

Preparation of ultrafine metal particles/polyurethane composites

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Summary

A new type of coordination polyurethane was prepared by incorporating the transition metal ions into the pyridine containing thermoplastic polyurethane films. Then the metal ions dispersed in the polyurethane matrix were reduced by controlling the exposure of the metal sites to NaBH_4 under mild condition. The reduction of the polyurethane metal complex films resulted in the production of amorphous ultrafine metal powders. The size of these powders was controlled by the content of the metal ions and the polarity of the polymer matrix. A polar polymer backbone and lower metal ion concentration favored to achieve a smaller particle. It was also found that the polymer chains prohibited the excessive aggregation of the metal atoms and have protective effect on the final metal powders.

Introduction

Interest in the physics of condensed matter at size scales larger than that of atoms but smaller than that of bulk solids has grown rapidly in the past two decades. Materials with particles in the range from 10 to 100Å exhibited novel electronic, optical, magnetic, and chemical properties due to their extremely small dimensions. Among the various nanostructures, ultrafine metal particles have attracted considerable interest in view of their potential applications (1,2). Until today, there are many methods have been proposed to produce the ultrafine metal powders. One of these methods is to prepare the nanoscale materials by consolidation of small clusters (3).

It has been proved that the metal ions in the ionomers and some other macromolecule metal complexes have a tendency to form the ionic clusters within polymer matrix (4,5). The metal ions and their associated pendent groups were microphase separated from the typically hydrophobic portions of the polymers (6). As a result, the ionic clusters, which ranged over 20-100Å in diameter and were largely surrounded by a medium of low dielectric constant polymer network, were achieved.

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analysis proved that the composition of the final products was in accordance with the designation (10).

Blends of pyridine group containing polyurethane with metal salts (FeCl_3 , CoCl_2 , NiCl_2 , CuCl_2) were prepared by dissolving the precursor polymer in DMAc (10%), then mixing with a stoichiometric amount of the appropriate metal salts dissolved in DMAc at 50°C. The mole ratios of pyridine nitrogen to metal ions and the ratio of the components of the base polyurethanes are listed in Table. I. The sample code XOPabcMR represents the composition of the sample (X:PTMO1000; O:ODI; P:BIN; abc:PTMO/ODI/Pyridine; M: metal ion; R:reduction).

The solutions were poured into Teflon-casting plates and the solvent was evaporated in an air oven at 80°C for 48h, then the films were dried in vacuum at 70°C for at least 2 days. The test pieces of polyurethane metal chelate films, 20 μm thickness, which allowed the reducing agent to reach the center of the film, were reduced by 25 ml of 1wt% sodium borohydride aqueous solution at room temperature for about 1 h. The reduced films were washed with distilled water and dried in a vacuum oven at room temperature and stored in a desiccator for subsequent use.

Tab.1. Composition of the Samples

<i>Sample Code</i>	<i>Pyridine Content (wt%)</i>	<i>PTMO /ODI /Pyridine</i>	<i>Metal/Pyridine</i>	<i>Cation Type</i>
POP132FeR	7.7	1/3/2	1/3	Fe^{3+}
POP132CoR	7.7	1/3/2	1/2	Co^{2+}
POP132NiR	7.7	1/3/2	1/2	Ni^{2+}
POP132CuR	7.7	1/3/2	1/2	Cu^{2+}
OP11FeR	20.3	0/1/1	1/3	Fe^{3+}
POP143FeR1	9.7	1/4/3	1/3	Fe^{3+}
POP143FeR2	9.7	1/4/3	1/6	Fe^{3+}
POP143FeR3	9.3	1/4/3	1/9	Fe^{3+}

Instrumental Analysis

Transmission electron microscopic (TEM) measurement was carried on JEOL JEM-200CX. The compositions for the ultrafine powders were obtained by use LINK-860-II model energy disperse X-ray spectrometer (EDS). Electron spectroscopy for chemical analysis (ESCA) spectra were obtained by using a VG Scientific LTD model ESCA LAB MK-II spectrometer.

Results and Discussion

It has been proved that the interaction was achieved by blending the base polyurethanes with metal salts (10). This interaction existed between the

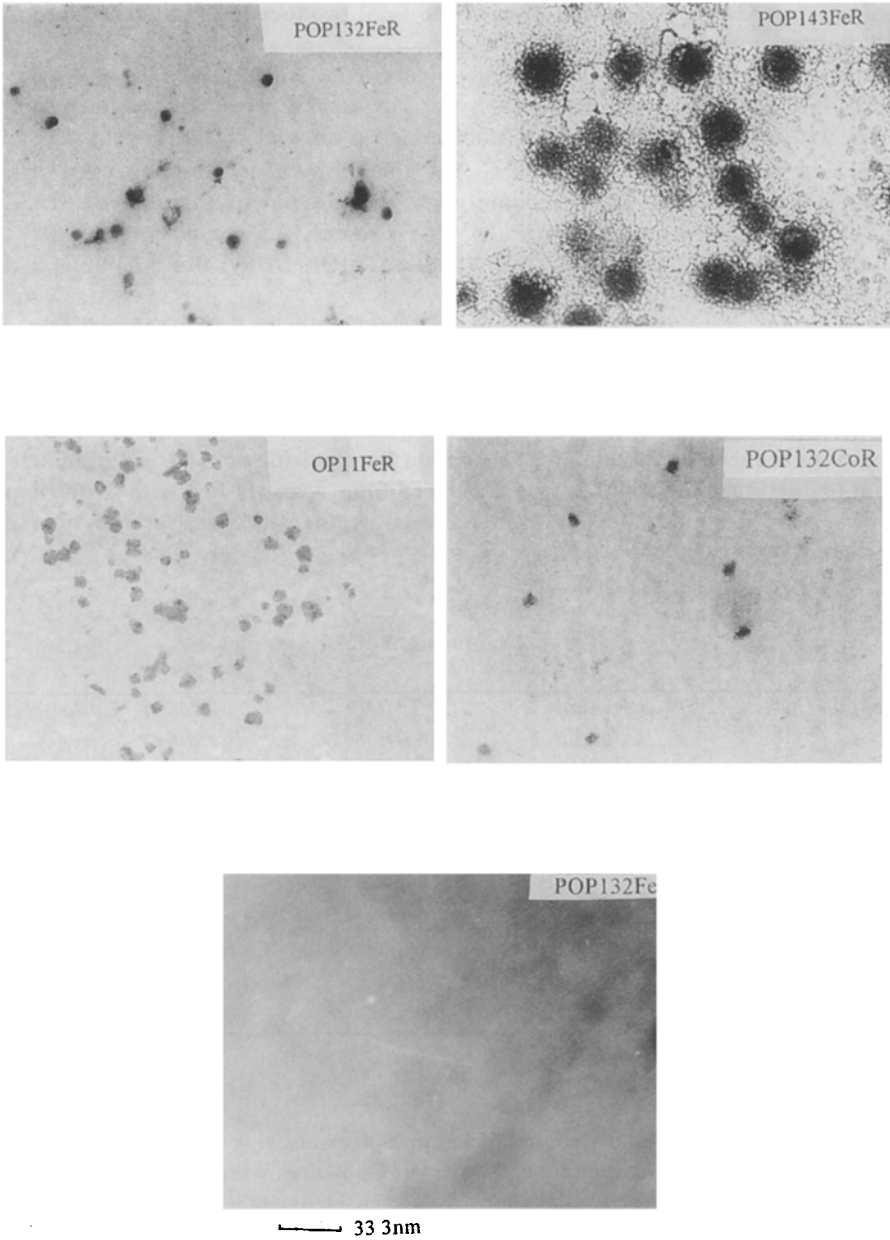


Fig.1. Transmission Electron Microscope Photographs of Polyurethane Films

pendent pyridine group and metal ions in the hard segments and increased hard domain cohesion. In addition, the metal ions were believed to aggregate together forming a nanomicrostructure because of the electrostatic or dipole-dipole interactions[6]. Those metal ion aggregates which have been named as ionic clusters, were difficult to be characterized, owing to their vary small size scale involved. On the other hand, they had a further aggregate tendency to reduce the energy associated with the high ratio of surface area to volume. By use of polymer matrix, it is possible to isolate and stabilize these metal ion clusters. The hard segments in the samples exhibited an interconnected hard domain or a continuous phase since the weight percentage of hard segment is 54% or more (9). No microstructure was found in these coordination polyurethane films under TEM before any chemical treatment. Upon reduction, the metal atoms in the local structure aggregated to form the ultrafine metal particles and could be observed easily by TEM (Fig.1). The size of these metal particles ranged from 10-100nm which was larger than that of the ionic clusters (6), showing there were some cluster-cluster aggregation during the chemical reduction proceeding. Energy disperse X-ray spectrometer (EDS) connected with TEM proved that the dispersed particles were metal aggregates (Fig. 2).

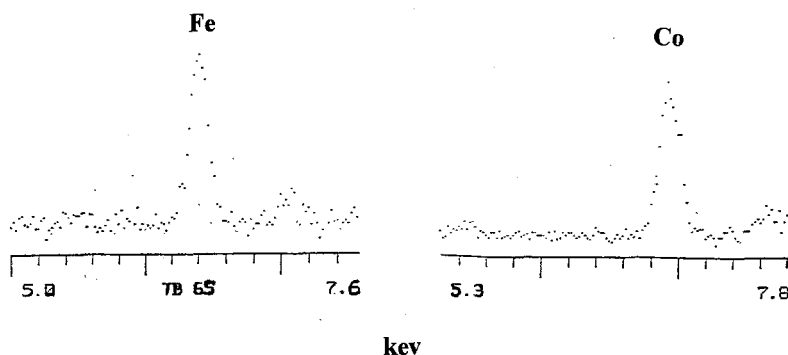


Fig.2 EDS traces of the samples based on Fe and Co

Furthermore, ESCA was used to characterize the valence of the metals. For POP132NiR(Fig.3) the electron binding energies of Ni 2p_{3/2} is 853.3ev which was lower than that of the POP132Ni and both of the two shake up bands near Ni 2p_{3/2} and Ni2p_{1/2} disappeared after reduction. These features showed that Ni²⁺ have been reduced to metallic Ni atoms in the film as indicated. After 15 days, some Ni atoms on the surface of the film were oxidized by air. However as the surface of this sample was peeled off with argon ion beams, it was found that the Ni ions in the bulk were not oxidized because of the protective effect of the polymer cover. The role of the polymer matrix was similar to the protective effect of the nitrogen gas for the ultrafine metal powders.

The study of the size and shape of the metal particles dispersed in polyurethane matrix showed (Fig.1) (Tab.2) that the nature of the metal ions played little effect on the morphology of the powders. However, the shape and size of the

metal particles varied with the concentration of the metal ions in the polymer

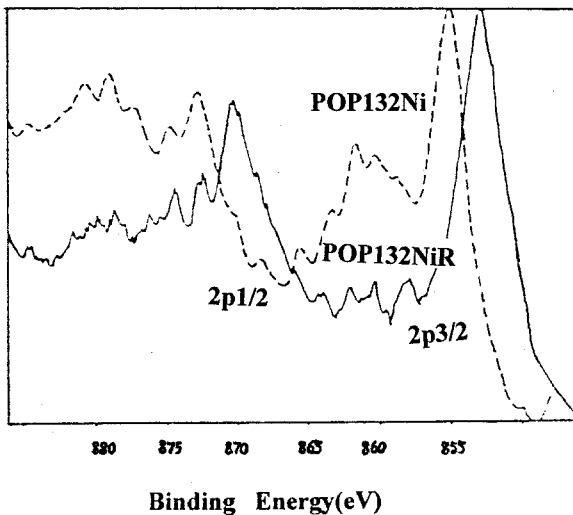


Fig.3 ESCA spectrum of metallized polyurethanes

matrix and the morphology of the base polymers. As the fraction of the hard segment was increased, a more regular lamella morphology was developed (10), thus the metallic powders produced from POP143FeR were larger than the powders in POP132FeR. Apart from the base polymers, the size of the metal particles was also influenced by the concentration of the metal ions. The observation of POP143FeR1, POP143FeR2 and POPFe143R3 showed that the diameter of the metal particles increased with the metal ion content and the shape of these aggregates changed from the polyhedron to a ball.

Tab.2. The size of the particles

<i>Sample Code</i>	<i>Diameter (nm)</i>
POP132FeR	10-30
POP132CoR	10-30
POP132CuR	10-50
POP143FeR1	20-30
POP143FeR2	70-90
POP143FeR3	100-150
OP11FeR	30-60

Electron diffraction patterns proved that the ultrafine metal particles are not in crystal or polycrystal state.

The above discussions focused on the study of the ultrafine metal powders made from the hard segment domain in the multiphase polyurethanes. It is interesting to know if it is possible to produce the ultrafine metal particles from the homopolyurethanes. The TEM observation of OPFeR was shown in Fig.1c. To our surprise, although the iron content in OPFeR was higher than that of POP143R, the size of the powders dispersed in OPFeR which did not possess

polyether soft segment was smaller than that of the powders in POP143FeR indicating that the size of the metal powders did not always increase with the length of the hard segment and the content of the metal ions. The choice of the soft segment also played an important role on the formation of the metal particles. A polar polymer matrix favored to disperse the ionic aggregates and resulted in a smaller metal particle.

Finally it should be noted that the fraction of the metal powders found in the polymer matrix was larger than the concentration of the metal ions in the sample, implying the metal atoms in the aggregates were not tightly compacted and there could be about 5-25% porosity in these powders.

Conclusion

A series complexes of metal chlorides and polyurethanes containing pyridine groups was synthesized. The metal ions in the polyurethane matrix trended to form nanoscale ionic domains. Upon reduction, the metal atoms aggregated to form the ultra-fine metal powders which were proved by TEM EDS and ESCA analysis. TEM observation indicated that the size and shape of these metal powders were affected by the concentration of the metal ion, the morphology of the polyurethanes and the polarity of the polymer matrix. The polymer chains around the metal particles prohibited the final metal particles from the excessive aggregation and oxidation.

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