

## Characterization and Properties of Hybrid Nanoparticle “inactive and active” Metal Polymer Films

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**Summary:** A single stage in situ process using a precursor complex has been used to create a uniform dispersion of nanoparticles. The size and interparticle distance varies with the nature of the composition of the nanoparticle and the precursor complex-polymer system. The process was used to create a uniform dispersion of inert, lanthanum oxide, as well as reactive, palladium and silver, nanoparticles.

For all three of these low 1 percent by volume nanoparticle polymer systems significant changes occurred in a range of properties. The nanoparticles increase the glass transition, in some cases creating in addition a broader temperature range for the glass transition. They also increase the crystalline-melting transition temperature and produce a large decrease in the per cent crystallinity in the PVDF system.

The nanoparticles decrease the gas permeability by a factor of ten or more compared to the predicted result. Further, the nanoparticles made from reactive metals to certain gases displayed unique reactive characteristics with regard to selectively changing solubility and diffusivity.

**Keywords:** gas permeability; lanthanum oxide; nanoparticle; palladium; polyimide; PVDF; silver

### Introduction

Nanoparticles have been shown to have a significant effect on a range of polymer properties including pronounced changes in thermal expansion, gas permeability, glass transition temperature, strength, heat distortion and modulus (1-51). A comprehensive fundamental study is needed in which the size, inter particle distance and composition of inert nanoparticles and the polymer is controlled and varied. Thereby the nanoparticle's size, separation, chemical identity and the polymer-particle interfacial interaction on enhancing these properties can be understood and used to design optimum material properties for a particular application. Further the use of reactive nanoparticles should be

examined as they can lead to unique membrane applications regarding hydrogen in the case of palladium and olefins in the case of silver.

The major portion of the literature on incorporating nanoparticles into polymers has focused on hybrid systems derived from organically modified montmorillonites and other types of clay particles (9-25). These hybrid systems are difficult to create because it is extremely challenging to separate and fully exfoliate the particles to form a uniformly dispersed, homogeneous distribution of nano sized particles in the polymer. In addition, it is difficult to isolate individual effects and thereby fully understand the fundamental reasons why the montmorillonites improve the polymer's properties. This is because of the complex electrostatic interactions on the surface of the silicate sheets and the residues that are often left after processing to delaminate when using large organic cations such as ammonium or phosphonium.

This initial report focuses on making and characterizing nano-materials comprised of nanometer-sized metal and metal oxide particles in polymers which were made using our novel recently developed single state in situ synthesis (4-8, 40). The objective is to develop nanoparticle containing polymers which achieve both exceptional gas permeability and improved mechanical properties. Based on successful preliminary work in our laboratories, we have made inorganic-polymer systems with nanoparticle inorganic phases of two types: 1) inert nanometer-sized rare earth lanthanum oxide nano clusters and 2) reactive nanometer-sized palladium and silver metal clusters. For the polymer matrix, we have used aromatic poly (amic acid)s-polyimides and a high performance thermoplastic polyvinylidene difluoride (PVDF) because of these polymers' strength and chemical-thermal stability. The fabrication techniques are distinctive in that they are in situ and single step routes dispersing nanoparticles uniformly within the polymer.

Our work has two major fundamental goals: 1) why and how does each of these factors, the polymer's chemical structure, the nanoparticle's chemical composition, the complex precursor, the cure time-temperature history and the gas environment affect the growth, size and dispersion of the nanoparticles as well as migration to the surface; 2) how does the very low volume percent nanoparticles, the size and the dispersion of the nanoparticles and particularly the nanoparticle polymer interfacial interactions affect the polymer's gas permeability, dynamic and mechanical properties.

## Experimental

### Lanthanum Oxide Nanoparticle Polyimide Films

**Materials.** 2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) was obtained from Hoechst Celanese and vacuum dried for 17 h at 110 °C. 1,3-Bis(3-aminophenoxy)benzene (1,3(3)-APB) was purchased from National Starch and used as received. 2,4-Pentanedione and lanthanum(III) oxide were obtained from Fisher and Aldrich, respectively. DMAc (HPLC grade) was purchased from Aldrich and stored over 4A molecular sieves.

Imidized 6FDA/1,3(3)-APB was prepared by the addition of 6FDA (0.5% molar excess) to a DMAc solution of 1,3(3)-APB to first prepare the poly(amic acid) at 15 % solids (w/w). The reaction mixture was stirred at the ambient temperature for 7 h. The inherent viscosity of the poly(amic acid) was 1.4 dL/g at 35 °C. This amic acid precursor was chemically imidized at room temperature in an equal molar ratio acetic acid-pyridine solution, the pyridine and acetic acid each being three times the moles of diamine monomer. The polyimide was then precipitated in water, washed thoroughly with deionized water, and vacuum dried at 200 °C for 20 h after which no odor of any solvent was detectable. The inherent viscosity of the polyimide in DMAc was 0.81 dL/g at 35 °C.  $M_n$  and  $M_w$  were determined by GPC to be 86,000 and 289,000 g/mol, respectively.

**Preparation of the diaquotris(2,4-pentanedionato)lanthanum(III) nanoparticle precursor complex.** The title complex was made following the approach of Pope et al.,<sup>42</sup> Stites et al.,<sup>43</sup> and Phillips, et al.<sup>41</sup> Redistilled 2,4-pentanedione (50 mL) was combined with 15 M ammonia and water until the diketone went into solution as the ammonium salt. Lanthanum(III) chloride was prepared by dissolving lanthanum(III) oxide in 6M hydrochloric acid. The pH was adjusted to 5.0 with sodium hydroxide. The ammonia solution of 2,4-pentanedione was added drop wise to the stirring lanthanum(III) chloride solution. The pH of this final solution was allowed to rise to six and held constant at this value. The solution was stirred for 24 h during which time the colorless crystalline complex formed. The product was filtered, washed twice with deionized water, and dried in air for 4 h after which it was recrystallized from 95 % ethanol. The final crystals were dried in air at the ambient temperature.

**Preparation of Films:** Metal doped 6FDA/1,3(3)-APB polyimide solutions were prepared by first dissolving the metal complex in DMAC and then adding solid imide powder to give a 15% solids (excluding the lanthanum(III) additive) solution. The solutions were stirred 2–4 h to dissolve all of the polyimide. The clear complex-doped resins were cast as films onto soda lime glass plates using a doctor blade set to give cured films ca. 25  $\mu\text{m}$  in thickness. The films were allowed to sit for 15 h at room temperature in flowing air at 5% humidity which resulted in a film that was tact free. The films then were cured in a forced air oven and removed from the plate by soaking in warm deionized water. The cure cycle for films used in permeability studies was 100 °C for 1 h, 30 min to 200 °C for 1 h; 30 min to 300 °C for 1 h. This cure cycle allowed to minimize the amount of residual solvent in the film. The films for SAXS analysis were cured as follows: 30 min ramp from room temperature to 100 °C; hold for 1 h at 100 °C; 100–300 °C over a 2 h linear ramp; hold at 300 °C for 1 h.

All of the results in this report concern films prepared at a molar concentration of polymer repeat unit-to-metal of 5:1, corresponding to 4.4 weight percent of  $\text{La}_2\text{O}_3$  in the polyimide (ca. 1.1 volume percent assuming the  $\text{La}_2\text{O}_3$  density to be 6.3  $\text{g}/\text{cm}^3$  with the 6FDA/1,3(3)-APB density at 1.43  $\text{g}/\text{cm}^3$ ).

### Palladium Metal Nanoparticle Polyimide Films

**Preparation of Films:** The following procedure was used to prepare 5.2% weight percent, 1.1 per cent by volume, palladium-BTDA/4,4'-ODA films using the  $\text{PdBr}_2(\text{SMe}_2)_2$  complex. The complex was prepared without isolation by reacting at room temperature in a small vial  $\text{PdBr}_2$  with four equivalent of dimethylsulfide in 1 g of DMAc. The complex solution was transferred via syringe (rinsing the vial with an additional 0.5 g of DMAc) to 10.00g of the poly(amic acid) solution prepared at 15.0% solids from the two monomers by the standard protocol of dissolving at the ambient temperature the diamine first followed by addition of the dianhydride. (All undoped initial poly(amic acid) solutions were first stirred for =5h before proceeding further.) The resulting Pd(II)-poly(amic acid) solution was stirred for 2h to ensure a homogeneous solution. Doped poly(amic acid) solutions were cast as films onto soda lime glass plates using a doctor blade set at 600 microns to obtain ca. 25 microns after thermal curing. After remaining in an atmosphere of slowly flowing dry air (4% relative humidity) for 18 h, the films were thermally cured in a forced air oven with the intake vent of a GS Blue M oven closed and exit vent opened

slightly at 15% of maximum. The cure cycle involved heating over 10 min to 100 °C and holding for 1 h, heating over 30 min to 200 °C and holding for 1h, and finally heating to 300 °C over 30 min and hold for 1h. The film was allowed to cool to cool to 75 °C over ca. 1h and then removed from the oven.

### **Silver Metal Nanoparticle Poly(vinylidene difluoride) Films**

**Preparation of Films:** The following procedure was used to prepare 8.0% by weight, 1.4 percent by volume, silver-PVDF films using silver(I) trifluoroacetate. Silver(I) trifluoroacetate (0.134 g) was dissolved in a small vial containing 1.5 g of DMAc. The silver(I) trifluoroacetate solution was transferred to the PVDF solution via syringe. The resulting doped polymer solution was stirred 2h and then cast as a film and cured as described above.

## **Results and Discussion**

### **Verification of In Situ Formation of a Uniform Dispersion of Nanoparticles in the Polymer**

In order to verify that the in situ process using a precursor complex generated a homogeneous dispersion of nano sized particles, TEM images were taken of each of the three systems. Figure 1 is the TEM image of the 1% by volume  $\text{La}_2\text{O}_3$  polyimide film. The image shows discrete, well separated nanoparticles with diameters in the range of 3 to 8 nm. These results are in good agreement with SAXS results which when analyzed using the Beucage approach showed a mean particle diameter of 7.2 nm and an average interparticle distance of 10 nm(52) .

The TEM image of the reactive Pd polyimide film is shown in Figure 2. Here the nanoparticles formed by the in situ degradation process of the Pd complex are again uniformly dispersed. The particle diameters are larger than in the  $\text{La}_2\text{O}_3$  system and have a mean diameter estimated from the TEM picture of 10 to 15 nm. SAXS experiments were also performed on this film and the average diameter was estimated by the SAXS analysis using the Beaucage approach to be 15 nm (52). The interparticle distance was large relative to the particle size and thus there was no scattering peak in the SAXS spectrum

characteristic of an interparticle distance. Since both the  $\text{La}_2\text{O}_3$  and the Pd film are approximately 1% by volume, the much larger volume of the Pd nanoparticles supports the result that the particles will be further apart than in the  $\text{La}_2\text{O}_3$  system.

The silver PVDF film was also characterized by TEM. The results are shown in Figure 3. The TEM results show that most of the silver particles are approximately 18 to 23 nm, although a few particles appear to have joined together to form a larger aggregate. SAXS measurements were also made on this film. The SAXS results show that the particles are again much larger than the interparticle distance as there was no peak in the SAXS spectrum indicating scattering characteristic of the interparticle distance. The SAXS results when analyzed using the Beurcage approach indicate that the mean particle diameter is 20 nm.

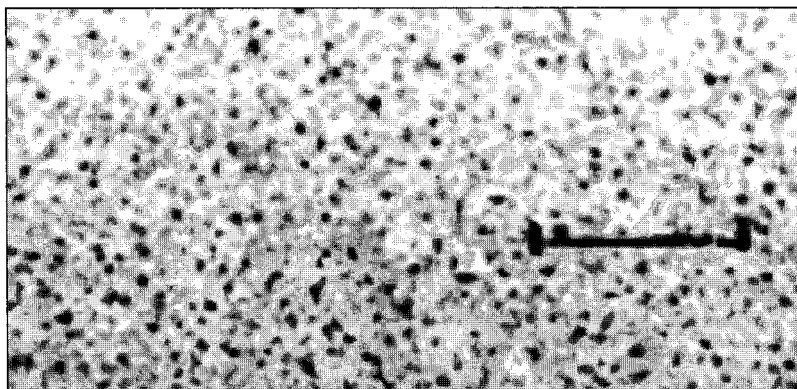


Figure 1. TEM image of the  $\text{La}_2\text{O}_3$ -6FDA/1,3(3)-APB hybrid film. The scale bar is 100 nm.

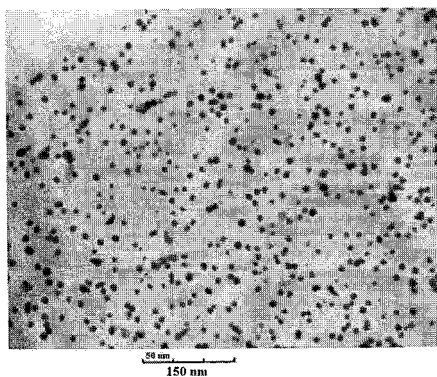


Figure 2. 5.2 weight % Pd ( $\text{PdBr}_2$  complex) nanoparticles in BTDA/ODA.

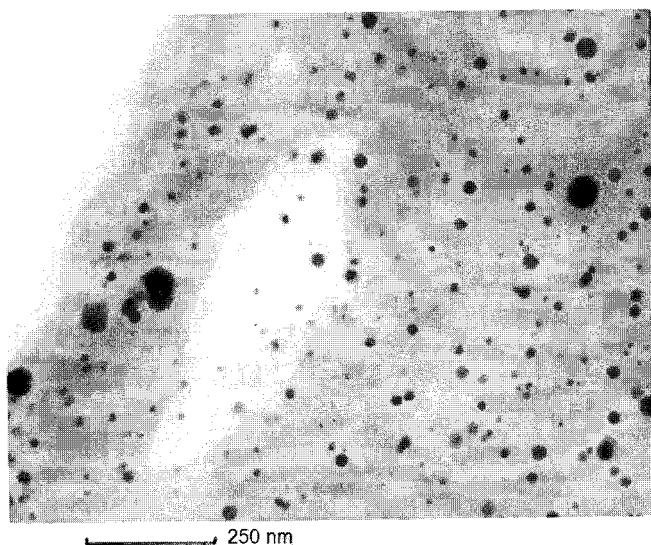


Figure 3. 8% by weight Ag (Trifluoroacetate complex) nanoparticles in the PVDF film.

### Characterization of Thermal Transitions

Thermal transitions in each of these three nanoparticle film systems have been characterized using a TA instruments modulated differential scanning calorimetry (DSC). This is a convenient, traditional experiment to assess the extent to which the nanoparticles affect the dynamical behavior of the polymer and thereby properties such as the glass transition, the temperature width of this transition and its characteristic temperature  $T_g$ . The effect of the nanoparticles on the ability of the chains to crystallize in the semicrystalline polymer PVDF can be characterized by the melting temperature, the width of that transition, and the heat of crystallinity.

These properties were determined during a  $3^\circ/\text{min}$  ramp to  $230^\circ$ ; a  $3^\circ/\text{min}$  cool down to  $130^\circ$ ; a  $3^\circ/\text{min}$  ramp back to  $230^\circ$  and a  $3^\circ/\text{min}$  cool down back to  $130^\circ$  to characterize the glass transition in the polyimide systems and the melting transition in the semi crystalline PVDF systems. A similar temperature ramp sequence between  $-65^\circ\text{C}$  and  $0^\circ\text{C}$  was used to try to characterize the glass transition in the PVDF systems.. These thermal procedures were used to characterize the effect of the nanoparticles on these transitions by comparing



the neat films to the hybrid La, Pd and Ag polymer films.

For the 1% by volume  $\text{La}_2\text{O}_3$  nanoparticle 6FDA/1,3(3)-APB polyimide system, the glass transition temperature increased 3°C. Furthermore, the temperature width of this transition increased from 199.6°C–204.5°C in the neat system to 201.5°C–208.1°C in the nanoparticle system. This supports the view that there are strong interactions between the polyimide matrix and the inert  $\text{La}_2\text{O}_3$  particles.

The effect of the Pd nanoparticles on the glass transition in the BTDA-4,4' ODA polyimide was also observed to increase the transition from 197°C to 204°C in the neat polyimide film to 200°C to 207°C in the Pd nanoparticle film.

It was not possible to detect the PVDF's glass transition temperature using calorimetry. But the effect of the silver nanoparticles on the crystalline-melt transition in the semicrystalline PVDF's was characterized. The presence of 1% by volume silver nanoparticles increased the melting point by 2°C. The width of the transition, 18°C, only increased by 1°C. But the heat of fusion decreased from 46 J/g to 35 J/g, a 25% decrease in the percent of crystallinity. Thus, the silver nanoparticles have a modest effect on increasing the melting temperature, a measure of the crystalline packing strength, but a strong effect on decreasing the volume of the crystalline regions. This suggests the particles inhibit polymer mobility in the vicinity of the nanoparticles.

### **Effect of Nanoparticles on Gas permeability**

Gas permeability measurements have been performed on the lanthanum oxide and the palladium metal nanoparticle films along with their neat counterparts using techniques previously described (53-57). The precision on permeability(P) and diffusivity(D) values are respectively 0.02 barrer and  $0.02 \cdot 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ .

Gas permeability of a polymer is known to be correlated with the free volume and the dynamic behavior of the polymer chains.(53). It is therefore, our belief, that characterizing the changes in the gas permeability of a polymer due to the incorporation of nanoparticles is not only of practical interest as a potential means to reduce gas permeability but also as a means to fundamentally characterize and thereby understand the effect of a particular nanoparticle's size, inter particle distance and the interactions at the particle polymer interface. It is also interesting to point out that the  $\text{La}_2\text{O}_3$  particles are inert to all the gases studied and the Pd nanoparticles are reactive with respect to hydrogen and oxygen.



Table 1 reports the change in the gas permeability(P) of oxygen, hydrogen and carbon dioxide due to the presence of the lanthanum oxide nanoparticles. These inert nanoparticles decreased the permeability of all three gases 14% and produced a reduction which is ten times that predicted for inert spherical particles using the Maxwell equation(53).

Table 2 shows the effect of the reactive Pd particles on the permeability, diffusivity(D) and gas solubility(S) for the gases helium, oxygen and hydrogen. The effects are large and vary between all three gases as the helium is inert and the oxygen and hydrogen can interact with the palladium but in differing ways.

Table 1. La<sub>2</sub>O<sub>3</sub> 6 FDA-APB Films Gas Permeability (units of Borrer).

Vol. %	Gas	Exp.	%Decrease	Theo.	%Decrease
0	Oxygen	0.38	--	0.38	--
1	Oxygen	0.33	13.2	0.37	1.5
0	Hydrogen	8.42		8.42	--
1	Hydrogen	7.25	13.8	8.29	1.5
0	Carbon dioxide	1.48		1.48	--
1	Carbon dioxide	1.27	14.2	1.46	1.5

Table 2. Pd BTDA-ODA Film's Gas Permeability, Diffusivity and Solubility.

1% by vol.	Neat film	Pd Bulk (sample 1)	Pd Bulk (sample 2)	Average Pd Bulk values	% Decrease on addition of Pd	Change in P ratio of expt/theo
P He (barrer)	4.52	Not measured	3.05	3.05	32.5	21.8
P O <sub>2</sub> (barrer)	0.14	0.106	0.108	0.11	23.6	15.8
D O <sub>2</sub> (10 <sup>-9</sup> cm <sup>2</sup> s <sup>-1</sup> )	2.13	2	1.6	1.80	15.5	
S O <sub>2</sub> (10 <sup>-3</sup> cm <sup>3</sup> cm <sup>-3</sup> cm Hg <sup>-1</sup> )	6.6	5.3	6.75	6.03	8.7	
P H <sub>2</sub> (barrer)	3.48	2.07	2.05	2.06	40.8	27.4
D H <sub>2</sub> (10 <sup>-9</sup> cm <sup>2</sup> s <sup>-1</sup> )	700*	120	206	163.00	76.7	
S H <sub>2</sub> (10 <sup>-2</sup> cm <sup>3</sup> cm <sup>-3</sup> cm Hg <sup>-1</sup> )	0.05	0.17	0.099	0.13	-169.0	

## Conclusions

The single stage in situ process using a precursor complex does create a uniform dispersion of nanoparticle. The size and interparticle distance varies with the nature of the composition of the nanoparticle and the precursor complex-polymer system. The process

can be used to create a uniform dispersion of nanoparticles in both an amorphous and a semi crystalline thermoplastic. And the process can create a uniform dispersion of inert, lanthanum oxide, as well as reactive, palladium and silver, nanoparticles .

For all three of these low 1 percent by volume nanoparticle polymer systems significant changes occurred in a range of properties The nanoparticles increase the glass transition, in some cases creating in addition a broader temperature range for the glass transition. They also increase the crystalline-melting transition temperature and produce a large decrease in the per cent crystallinity in the PVDF system.

The nanoparticles decrease the gas permeability by a factor of ten or more compared to the predicted result. Further nanoparticles made from reactive metals to certain gases do display these unique reactive characteristics with regard to selectively changing the polymers solubility and diffusivity.

Future work will focus on characterizing the kinetics of the in situ nanoparticle formation process, thereby controlling and varying the particle size and interparticle distance for a given particle polymer system. Then studies will be conducted on the relation of particle size, inter particle distance, and the nature of the particle's and the polymer's chemical composition to the nanoparticle polymers final properties.

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