

Novel Nano-metal Polymeric Composites Fabricated via In-Situ Self Assembly

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ABSTRACT

Current research in the field of nanotechnology and the fabrication of polymeric composites is often complicated by the inability to obtain well dispersed nano-particles within polymeric matrices. Current methods require that nanoparticles be protected by organic ligands that affect many of the properties inherent to unprotected nanoparticles (e.g., catalytic activity). In this paper we describe a new in-situ method for directly growing and assembling metal and metal oxide nano-particles within the free volume of polymeric materials without the use of solvents, supercritical fluids, or organic stabilizers.

Keywords: polymeric free volume, metallic nanoparticles, polymeric nanocomposites, fluoropolymer, nanoparticle dispersion

1. INTRODUCTION

In this paper we will describe a revolutionary synthesis technology for producing unlimited numbers of polymeric materials containing interpenetrating networks of metal, metal oxide, and organometallic nanoparticles.

Integument Technologies, Inc. has developed a new infusion method⁽¹⁾, which allows metals, metal oxides, and organic materials to be controllably grown within the internal structure of almost any polymer thereby affecting both surface and bulk properties. This new nanotechnology permits a polymer composite material to be easily modified for specific uses that may require: (1) Controlled adhesion or foul release properties, (2) Improved mechanical and thermal stability, (3) Surface and bulk chelation of catalysts, anti-microbials, and recognition elements, and (4) Selective Ion and gas Permeable Barriers.

Before describing this technology a few general comments on synthesis of nano-composites are warranted. Specifically, there are two approaches to nano-scale polymeric composites: (i) powder blending, and (ii) *in-situ* synthesis⁽²⁻⁴⁾. In the former, nano-scale materials are formed by wet chemistry (e.g., sol gel), gas phase synthesis or surface science routes and combined with the polymeric matrix material in a subsequent blending operation. Although there are advantages to the powder blending approach, working with nano-powders presents materials purity, safety, scale-up, and compositing challenges that are often difficult to overcome for specific applications. In

particular, the prospects for synthesizing and blending nano-scale metals or other reactive materials into polymers in production quantities are remote. For this reason, it is our belief that for applications where polymeric nanocomposites might be desired, development of one step, *in-situ* processing is the preferred route. Another compelling argument for pursuing *in-situ* synthesis is that the transition from “grams-to-kilograms” and “kilograms-to-tons” quantities should not be technologically limited.

The following sections of this paper will describe what our team refers to as an infusion method that effectively utilizes the inherent free volume contained in a fully cured organic polymer. This method allows us to infuse and then form interpenetrating networks of metal, metal oxide, and organometallic nanoparticles within pre-formed polymeric sheets, films, objects or resins without significantly disrupting the initial structure of the polymer. This infusion technique utilizes no solvents or supercritical fluids and is thus not limited to the use of inorganic precursors that must be compatible with the solvents used to either swell or solubilize the starting polymeric material. This technique enables one to incorporate virtually any metal or metal oxide into any polymeric system, including fluoropolymers and polyolefins. The infusion process is limited by: 1) the free volume contained within the polymer, (i.e., polymers having crystallinity greater than 95% do not lend themselves to this process without using methods that can lower the polymer’s crystallinity), and 2) the incorporation of inorganic materials that have precursors (e.g., organometallic complexes) that can be volatilized below the polymer’s decomposition temperature⁽⁵⁾.

2. Control of Metal and Metal-Oxide Material into Polymer Free Volume

In practice, the polymer to be infused is evacuated under vacuum followed by the introduction of a volatile precursor material into the evacuated free volume of the polymer. A subsequent thermal or chemical transformation of the infused precursor results in the formation of nano-scale particles within the polymer’s free volume. As previously mentioned this process requires that the polymeric material possess free volume; i.e., the polymer contains a degree of amorphous character and is not 100% polycrystalline. Thus, in order to gain a full understanding of how this process works it is important to understand the nature of free volume that exists within solid polymers below their

glass transition temperatures (T_g). References 6-7 are cited and describe both the theoretical and practical aspects of polymeric free volume and how it relates to diffusional characteristics associated with a particular polymeric system.

Note that polymeric free volume is not the same as unoccupied or empty volume like pores that are produced in materials like filters. The free volume of a polymer relates to the volume in amorphous regions of a polymer that allow the polymeric chains the ability to move depending on how the chains are packed. For example a solubilized polymer (or one that is heated above its T_g) has a high degree of free volume due to the fact that the polymeric chains can readily move and fluctuate. By removing the solvent, or decreasing the polymer's temperature below T_g , the polymeric material forms a glassy state where the free volume is decreased but still present to varying degrees depending on its amorphous character. The free volume of a polymer in its glassy state then determines its diffusional characteristics that allow gaseous molecules to freely diffuse into and out of the polymeric matrix.

By first evacuating the ambient gas that resides within a polymer's free volume other molecules can be transferred into this space with little difficulty as long as the precursor molecules are sufficiently small enough to easily diffuse or infuse into the free volume space. In essence, the polymeric matrix acts as a three dimensional molecular template or surface that

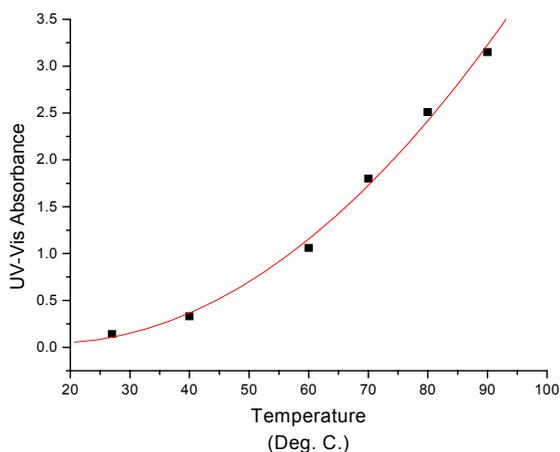


Figure 2.1 Concentration of Infused V_2O_5 vs. Infusion Temperature

controls: 1) the amount of inorganic precursor that can be added and 2) the physical structure and size of the nano particle network that is subsequently formed within the polymer.

For example, because an increase in temperature results in an increase in free volume, we have used the infusion temperature to control the concentration of inorganic

material formed within a polymeric system. By increasing the temperature during the first step of the process, more free volume is created which allows the infusion of more inorganic precursor into the polymer. This provides the ability to control the amount of inorganic material that is subsequently formed within the polymer after the precursor is converted to a metal or metal oxide. To demonstrate this, $VOCl_3$ was infused into polytetrafluoroethylene-co-hexafluoropropylene (FEP) at different infusion temperatures and, after subsequent hydrolysis to V_2O_5 , the film's absorbance at 225 nm was measured (Figure 2.1). The plot shows an increase in V_2O_5 concentration with increasing temperature. Note that the behavior corresponds well with diffusion behavior observed in measurements of polymeric free volume as a function of temperature (6,7).

Step 2 of the infusion process, a thermal, photochemical or chemical transformation of the precursor, also affects the resulting particle size and distribution of the infused metal or metal oxide. TEM results (not shown) have provided images showing particle size and distribution of Pd metal and V_2O_5 nano particles incorporated into FEP. The hydrolysis used to form V_2O_5 was performed slowly at room temperature. This results in a distribution of particles which are ~ 100 nm and non-uniform in size, shape and distribution. The slow hydrolysis allows the hydrolyzed precursor the mobility to form large, irregular shaped aggregates before condensing to the metal oxide. A more rapid hydrolysis using steam results in smaller, more uniform particles, which are uniformly distributed. Alternatively, Pd metal nano particles formed through thermal decomposition, are ~ 10 nm with uniform distribution (within the polymer matrix and size. Because the thermal decomposition of the precursor proceeds quickly, there is not significant mobility or agglomeration prior to formation of the metal particle.

The infusion process can also be repeated multiple times in order to controllably increase the amount of infused metal or metal oxide. Figure 2.2 shows a plot of the measured absorbance of infused TiO_2 in a thin (0.5 mil) film of MFA fluoropolymer vs. number of infusion cycles. Because the free volume is filled with a gaseous precursor, (and then condensed via hydrolysis to a solid), most of the original free volume remains after one infusion cycle. This allows one the ability to perform multiple infusion cycles results in an increasing amount of infused material.

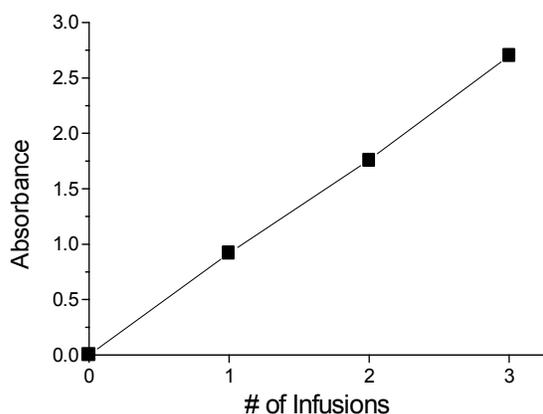


Figure 2.2 Absorbance of TiO₂ vs. Number of Infusion Cycles

3. Demonstrative Applications of the Infusion Process

3.1 Anti-Fouling and Release Applications

A number of different precursors have been infused into a variety of base polymers to produce resultant materials that possess enhanced release characteristics. For example, 13-FT, a fluoroalkyl-containing organosilane, was infused into silicone rubber. Because of thermodynamics, the fluorinated silicate blooms to the near-surface region during hydrolysis. The resulting material exhibits oleophobic properties not present in the base silicone material. In addition, because the silicate network extends into the bulk of the polymer and is not simply a coating, the oleophobic properties persist even after significant wear of the silicone rubber material. The 13-FT precursor has also been infused into polyester and nylon polymers to produce materials with oleophobic as well as hydrophobic properties.

Alternatively, dimethyldichlorosilane has been infused into fluoropolymers. After hydrolysis, the fluoropolymer contains a network of silicone oligomers – essentially low molecular weight silicone oil. Because the precursor possesses only two hydrolyzable groups, a permanent, three-dimensional network does not form and the silicone oil can slowly release from the surface of the film. The resultant material combines the low surface energy and excellent corrosion protection inherent to fluoropolymer films with the foul-release characteristics marine silicone coatings.

3.2 Enhanced Interfacial Bonding and Adhesion

Many polymers such as polyolefins, silicones and fluoropolymers, are difficult to bond to because of their low surface energies and lack of bonding sites at the air-polymer interface. Therefore these polymers are often

treated by plasma, corona or chemical etchants to facilitate bonding. These treatments can effectively increase surface energies which promote adhesion of other materials however, since these treatments are limited to very thin surface regions, their bonding characteristics often diminish with time and suffer under severe environment, mechanical strain, or long term use. Alternatively, the infusion process described in this paper can be used to introduce functional groups (amine, thiol, vinyl, epoxy and isocyanate) to the surface as well as near-surface region of these treated polymers. Furthermore, these functional groups, although present at the polymer's surface, are anchored into the bulk of the polymer via the interpenetrating network that is formed during the infusion process. By choosing an organosilane starting material (i.e., "precursor" as described earlier) that has an organic functional group capable of chemically reacting with chemical functionality contained within a given coating or adhesive layer, one can effectively facilitate the bonding of any coating or adhesive to polymer surfaces that are normally difficult to bond to. Essentially, because the reactive functional chemistry contained within the organosilane starting material is placed both at the polymer's surface and interpenetrated throughout the polymer's bulk via the formation of the polysiloxane network, subsequent chemical bonding of another material (e.g., an adhesive system) results in the fusion of both the infused polymer and the other material at their respective interfaces.

For example, we have previously demonstrated the use of this infusion technology in order to tenaciously bond a fluoropolymer to a platinum-catalyzed silicone adhesive. This was facilitated by first infusing polytetrafluoroethylene-co-hexafluoropropylene (FEP) fluoropolymer (5 mil) with vinyltrimethoxysilane. After subsequent hydrolysis, a polysiloxane network containing pendant vinyl groups were formed and extended from the bulk to the surface of the polymer. A platinum-catalyzed silicone adhesive was then used to bond two pieces of the infused fluoropolymer together. During the cure of the adhesive, the platinum catalyzes the covalent coupling of vinyl groups attached to the surface to those in the silicone adhesive. The resulting bond strength was such that attempts to disbond the films resulted in stretching and ultimate tearing of the fluoropolymer films (ca. > 15 PLI).

3.3 Anti-microbial Polymers

Ligand-bearing organosilanes have been infused into polymers to form long lasting, dynamic anti-microbial polymeric materials. The ligands, which are covalently attached to the silicate-interpenetrating network, function as chelating sites for reversible attachment of silver ions, which function as anti-microbial agents. After infusion of the ligand-bearing organosilane, such as EDA-Si, and subsequent hydrolysis, the infused polymer is immersed in an aqueous solution of silver ion. Silver ions are abstracted from the solution and are bound to the ligands within the

polymer. Although the silicate-ligand network cannot leach out of the infused polymer, the silver-ligand complex slowly releases silver ions out of the polymer resulting in anti-microbial properties. The controlled release of silver ion is governed by the formation constant of the silver-ligand complex and can be tuned by choice of ligand. Because the formation constant for EDA-Ag complex is very large ($K_f \sim 10^{15}$), the rate of release of silver ion is very slow so that anti-microbial properties of the infused polymer are long-lived. Additionally, because the ligand cannot leach, one may simply recharge the polymer with silver ion when necessary. Fabrics made from polypropylene and polyester have each been treated as above and tested for their anti-microbial properties. The treated polymeric fabrics exhibited 100% microbe kill activity even after multiple industrial washing cycles.

3.4 Dyeing of Polyolefins

The dyeing of polyolefins is a difficult technological barrier to surpass. Although many polymers such as polyesters may be dyed using aqueous dye solutions, polyolefins cannot be dyed using traditional dye solutions and therefore are pigmented during compounding prior to extrusion. Traditional acidic or basic dyes will indeed migrate into polyolefins, however these dyes readily leach back out again because there are no functional groups available to act as suitable receptor sites for the dye molecules. Attempts have been made to introduce suitable receptor sites in polyolefins, usually by graft or copolymerizations, so that the polymer may be dyed. These attempts have met with limited success. Polyolefins are low surface energy polymers and any attempt to introduce receptor sites into these materials prior to extrusion, will likely result in the higher energy functionalities being largely segregated to the bulk polymer regions. Therefore these added functionalities are not present at the free volume – polymer interface and cannot effectively interact with the incoming dye molecules.

Because the infusion process specifically takes place within the free volume of the polymer, suitable functional groups introduced by this process should be available to accept the dye molecules. Indeed, the infusion process has been utilized in a number of different permutations to demonstrate the dyeing of polyolefins and, in particular, polypropylene.

Basic functionalities, in the form of amines, can be introduced by infusing any number of amine-functionalized organosilane precursors. After hydrolysis of the precursor to form organosiloxane network within the polypropylene free volume space, the polymer may be effectively dyed using an aqueous acidic dye solution. The electrostatic interaction between the amine receptor and the acidic dye molecule is sufficiently strong to prevent leaching of the dye when immersed for extended periods in boiling water.

Alternatively, infusion of SiCl_4 or tetraethoxyorthosilicate, followed by hydrolysis results in the formation of an SiO_2 network within the polypropylene free volume. The silica is acidic enough to accept a basic dye molecule that does not leach out when exposed to boiling water.

Lastly, infusion of glycidoxypropyltrimethoxysilane (GOPS) results in, after hydrolysis, an organosiloxane network containing an epoxide pendant group. The epoxide group of GOPS is susceptible to ring-opening attachment of either acidic or basic dyes resulting in a covalently bound dye molecule. Dyeing of polypropylene by this method allows strong covalent anchoring of the dye molecule using either acidic or basic dyes.

3.5 Polymerizations Within a Base Polymer's Free Volume

The free volume of a polymer is responsible for the transport of gaseous molecules through the polymer. The infusion process, as described above, adds material to the free volume of polymers. However, the gaseous precursors used for infusion condense to solid materials, and therefore, do not fill a significant portion of the free volume. In fact, the oxygen and water vapor transport properties of an infused polymer do not show significant differences when compared to the base polymer.

Although multiple infusion processes can be used to significantly reduce free volume another more interesting method involves the use of infused metal oxides as catalysts for polymerizing various organic monomers within the free volume. For example, V_2O_5 was chosen as a catalyst for the initial studies because it provides catalytic sites capable of promoting various anionic polymerizations. Styrene was chosen as the monomer for this investigation. The infusion process places the V_2O_5 catalyst in the free volume and subsequent infusion of styrene monomer results in polymerization of styrene within the free volume. Based on weight gain and IR characterization, approximately 10% (by weight) of polystyrene polymerized into the fluoropolymer film. No unreacted styrene monomer was measured in the IR spectrum of the resulting film. Additionally, a sample of fluoropolymer film that did not contain V_2O_5 was infused with styrene monomer. IR did not detect polystyrene in this sample.

Measurement of the oxygen and water vapor transport properties of this sample produced some unexpected results. The rate of water vapor transmission was unaffected by the added polystyrene, but the rate of oxygen transmission increased by a factor of 10. We expected to see an overall decrease in transport rates due to a physical blocking of the free volume. The increase in rate of oxygen transport was unexpected. Work is ongoing to further study these polymer hybrid systems and to determine the selectivity of this effect on different gases.

3.6 Flexible Broad band Radiation Absorbing materials

Figure 3.6.1 below illustrates a fluoropolymer (ETFE) film (10 mils in thickness) that was infused several times in order to obtain a polymer film having a 2.5% by volume loading of Pd nanoparticles. Note the homogeneous distribution and uniformity in size of the Pd nanoparticles throughout the bulk of the ETFE film.

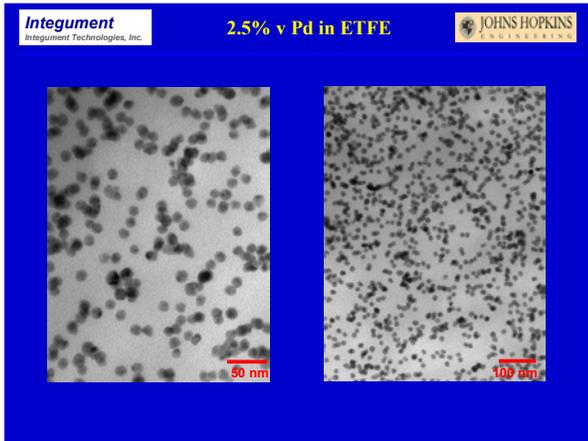


Figure 3.6.1 Multiple infusions of PdCl₂ with subsequent reduction to Pd⁰ metal nanoparticles within a 10 mil Ethyl-trifluoroethylene (ETFE film)

Subsequent spectroscopy (Figure 3.6.2) of the film illustrated in Figure 3.6.1 above showed it to be a remarkable broad band black body absorber (Note: We measured several loadings which show the drop in wavelength transmission. Note that the spectrum baselines from 0.1um through 25um at the 2.5% by volume loading. In addition, although the color of the film was changed to black, no inherent changes in flexibility, toughness, T_g, or crystallinity could be measured due to the relatively low concentration of the nanoparticles grown via infusion into this film.

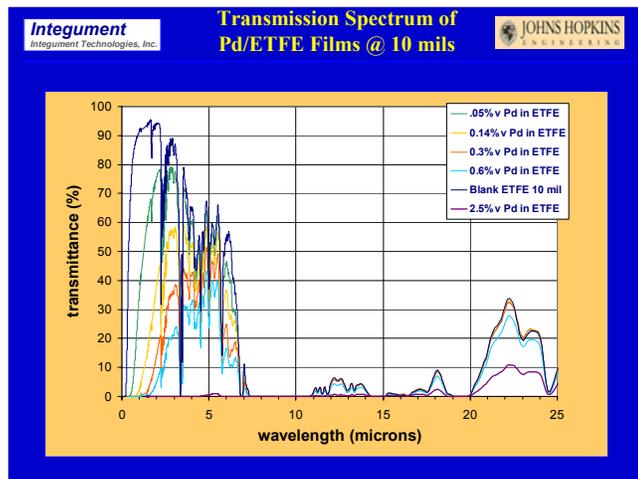


Figure 3.6.2 Transmission Spectrum of Pd nanoparticle ETFE composite film

In addition, our team has published other results investigating optical effects of Ag nanoparticle fluoropolymer composites⁸, as well as linear and nonlinear effects of Pd nanoparticle fluoropolymer composites⁹.

3.7 Control of Gas Permeation

The free volume of a polymer is responsible for the transport of gaseous molecules through the polymer. The infusion process, as described above, adds material to the free volume of polymers which obviously influences gas transport properties. Figure 3.7.1 below shows an example or means for not only attenuating radiation but also for controlling gas permeation. In this case we controllably created a surface rich region of Pd metal nanoparticles which effectively eliminates O₂ permeation while allowing H₂O permeation¹⁰. Looking clockwise from top to bottom the first picture shows a case where we controllably synthesized Pd nano particles near the interface. The metallic crust seen on the first picture is actually below the polymer interface but can be used to subsequently bond another metal or metal oxide layer at the interface thus improving scratch resistance and gas permeation characteristics without altering the host polymer's flexibility. The second picture to the right of the first one is a higher resolution image the first image showing that the crust is actually comprised of Pd nanoparticles. The two pictures on the bottom of Figure 3.7.1 are identical but at different magnifications that show the ability to synthesize similar size Pd nanoparticles homogeneously into the bulk of the polymer.

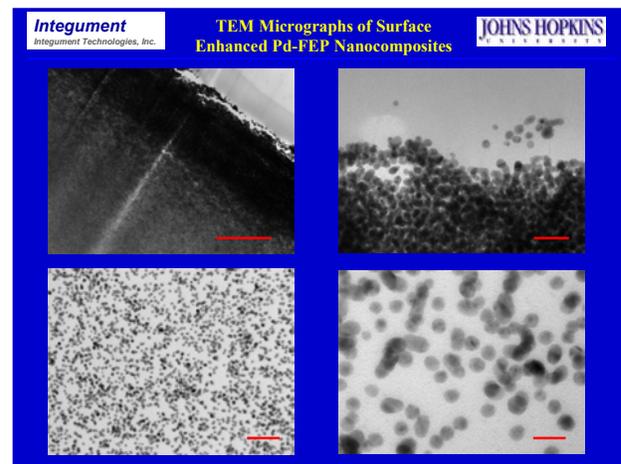


Figure 3.7.1 Bulk and surface percolated Pd nanoparticles in FEP fluoropolymer

3.8 Conductive nano-polymer composites

As described above various nano-metallic particles have been formed in a number of base polymeric resins including fluoropolymers, polyolefins, and others. To date our team has demonstrated loading capabilities of Pd, Pt, Au, and Ag nanoparticles that can lead to both bulk and surface percolation and thus electrical conductivities. For example,

Au, Ag, and Pd polymer nano-composites have been fabricated having a range of surface resistances ranging from mega ohms per square to 0.01 ohms per square cm.

In addition, our team has recently started to demonstrate the inclusion of micro metallic whiskers and platelets for creating desired electrical conductivities for potential sensor and optical switching characteristics. More recently we have begun examining the capability for selectively growing (via infusion) nanometals onto non-conductive micro whiskers and fibers (used for polymer reinforcements). For example, Au nanoparticles have been coated onto non-conductive ceramic fibers previously incorporated into fluoropolymer film. Subsequent thermal treatment has demonstrated that these Au nanoparticles can be controllably melted to form a conductive coating onto these micron sized fillers. We refer to this as nano-welding within our ongoing research program.

4. Conclusion

This paper reports on novel nano-technology that can be used to fabricate an endless number of polymer nanocomposite materials. The methods described require no solvents or use of supercritical fluid technology and are useful for a wide range of polymeric materials including fluoropolymers and polyolefins.

The infusion process produces materials that exhibit a variety of unique chemical, biochemical, optical, and electrical characteristics that make them commercially attractive for many technological applications. The process allows certain characteristics of a polymer to be enhanced or altered for improved performance, while leaving other polymer properties unchanged. Desirable attributes can be added to polymeric materials with the addition of only 1-2% by weight of infused material.

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