure 1 shows the particle shape and distribution for a sample that has been infused 15 times resulting in approximately 2 v/o Pd in the composite. Under various processing conditions, particle size and particle density can be higher near the surface due to the higher flux of precursor that passes through this region during infusion and decomposition. This is shown in Fig. 2 where the surface and near surface regions of one of the composites contains a densely packed population of Pd nanoparticles.

Nanocomposite systems processed through high temperature decomposition favor near surface nanoparticle nucleation and growth. Through repeated infusions under these processing conditions, it is possible to produce an interconnecting network of particles that give the particles a percolative structure. In the literature, percolation for randomly packed, impenetrable spheres has been observed for volume fractions as low as 16 % [15,16].

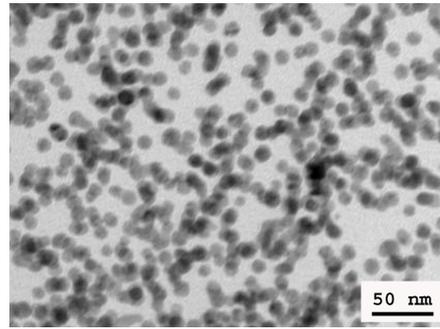


Figure 1: TEM micrograph of Pd-FEP nanocomposite with approximately 2 v/o Pd content. The Pd particle diameter is approximately 10 nm.

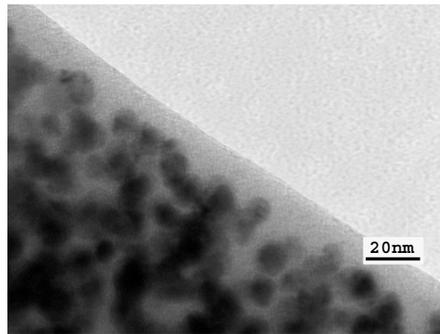


Figure 2: TEM Micrograph of Pd Particles near the FEP surface showing high population density. The decomposition temperature used for the infused precursor gas was 207 °C for this sample.

For our samples, percolation was only observed in two heavily infused samples within a sample set produced at higher decomposition temperatures. A second set of samples was processed at a slightly lower temperature that did not favor near surface nucleation and growth. This set consisted of four samples: two lightly infused (3,5 times) and two heavily infused (15,17 times). Volume percentages range between 0.27% and 3.3% and vary linearly with the number of infusion cycles carried out during material production for fewer than 18 cycles. Although the two sample sets were synthesized through slightly different processing conditions and were visually distinguishable, the weight fraction gains with successive infusion cycles were similar for both.

3.2 Linear Optical Property Measurements

Having performed baseline structure analysis of these nanocomposites, additional studies were carried out to determine the optical properties of these materials. Since macroscopic sample curvature deformed the shape of the reflected beam, an integrating sphere, reflectivity apparatus was used to measure the reflectivity of the PMNCs. A schematic of the apparatus is shown in Fig. 3.

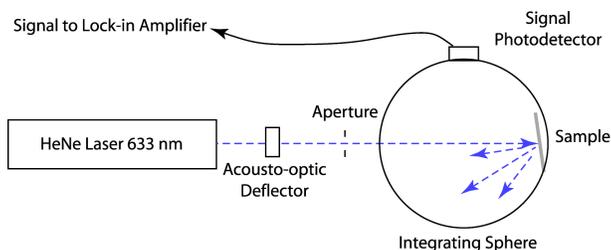


Figure 3: Integrating sphere reflectivity setup.

The reflected power measured using the integrating sphere contains contributions from both the diffuse and the specular components [17], however, since the diffuse component was small compared to the specular reflection, the total power measured from the integrating sphere is a good estimate of the specular reflectivity of the nanocomposite system [18].

Although the PMNCs had low average volume percentages determined using simple mass gain measurements, baseline characterization showed that samples with percolated layers exhibited much higher local volume percentages. Figure 4 shows the measured and calculated optical reflectivities of PMNCs as a function of the Pd content and indicates that the introduction of nanoparticles into the polymer matrix caused the reflectivity to decrease compared with that of the unfused FEP – a result not predicted by the TKF model. Beyond a certain volume fraction, the reflectivities for both sets of samples increased with increasing volume fraction of nanoparticles.

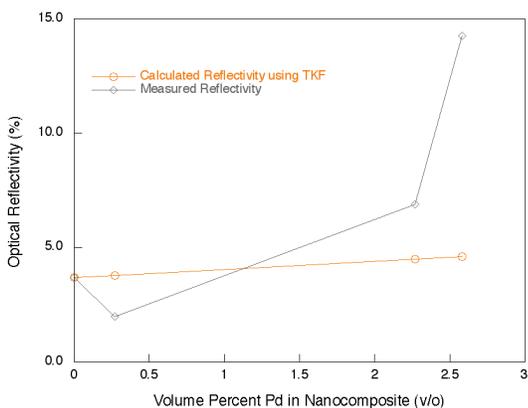


Figure 4: Measured and calculated optical reflectivities of Pd reinforced PMNCs as a function of the Pd content.

Samples processed to yield percolated surfaces exhibited much higher reflectivities than calculated using TKF owing to the high local concentration of particles in the near-surface region of the composite. Materials processed at relatively low temperatures with similar volume percentages displayed optical reflectivities that followed trends similar to that shown in Fig. 4.

3.3 Nonlinear Optical Property Measurements

To complement the linear optical property measurements, nonlinear optical properties were also investigated using simple optical limiting measurements. These were performed using the apparatus shown schematically in Fig. 5 where the transmittance of a Nd:YAG laser pulse (1064 nm, 8ns pulse duration) was measured as a function of the laser pulse fluence.

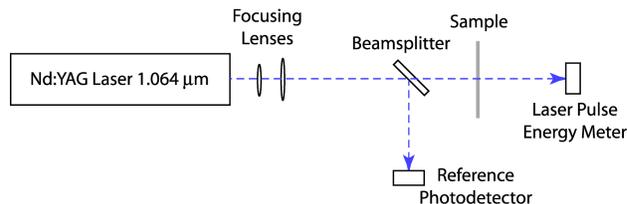


Figure 5: Experimental apparatus used for performing optical limiting experiments on Pd-FEP nanocomposites.

These measurements were completed only on those samples containing the lowest content of Pd (1 or 3 infusions) since these transmitted sufficient laser pulse energy to be measured using standard laser pulse energy meters.

The results of these measurements are shown in Fig. 6 where the absolute transmissivity is shown as a function of the incident laser pulse fluence. At low fluences, nonlinear effects are small and the linear transmittance is measured.

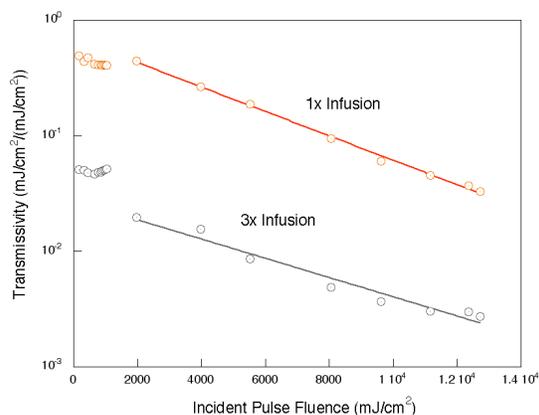


Figure 6: Results for the optical limiting performance of Pd-ETFE nanocomposite materials as a function of laser pulse fluence.

These results show that the material infused once (1x) transmits approximately ten times as much optical energy as the material produced using three infusion cycles (3x) – this is in rough agreement with the Beer-Lambert Law. As the laser pulse fluence increases, the transmitted pulse energy generally decreases. Above a certain incident pulse fluence, plasma formation at the PMNC surface is initiated and is responsible for significant reductions in the transmitted pulse energy owing to the optical properties of plasmas. This decrease appears to be exponential as is shown in Fig.

6 by the solid lines fit to the data. Below this plasma formation threshold, the material behavior is quite complicated and is currently being explored using more sophisticated measurement techniques.

4. DISCUSSION

For samples with a homogeneous distribution of nanoparticles, our system satisfies the conditions assumed for TKF, yet the introduction of nanoparticles in the polymer matrix causes significant changes not predicted by this model. Qualitatively, as metal nanoparticles with high dielectric constant are added to a polymer matrix, the overall effective dielectric constant should rise. Instead, for all of the lightly infused samples, we observed ~ 45% reduction in the reflectivity from the uninfused FEP. This suggests that as small amounts of nanoparticles are added to the polymer matrix, the overall dielectric constant of the nanocomposite decreases. The opposite result is expected based on most composite models including TKF and Maxwell-Garnett. Since the volume fraction of the nanoparticles was low, this effect might be attributed to the changes in the dielectric constant of the matrix.

This decrease in the dielectric constant in the matrix could result from chemical interactions that exist between the palladium particles and the polymer matrix that lead to long range variations throughout the materials system. Clearly, percolation phenomena as well as strong chemical interactions between the matrix and the polymer make it difficult to simply model these polymer nanocomposite material systems using effective medium theories.

5. CONCLUSION

The linear and nonlinear optical properties of palladium-polymer matrix nanocomposite systems were investigated using optical reflectivity measurements and optical limiting measurements. These polymer-metal nanocomposites were fabricated using a chemical infusion synthesis technique capable of producing stable, crystalline, spherical palladium nanoparticles in an insulating polymer matrix. By choosing specific processing conditions, it was possible to produce samples with near surface percolation of nanoparticles. Samples with percolated layers exhibited much higher reflectivities than non-percolated samples of similar volume fraction. The most heavily loaded percolated sample had a reflectivity of 14.3%. It was also shown that chemical interaction between the polymer matrix and the palladium nanoparticles can decrease the effective dielectric constant of the polymer matrix for the lightly infused samples. Chemical interactions between the fluorinated polymer matrix and the palladium nanoparticles, as well as near surface percolation phenomena make it difficult for current

effective medium theories to simply model the behavior of these materials systems.

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