Preparation of Pd Cluster/Polymer Composites Using Bis(acetylacetonato)palladium(II) Vapor

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Composites consisting of Pd clusters and commodity polymers such as Nylon 6 and poly(ethylene terephthalate) are easily prepared by exposing the polymers to bis(acetylacetonate)palladium(II) vapor.

Metal clusters are known to show remarkable properties when well dispersed.[1] Thus, many efforts have been devoted to fix the dispersions of metal clusters in solid materials.[2] Polymers might provide the most suitable matrix material for such a purpose because of their light weight and transparency, as well as their easy processibility.[3] Here we describe a simple method to prepare Pd cluster/polymer composites using bis(acetylacetonato)palladium(II) (Pd-AA) vapor. This method allows the easy creation of composites with Pd concentrations of more than 20% or composites in which Pd clusters are locally distributed.

Pd-AA was chosen as the starting material because it is smoothly sublimed at temperatures at which many commodity polymers usually show soft property. A tentative procedure is as follows: In a flat-bottomed test tube of 28 mm diameter, Pd-AA previously placed on the bottom was sublimed under reduced pressure(ca. 2 Torr) by heating the bottom locally at 180 °C, and the Pd-AA vapor thus generated was condensed on the cold sidewall of the test tube. A polymer sheet(12 mm × 19 mm) was then placed on the bottom of the test tube, and after the atmosphere was replaced with N_2, the entire test tube was immersed in a 180 °C oil bath. The Pd-AA on the sidewall then began to be sublimed. Some sheets of commodity polymers[4] gradually turned black or dark brown on exposure to the Pd-AA vapor generated by sublimation.

Heating a nylon 6 (NYL) sheet for 0.5 h gave a sheet consisting of a black upper layer and a colorless lower layer. The TEM image of the black layer of the sheet shows that the Pd clusters are homogeneously dispersed (Figure 1). Further heating of the sheet under N_2 resulted in no change in color. This indicated that the Pd cluster formation had been completed at that time. Using a poly(ethylene terephthalate) (PET) sheet, a black layer was also generated containing Pd clusters. Other polymers including poly(styrene), poly(propylene), polycarbonate resin and poly(vinyl alcohol) were applicable to the preparation of Pd cluster-containing composites. In some cases, further postheating treatment for 0.5 h or so under N_2 was required to complete Pd cluster formation.

Exceptionally, heating of a poly(methyl methacrylate) (PMMA) sheet with Pd-AA vapor resulted in the formation of a pale yellow upper layer containing a considerable amount of Pd-AA which showed an absorption band at 325 nm and only a small amount of Pd clusters. At 180 °C, PMMA (Tg=105 °C) in the glass state is regarded as a viscous liquid which is favorable to dissolve Pd-AA. During further heating for 16 h under N_2, the upper layer of the PMMA sheet turned dark brown very slowly due to the formation of Pd clusters. After heating for 16 h, the UV–vis spectrum of the sheet showed the presence of only a trace amount of Pd-AA. During the postheating treatment, Pd-AA dissolved in PMMA would be converted to Pd clusters. It is known that a similar decomposition of Pd-AA occurs in organic solvents to give colloidal palladium.[5]

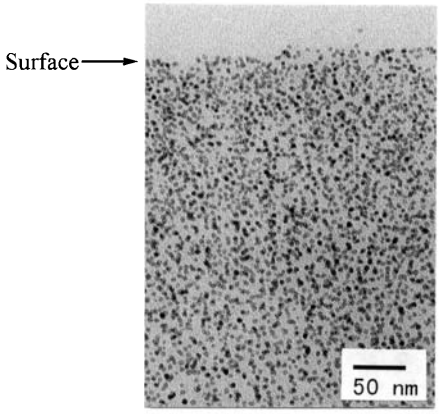

Figure 1. TEM image of the ultrathin slice of NYL sheet treated with Pd-AA vapor.

The processes using other polymers such as NYL and PET might also involve the dissolution of Pd-AA followed by conversion to Pd clusters in the polymers in a glass state, although Pd-AA could not be detected by UV–vis spectroscopy during the present experimental course due to the strong absorption by Pd clusters near 325 nm.

The Pd contents of the colored layers were estimated on the basis of the Pd analysis of the entire sheets and the depth measurement of the layers by the optical microscopy of their cross sections. The results are summarized in Table 1. These results indicate that both the Pd content and the depth of Pd cluster-containing layers were considerably influenced by the diffusion of Pd-AA in the polymers. As previously reported,[6] through the use of an alternative method starting from the solution of Pd-AA in MMA, the Pd content of Pd cluster/polymer composites is no more than 0.5% owing to a limit in the solubility of Pd-AA. In contrast, via the present method, composites containing even ca. 40% and ca. 20% Pd were obtained by prolonged treatment with Pd-AA vapor and the use of thinner sheets of NYL(15 μm thick) and PET(16 μm thick), respectively.

Table 1. Composition of palladium cluster/polymer composites prepared using Pd-AA vapor

Polymer	Heating time[a]/h	Depth of the layer[b] / μ m	Pd content of the layer[b] /%	Size of Pd clusters/nm
NYL	0.5	35	5	4.3 ± 0.4
PET	0.5 + 0.5[c]	90	0.8	3.9 ± 0.9
PMMA	0.5 + 16[c]	60	0.6	4.2 ± 0.9

[a] Time of heating at 180 °C with Pd-AA vapor. [b] The colored layer containing Pd clusters. [c] Time of postheating at 180 °C under N_2 in the absence of Pd-AA vapor.

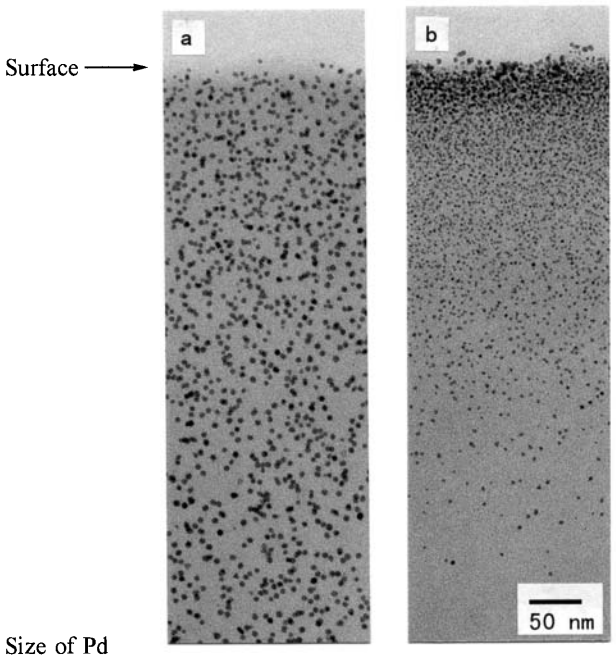

Figure 2. TEM images of the ultrathin slices of epoxy resin sheets treated with Pd-AA vapor, a: EP-5, b: EP-15.

Sheets of epoxy resins (EP-5 and EP-15)[7] with differing degrees of cross-linking were prepared by the use of 5 and 15 phr (parts per handred of resin) of triethylenetetramine, respectively, and treated with Pd-AA vapor in the same manner as described above. The TEM images of the resulting sheets and the sizes of Pd clusters measured from the pictures are shown in Figure 2. These profiles indicate that the degree of cross-linking of the epoxy resins strongly influence both the size of Pd clusters and the depth of Pd cluster-dispersed layers. Thus, in EP-15, much smaller Pd clusters are distributed in the surface layer of ca. 500 nm depth with a steep gradient in density. This is presumably because either the growth of Pd clusters or the diffusion of Pd-AA might be depressed by the close network of such a highly cross-linked polymer.

Composites containing clusters of other metals including Pt and Cu were obtained using the acetylacetonato complexes of the corresponding metals in a quite similar manner.

References and Notes

1 G. Schmid, *Chem. Rev.*, **92**, 1709 (1992).
2 R. Dagani, *Chem. Eng. News*, **1999 (June 7)**, 25.
3 Y. Nakao, in "Macromolecular Science and Engineering," ed. by Y. Tanabe, Springer, Berlin (1999), p. 125.
4 Among them, an NYL sheet 135 μm thick was supplied as Novamid, and a PET sheet 350 μm thick as Diafoil. A PMMA sheet of 500 μm thick was prepared by cast polymerization of methyl methacrylate(MMA) under N_2 using 0.05% AIBN as an initiater.
5 K. Esumi, T. Tano, and K. Meguro, *Langmuir*, **5**, 268 (1989).
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7 Epoxy resin sheets 500 μm thick were prepared from Epikote 828 by hardening with triethylenetetramine at room temperature.