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Polymer/Metal Nanocomposite Synthesis in Supercritical CO$_2$

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The synthesis of polymer/metal composites is an ongoing challenge in materials research, and a spectrum of techniques tailored to specific applications has emerged, but to date no general preparative method exists. An elusive but potentially rewarding goal is the synthesis of polymer/metal nanocomposites: metal and semiconductor clusters having dimensions of tens of nanometers or less exhibit size-dependent electrical, chemical, and magnetic properties.[1,2] Stabilization in a polymer matrix prevents agglomeration and facilitates fabrication into useful catalytic, optical, and electronic devices. Reports of the synthesis of these materials are limited and highly specific.[3-14] We have developed a simple, direct and versatile method for the synthesis of polymer/metal composites consisting of isolated metal nanoclusters distributed homogeneously throughout polymeric substrates. Organometallic precursors are dissolved in supercritical fluid (SCF) carbon dioxide and infused into solid polymers as SCF solutions (Scheme 1). Chemical or thermal reduction of the precursor (OM) to the base metal (M) either in the presence of the SCF or subsequent to its removal produces metal domains within the solid polymer matrix. In this report we demonstrate this technique by describing the synthesis of nanoscale platinum clusters within poly(4-methyl-1-pentene) (PMP) and poly(tetrafluoroethylene) (PTFE) using dimethyl(cyclooctadiene)platinum(II) (CODPtMe$_2$) as the metal precursor.

This work is part of a broader program in which we are preparing composite materials by conducting chemical reactions within polymer substrates swollen with-SCF CO$_2$. Our first reports described the free-radical polymerization of styrene in swollen polymers to produce polystyrene/substrate blends.[15,16] There are multiple advantages associated with this approach to composite materials: First, the high permeation rate of CO$_2$ in virtually all polymers and the wide range of organic and organometallic reagents which are soluble in CO$_2$ render this technique a generally useful scheme for the synthesis of polymer composites. Neither the polymer substrate nor the reaction product need be soluble in CO$_2$. Second, sorption of CO$_2$ can result in orders-of-magnitude increases in diffusion rates in the

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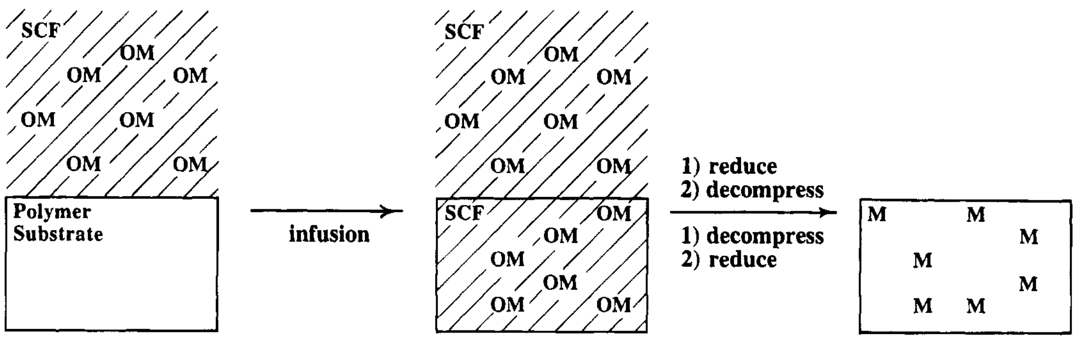
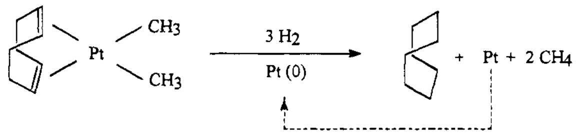
Scheme 1. SCF Strategy for Preparing Metal/Polymer Composites (OM = Organometallic)



substrate which significantly enhances the kinetics of penetrant absorption.[16-18] The degree of polymer swelling,[17-20] diffusion rates within the substrate,[17,18] and the partitioning of penetrants between the SCF and the swollen polymer[21] can be controlled by density-mediated adjustments of solvent strength via changes in temperature and pressure. Coupled with manipulation of reaction rates, SCFs offer unprecedented control over composite composition and morphology. Third, SCFs such as CO_2 are gases at ambient conditions and the solvent dissipates rapidly upon the release of pressure. Finally, CO_2 is an environmentally acceptable process solvent. In the case of metalation using $CODPtMe_2$, the process effluent consists solely of CO_2 and the light hydrocarbons (methane and cycloooctane) derived from the precursor ligands.

The synthetic scheme described above requires that CO_2 serve as both an effective medium for the transport of reagent and an inert solvent for the reaction that produces the second phase. Recent reports[22-25] have highlighted technical and environmental advantages of CO_2 as a process solvent and provide examples of reactions that proceed cleanly in CO_2. These include hydroformylations, oxidations, enzymatic reactions, Diels–Alder reactions, photochemical activations of alkanes, and free-radical reactions.[26-32] This is the first report of the reduction of an organometallic compound to yield pure metal[33] in CO_2. We chose $CODPtMe_2$ as the precursor for this study for the following reasons: High-purity Pt films have been obtained from the precursor by chemical vapor deposition (CVD) in the presence of H_2.[34] Unlike most CVD precursors, detailed information regarding the thermal decomposition and the reduction of $CODPtMe_2$ with H_2 is available.[35-37] The reduction of $CODPtMe_2$ with H_2 over platinum is autocatalytic (eq 1); this is exploited to nucleate and grow platinum clusters. Finally, $CODPtMe_2$ is attractive due to its high platinum content (58.5 wt %), heptane solubility (which is a good indicator of solubility in CO_2[38]), and low toxicity of the ligands. Additionally, the ligand-derived products are easily removable from the composites; methane should spontaneously desorb and cyclooctane is easily extracted with CO_2.



(1)

Platinum/PMP composites were prepared by the sequential impregnation and reduction of $CODPtMe_2$. 1 × 5 cm sections of thick (90 mil) PMP films (~1.0 g) were exposed to solutions of 50 mg of $CODPtMe_2$ in CO_2 (1.3 wt % $CODPtMe_2$) at 80 °C and 155 bar for 4 h in high-pressure stainless steel reactors that consist of ~1.2 cm (i.d.) by 10 cm sections of ½ in. schedule 160 seamless pipe with a plug at one end and a high-pressure needle valve at the other. In three parallel experiments, the precursor was reduced by (a) hydrogenolysis (24 h) subsequent to depressurization, in a clean stainless steel reactor at 60 °C, 70 bar of H_2, (b) hydrogenolysis (4 h) in CO_2 at 80 °C, 155 bar induced by the addition of a ~10-fold excess of H_2 to the reaction vessel prior to depressurization, and (c) thermolysis (20 h) in CO_2 induced by raising the temperature to 140 °C prior to decompression (final pressure ~265 bar).[39] The concentration of platinum in each sample was determined by the residual mass obtained after fuming

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(33) XPS analysis of Ar^+ ion sputter-cleaned platinum films prepared by reducing $CODPtMe_2$ from CO_2 onto polished silicon wafers indicates that extremely high-purity platinum is obtained in the reaction reported here.

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(38) The maximum solvent strength of CO_2 at elevated pressures has been compared to that of the light hydrocarbons.[25] While this generalization does not account for a number of notable exceptions in which solubility in CO_2 (and not in hydrocarbons) is attributed to specific solute–solvent interactions,[26,27,44] it is a useful guide for the selection of organometallic precursors.

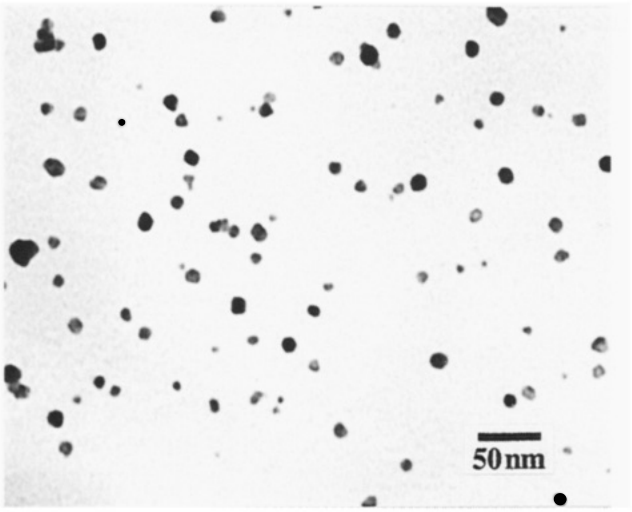

Figure 1. TEM image of Pt clusters in PMP deposited by reduction of $CODPtMe_2$ subsequent to removal of the SCF solution.

sulfuric acid digestion of the composites in platinum crucibles followed by ashing at 1000 °C in a muffle furnace. Platinum content varied between 1.8 and 2.0 wt % for the three samples. In a control experiment, a PMP sample gained 36.4 mg after decompression and isolation from a 1.3 wt % $CODPtMe_2$ solution in CO_2. This corresponds to 3.4 wt % $CODPtMe_2$ (2.0 wt % Pt). The control sample is a yellow transparent solid solution. We have not studied the fate of the ligand-derived products. Reduction of the impregnated substrate subsequent to depressurization produces a deep black composite. Transmission electron microscopy[40] of a microtomed section from the cross section of this composite revealed the presence of discrete platinum clusters having a maximum particle diameter of approximately 15 nm (Figure 1). Images of the composite cross section obtained by low-voltage SEM[41] confirmed that the clusters are present throughout the thickness of the substrate. The uniform distribution of the clusters throughout the composite indicates that the 4 h soaking period is of sufficient duration for complete permeation of the precursor to occur. This point may have been reached sooner than 4 h; we have not yet studied the kinetics of this absorption. SEM analysis of the composite surface indicated the presence of a small number of large platinum clusters (~100 nm diameter) in addition to a predominate population of clusters of less than 15 nm. The large clusters could be the result of surface deposition of precursor during the removal of the SCF.

Hydrogenolysis of the precursor in the presence of CO_2 produces a deep black composite with a silvery hue. TEM analysis of a section microtomed from the cross section of this composite (Figure 2) indicates the presence of discrete platinum clusters having a maximum diameter of approximately 50 nm. We attribute the larger particle size observed in the hydrogenolysis of the precursor in the presence of CO_2 to higher diffusion rates within the CO_2-swollen polymer. SEM analysis of the composite cross section revealed a sharp concentration gradient between a platinum-enriched surface layer and the bulk of the substrate which contained a uniform concentration of the <50 nm Pt particles. SEM images of the surface revealed a high concentration of larger platinum crystals (50–100 nm). We ascribe the surface enrichment to deposition of metal from precursor dissolved in the fluid phase.

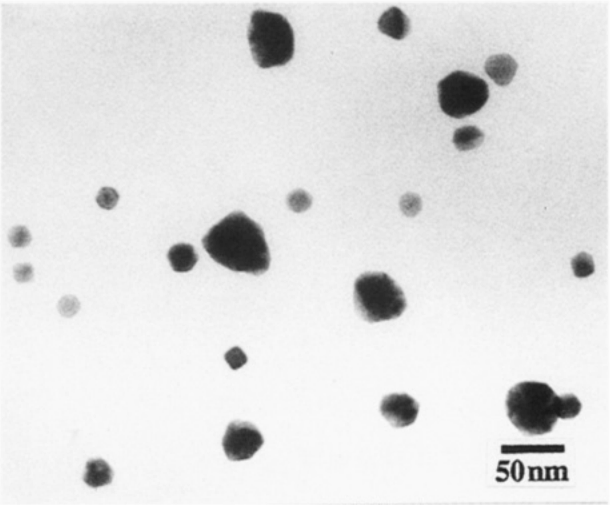

Figure 2. TEM image of Pt clusters in PMP deposited by reduction of $CODPtMe_2$ in SCF CO_2.

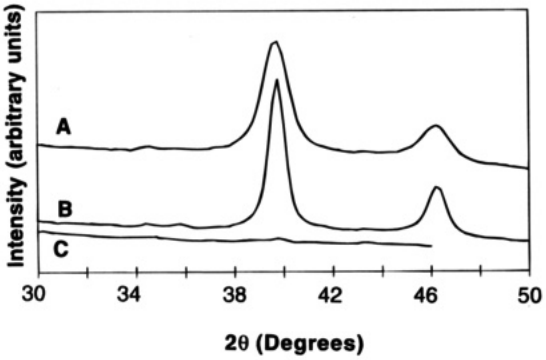

Figure 3. WAXD of Pt/PMP composites. (A) <15 nm clusters; (B) <50 nm clusters; (C) virgin PMP. The intensity of A has been shifted for clarity.

Thermolytic reduction of the precursor in CO_2-swollen PMP at 140 °C produces a deep black composite. TEM analysis revealed feathery platinum aggregates comprised of smaller primary particles. The aggregates, which are distributed throughout the substrate, have a maximum diameter of approximately 50 nm. The solid state thermolysis of $CODPtMe_2$ is reported to yield metallic platinum; the decomposition temperature as determined by differential scanning calorimetry is ~208 °C.[35]

The presence of metallic platinum in the composites was confirmed by wide-angle X-ray diffraction (WAXD, Figure 3). With the exception of the strong 111 and 200 reflections for metallic platinum, wide-angle scans ($2\theta = 5-50°$) for virgin PMP and the composite samples were identical.[42] The 15 nm clusters produce broader

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(39) It is likely that shorter reaction times will also render complete reductions; we have yet to study the kinetics of the hydrogenolysis and thermolysis reactions.

(40) Transmission electron microscopy (TEM) using either a JEOL 100 CX or a JEOL 1200 electron microscope was performed on thin sections obtained from the cross sections of the composites by microtomy using a glass knife.

(41) SEM analysis of the polymer/metal composites was performed using a JEOL 6400 FXV field emission SEM. Secondary electron images (1 kV) of the uncoated composite surface and back-scattered electron images (BSI) of composite cross sections (light carbon coating, 15 kV) were obtained.

reflections than the 50 nm clusters, which is in agreement with the Scherrer equation.[43] WAXD analysis of the thermally prepared composite revealed significantly weaker and significantly broader Pt reflections. WAXD analysis of the precursor/substrate control sample (prior to reduction or thermolysis) revealed only PMP reflections, indicating that the precursor is present not as a crystalline solid in PMP but as a solid solution and that reduction does not occur during the infusion of precursor into the solid substrate.

Platinum/PTFE composites were prepared by hydrogenolysis of CODPtMe$_2$ in the presence of CO$_2$ using the same conditions described above for the platinum/PMP composite. Platinum clusters (in much fewer number than in PMP) were observed throughout the bulk of the sample by TEM analysis of sections obtained from the interior of the composite by cryogenic microtomy (Figure 4). A significant amount of platinum (crystals, >100 nm diameter) was also deposited at the surface under these conditions. The successful deposition of platinum within PTFE confirms that the absence of surface tension in SCFs and the permeability of CO$_2$ in even the most solvent resistant polymers render this technique a powerful tool for the synthesis of polymer composites.

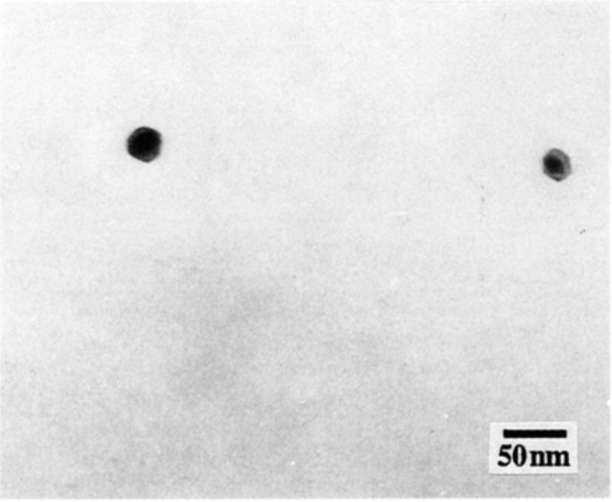

Figure 4. TEM image of platinum clusters within PTFE.

The distribution of metal and the size of individual metal clusters within the substrate are determined by the relative rates of permeation and reduction. Both of these rates can be controlled by adjusting experimental parameters. Homogeneous modifications are effected by equilibrating the SCF solution with the swollen polymer prior to reduction. Surface-selective depositions can be achieved by reduction of the precursor using conditions under which the rate of absorption of the precursor is slow relative to the rate of reduction. Gradient structures should be produced when the rates of absorption and reduction are competitive. We are currently studying these issues.

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(42) Wide-angle X-ray diffraction (WAXD) measurements were obtained using a modified Siemens D500 diffractometer operating in normal-transmission mode with Cu Kα radiation from a sealed tube.

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