

The Effect of Nanoparticle Distribution on the Structure and Properties of Palladium/Polycarbonate Nanocomposites

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ABSTRACT

We report the synthesis of palladium (Pd)/polycarbonate (PC) nanocomposites as well as their morphological and thermal properties. Pd nanoclusters were produced by the reduction of palladium chloride using a variation of the Brust's method. Isolated Pd nanoclusters were formed in the absence of PC in the reaction mixture (*ex situ* method) while agglomeration of Pd nanoclusters was noticed in the presence of PC in the reaction mixture (*in situ* method). The glass transition temperature (T_g), decreased by $\sim 15^\circ\text{C}$ for both the *ex situ* and *in situ* samples. Thermogravimetric analysis (TGA) indicated that the presence of Pd nanoclusters significantly improved the thermal stability of the nanocomposites, as evidenced by the enhanced onset of degradation by $\sim 30^\circ\text{C}$ and $\sim 50^\circ\text{C}$ for the *in situ* and *ex situ* nanocomposites, respectively.

Keywords: nanoclusters, nanocomposites, morphology, glass transition temperature, thermal stability.

1. INTRODUCTION

In the past few years, nanoclusters protected by polymers and organic ligands have gained increased attention in materials research as they offer immense opportunities to design materials with tunable properties. For example, these nanoclusters showed variations in optical, thermal, electrical and electrochemical properties based on their size.

Generally, nanoclusters protected by polymers can be prepared by two different synthetic methods. In the *ex situ* method, organic ligand-protected nanoclusters are initially prepared followed by homogenous mixing with a polymer solution. In contrast, the *in situ* method, involves the preparation nanoclusters in the presence of a polymer. This method generally involves no additional organic ligands as protecting agents other than the polymer. The resulting solutions from either method can subsequently be cast into films. Several variants

of the *ex situ* method (1) and the *in situ* method (2) have already been reported for the preparation of metal/polymer nanocomposites.

From earlier studies (3-5), it can be inferred that the morphology of the resulting nanoclusters depends on several factors such as molecular weight of the protecting agent; metal salt; protecting agent ratio; functional groups in the protecting agents; reaction temperature; reducing agent; and reduction rate. However, there have been few prior reports pertaining to examining the effect of synthetic method on the structure and properties of the resulting metal/polymer nanocomposite films. The present study was aimed at addressing this issue.

Here we report an *in situ* method for preparing nanocomposite films by reducing PdCl_2 in the presence of polycarbonate (PC) dissolved in dichloromethane. We also synthesized Pd/PC nanocomposite films by an *ex situ* method involving the dispersion of dodecanethiol-protected Pd nanoclusters in a solution of PC in dichloromethane. These nanocomposite films were characterized by transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). It was found that the synthesis method had a significant impact on the morphological characteristics and the corresponding thermal properties of the nanocomposite films.

2. EXPERIMENTAL SECTION

2.1 Materials

Palladium chloride (PdCl_2), conc. hydrochloric acid (HCl), and dichloromethane (CH_2Cl_2) were purchased from Merck, India. Sodium borohydride (NaBH_4) and dodecanethiol ($\text{C}_{12}\text{H}_{25}\text{SH}$) were purchased from Aldrich, USA. Polycarbonate (Caliber T303, (Mw: 1,600,000)) was obtained from Dow Chemicals, USA. De-ionized water with a resistivity of $18 \times 10^6 \Omega\text{-cm}$ was obtained from a Millipore unit.

2.2 Synthesis of Pd/PC nanocomposite films

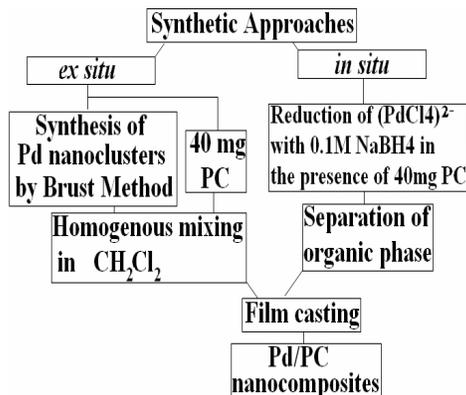


Figure 1. Synthetic approaches for preparing *in situ* and *ex situ* Pd/PC nanocomposites

A schematic representation of Pd/PC nanocomposite synthesis is shown in Figure 1. In the *ex situ* method, $C_{12}H_{25}SH$ -protected Pd nanoclusters were prepared using Brust method (3). The Pd nanoclusters were then homogeneously mixed with a solution of 40 mg of PC in 20 ml of CH_2Cl_2 ($1.6 \mu M$) followed by film casting at room temperature. In the case of the *in situ* method, PC (40 mg) was dissolved in CH_2Cl_2 (20 ml) ($1.6 \mu M$). 15 mg of $PdCl_2$ was first dissolved in 2 ml of conc. HCl so as to form a complex $[PdCl_4]^{2-}$, and was further dissolved in 48 ml water to form a 1 mM solution. This biphasic mixture was stirred continuously using a magnetic stirrer for 30 minutes. A freshly prepared solution of $NaBH_4$ in 20 ml water (0.1 M) was added drop-wise to the mixture. The color of the reaction mixture changed rapidly from golden yellow to black, indicating the formation of Pd nanoclusters. After stirring for 3 hours, the organic phase was separated, washed with water and was directly cast into film at room temperature. Soon after the reduction nearly all of the reduced Pd nanoparticles get themselves shifted from aqueous phase to organic phase.

2.3 Characterization of Pd/PC nanocomposite films

TEM micrographs were taken on a JEOL model 1200 EX instrument operated at an accelerating voltage of 120 kV. Samples for TEM analysis were prepared by casting nanocomposites from dichloromethane

dispersion on a carbon coated Cu grid (400 meshes) and dried slowly at room temperature. Thermogravimetric analysis was performed using Perkin-Elmer TGA-7 thermal analysis system, operated under nitrogen flow in the temperature range of 50 to $700^\circ C$ at $20^\circ C/minute$. The calorimetric measurements were carried out using a DSC-7 (Pyris 1, Perkin-Elmer) unit over a temperature range of 20 to $200^\circ C$ at $20^\circ C/minute$ under nitrogen atmosphere.

3. RESULTS AND DISCUSSIONS

3.1 Morphology of Pd/PC nanocomposite films

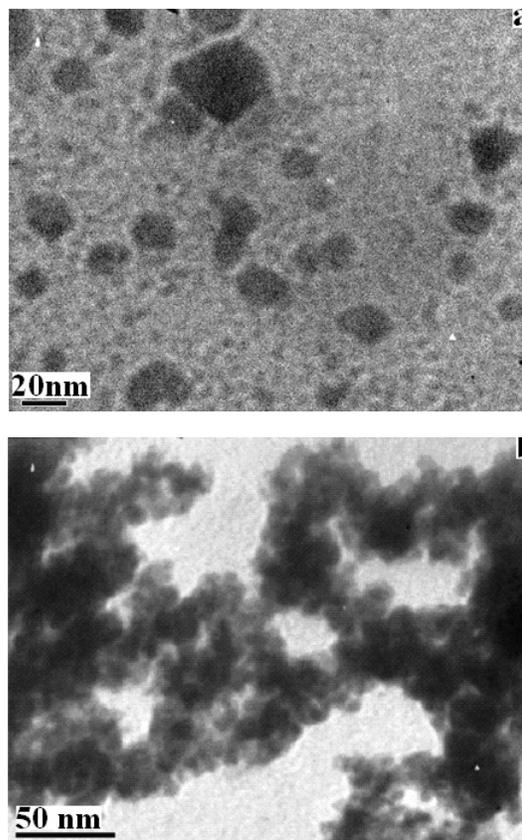


Figure 2. TEM image of the *ex situ* and *in situ* Pd/PC nanocomposites showing (a) dispersed Pd nanoclusters, and (b) agglomerated Pd nanoclusters, respectively.

The TEM image of the *ex situ* nanocomposite with 18.4 wt.% (2 vol%) Pd, (on a stoichiometric basis) revealed dispersed Pd nanoclusters of ~ 15 nm embedded in PC (mol.

wt. 1,600,000) matrix (Figure 2a). Based on earlier reports on the synthesis and morphology of n-alkanethiol-protected Pd nanoclusters, the presence of dodecanethiol on the surface of the Pd nanoclusters in the present study is likely to ensure the separation of the nanoclusters even after mixing with PC.

However, the average particle size of the Pd nanoclusters in previous studies was found to be ~ 5 nm size; using the Brust's biphasic method (3). Although identical metal salt: thiol ratio and reducing agent were used in the present study, an increase in the size of the nanoclusters was found. This may be due to the absence of the surfactant, tetraoctyl ammonium bromide, in the reaction mixture which helps in phase transfer of reduced Pd nanoclusters. The effect of increased temperature of the reaction mixture from ice-cold condition in the earlier studies in comparison to the reaction room temperature may have also contributed to the increased size of the nanoclusters. A difference in the concentration of reducing agent may have also contributed to the increase in the average size of nanoclusters.

In contrast to the above system, *in situ* nanocomposites of Pd nanoclusters (18.4 wt. % on a stoichiometric basis) in PC showed significant agglomeration (Figure 2b). Similar observations on agglomeration were reported by Chen et al using Pd/ mercapto-poly(ethylene glycol) (5), and Chatterjee et al with Au/poly(dimethylamino ethyl methacrylate-*b*-methyl methacrylate) copolymers (6). However, discrete nanoclusters were also noted by Tamilselvan et al in Au/ poly(styrene-*b*-vinyl pyrrolidone) copolymer systems (7), and Khanna et al (8) in Ag/poly(vinyl alcohol) systems. Thus, morphological changes in nanocomposites appear to be strongly dependent on the specific polymers system and reaction conditions.

Wang et al have suggested that in order to obtain discrete nanoclusters, the rate of adsorption of organic ligands on the surface of nanoclusters should equal the rate of nanocluster formation (9). Accordingly, organic ligands with lower molecular weight have generally been found to be more effective in limiting the nanoclusters size (10). The wide-ranging behavior of agglomeration in nanocomposites prepared by the *in situ* methods may be due to the differences in conformation of the polymer chain in the different systems. These differences can arise from variations in molecular weight, solvent, and temperature. Consequently, the mobility of the polymer during adsorption on the

nanocluster surface can be affected, thereby limiting the agglomeration of the nanoclusters. In addition, the nature of interactions between the polymer and the surface of the nanoclusters may also play a role in determining the morphology of the resulting nanocomposites. Further the following sections examine the consequences of the differences in morphology on the resulting properties of the nanocomposites.

3.2 Thermal Properties

3.2.1. DSC

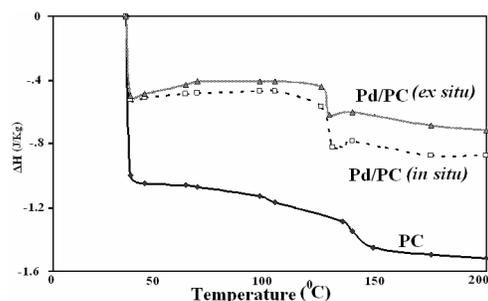


Figure 3. DSC measurements showing reduction in the T_g of *ex situ* and *in situ* Pd/PC nanocomposites and free PC.

A comparison of the DSC profiles of the nanocomposites is displayed in Figure 3. It was found that the T_g of both *ex situ* and *in situ* nanocomposites (with 18.4 wt% Pd on a stoichiometric basis) decreased by 16°C (from 146°C to 130°C).

Aymonier et al (2) observed $\sim 9^\circ\text{C}$ decrease in T_g for Pd/PMMA nanocomposites synthesized by a different route. Differences in concentration (≤ 0.1 wt. %) and nanocluster size (~ 2 nm) between their work and the present study may account for differences in the magnitude of the change in T_g . Earlier studies by Liu et al (4) using Au/PMMA and Hsu et al (11) with Au/polyurethane also showed a decrease in T_g by 20°C and 5°C respectively. Prior studies with fumed silica-based poly(4-methyl-2-pentyne) and poly(1-trimethylsilyl-1-propyne) nanocomposites indicated a substantial rise in gas permeability compared to the unfilled polymers suggesting an increase in free volume between the polymer chains (12). In a similar manner, the Pd nanoclusters embedded may have increased the free volume between the PC

chains, thereby reducing the T_g of the nanocomposites.

However, an increase in T_g by 7°C was also noted by Ash et al (13) in alumina/PMMA nanocomposites. The presence of strong interactions between the carbonyl groups of PMMA and alumina is well-known. Consequently, the polymer chains will be strongly pinned to the surface of the metal oxide, thereby increasing T_g . In contrast, relatively weak interactions exist in the Pd/PC nanocomposites as evidenced by the FTIR data and a corresponding decrease in T_g .

3.2.2. TGA

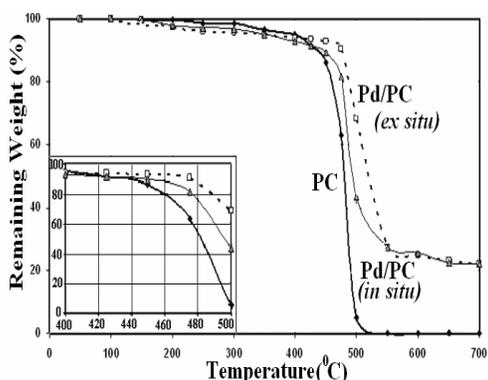


Figure 4. TGA of *ex situ* and *in situ* Pd/PC nanocomposites and free PC

Thermogravimetric analysis (Figure 4) indicated that the incorporation of Pd nanoclusters in PC for the *ex situ* nanocomposites increased the thermal stability of the PC matrix from ~ 425 to $\sim 475^\circ\text{C}$. In comparison, in the *in situ* nanocomposites an improvement in thermal stability from $\sim 425^\circ\text{C}$ to $\sim 455^\circ\text{C}$ was observed.

A similar increase in thermal stability was noted in earlier reports by Aymonier et al (2) for Pd/PMMA, and Hsu et al (11) for Au/polyurethane. They observed that the thermal stability of the nanocomposites increase with increase in the metal concentration and decrease with decrease in particle size and agglomeration. These results are based on changes in area of the polymer-nanocluster interface and are in close agreement with the present study. As an additional note, the stoichiometric yield of Pd after reduction was expected to be 18.4 wt% but after thermogravimetric analysis ~ 20 wt% residue was obtained. This may be attributed to the presence of impurities such as oxides of Pd.

4. CONCLUSIONS

Pd/PC nanocomposites prepared by the *ex situ* and *in situ* methods exhibited marked differences in their morphology. The Pd nanoclusters produced by the *ex situ* method were well-dispersed while the Pd nanoclusters produced by the *in situ* method were agglomerated. The nanocomposites exhibited a strong dependence of thermal properties on their morphology. The T_g of both the nanocomposites were lower than PC by 15°C . In addition, the onset of thermal degradation of the *ex situ* and *in situ* nanocomposites were higher than PC by 50°C and 30°C , respectively.

5. REFERENCES

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