Synthesis and characterization of poly(butyl acrylate-co-styrene)–silver nanocomposites by γ radiation in W/O microemulsions

Yadong Yin, Xiangling Xu,*† Chuanjun Xia, Xuewu Ge and Zhicheng Zhang

Department of Applied Chemistry, University of Science and Technology of China, Hefei 230026, PR China

Poly(butyl acrylate-co-styrene)–silver nanocomposites were prepared by γ-irradiation of microemulsions and metallic silver nanoparticles of near uniform size were found to be well dispersed in the polymer matrix.

Much attention has been paid to the synthesis and characterization of nanometer metal particle–organic polymer composites, owing to their intriguing optical, electrical and mechanical properties.[1–3] These composites are considered to be highly functional materials, with wide potential application in electromagnetic inference shielding films, non-linear optical materials and the like.

Several methods have been developed to synthesis the composites.[4–6] In general, two steps were needed: firstly, monomer was polymerized in the solutions, with metal ions introduced before or after the polymerization. Secondly, metal ions in the polymer matrix were reduced by a reducing agent or by calcining. Since polymerization and reduction were performed separately metal nanoparticles were not well dispersed in the polymer matrix.

Recently, Zhu *et al.*[7] developed a γ radiation method to prepare polyacrylamide–silver nanocomposites at room temperature. In this method, aqueous soluble monomer and metal salt were mixed homogeneously in aqueous solution. When the system was γ-irradiated, polymerization and reduction took place simultaneously, leading to a homogeneous dispersion of nanocrystalline metal particles in a polymer matrix.

However, in the above method, the compatibility of monomer and metal salt or metal salt aqueous solution was of importance. The application of the method was restricted when the metal salt was insoluble in the monomer or monomer solutions. In addition, the dimension of the metallic nanoparticles was not uniform, and size control was difficult. Furthermore, the polymer–metal nanocomposites were water absorptive, limiting their practical applications.

Here we report a novel method for preparing polymer–metal nanocomposites in microemulsions using γ radiation at room temperature. It was found that products formed by this method contained not only well dispersed but also monodisperse metal nanoparticles.

A W/O microemulsion was produced with Span 80 (sorbitanol monooleate) and SDS (sodium dodecyl sulfate) as emulsifier. The metal salt was dissolved in water before producing the microemulsion, and monomers (styrene or butyl acrylate) were dissolved in toluene. In order to reduce the emulsifier content in the microemulsion, 2-hydroxy-α-methacrylate (HEMA) was used as coemulsifier and comonomer simultaneously.

An aqueous solution containing 8.5 mass% $AgNO_3$ was prepared in advance. 10 g of the solution was then added to a mixture of 48 g toluene, 19 g butylacrylate (BA), 10 g styrene (St), 3 g SDS and 5 g HEMA. Span 80 was titrated into the mixture under stirring until a transparent microemulsion suddenly formed. After bubbling with N_2, the microemulsion was irradiated in the field of a ^{60}Co γ-ray source for 6 h with a radiation dosage of 1.8×10^4 Gy. After irradiation, the brown, semi-transparent microemulsion was de-emulsified by acetone and distilled water. The products were washed with distilled water, dried and ground into powder for further analysis.

The size and morphology of the P(BA-co-St)–silver nanocomposites were investigated by transmission electron microscopy (TEM) (Fig. 1) and X-ray diffraction (XRD) analysis. TEM images were conducted using a Hitachi Model H-800 transmission electron microscope and XRD patterns were recorded by a D_{max} γ_A X-ray diffractometer with graphite-monochromated Cu-Kα radiation (λ = 0.154 178 nm), using an accelerating voltage of 200 kV.

Fig. 2 shows the XRD pattern of the same sample as Fig. 1. The broad peak at $2\theta \approx 19.8°$ is attributed to the diffraction of non-crystalline co-polymer. The other three peaks with 2θ values of 38, 44.5 and 64° correspond to three crystal faces of 111, 200 and 220 of metallic crystalline silver, respectively (cubic system, a = 4.101 Å). The broadening in diffraction peaks shows that the product consisted of small metallic particles. The average size of silver particles estimated by Scherrer's equation[8] is 8.5 nm, which is in good agreement with the TEM result.

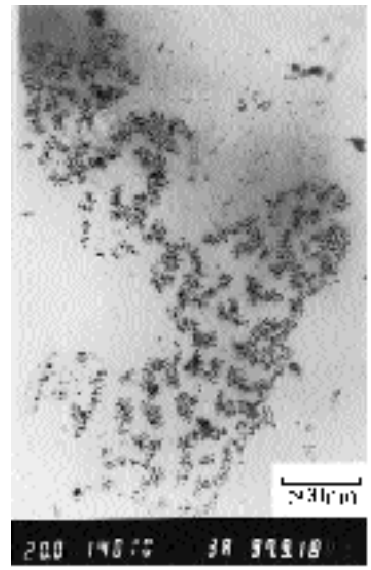

Fig. 1 TEM image of a poly(BA-co-St)–silver nanocomposite prepared by γ-irradiation of a microemulsion. Details in text.

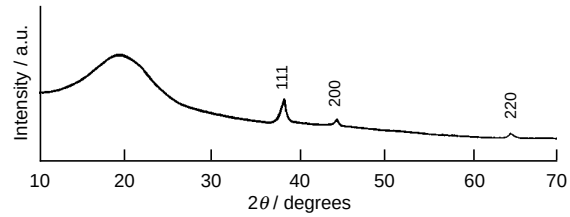

Fig. 2 XRD pattern of the same sample as in Fig. 1

In the conventional microemulsion method,[9,10] the metal salt was dissolved in one microemulsion system, and the reducing agent dissolved in another, in advance. When these two microemulsions were mixed together, only through interaction of two types of droplets could the metal ions be reduced to form metal clusters. However, control of particle size and distribution was difficult.

Another advantage of the new method is that polymerization of monomer and reduction of metal ions are both achieved by γ-irradiation. Radiolysis of the microemulsion system may produce radicals in the oil and aqueous phase. These radicals may effectively initiate the monomer in oil polymerization. Since the polymerization is a chain process it will be faster than the reduction process. With polymerization, the microemulsion system changes from liquid to viscous liquid, rubber or solid material, depending on the monomer type and the monomer content in the oil phase. The increase of the system's viscosity will certainly restrict water droplet aggregation and favour the synthesis of well-dispersed polymer–metal nanocomposites.

In summary, this novel method not only has all the advantages of the microemulsion and irradiation methods to produce metal nanoparticles, but also makes the process easier to control and gives near monodispersed nanoparticles. Furthermore, it makes it possible to synthesize versatile metal particles–polymer nanocomposites. It has advantages over the method developed in ref. 7, in which the monomer has to be soluble in water, because many more monomers are oil soluble than are water soluble. Moreover the composites prepared using oil soluble monomers have wider application.

Notes and References

† E-mail: xlxu@mail.ach.ustc.edu.cn

1 D. M. Bigg, *Polym. Composites*, 1996, **7**, 125.
2 L. T. Chang and C. C. Yen, *J. Appl. Polym. Sci.*, 1995, **55**, 371.
3 K. Ghosh and S. N. Maiti, *J. Appl. Polym. Sci.*, 1996, **60**, 323.
4 H. Tamai, S. Hamamoto, F. Nishiyama and Hajmeyasuda, *J. Colloid Interface Sci.*, 1995, **171**, 250.
5 C. C. Yen, *J. Appl. Polym. Sci.*, 1996, **60**, 693.
6 Y. Nakao, *J. Colloid Interface Sci.*, 1995, **171**, 386.
7 Y. J. Zhu, Y. T. Qian, X. J. Li and M. W. Zhang, *Chem. Commun.*, 1997, 1081.
8 C. N. J. Wagner and E. N. Aqua, *Adv. X-Ray Anal.*, 1964, **7**, 46.
9 P. Barnickel, A. Wokaum, W. Sager and H. F. Eicke, *J. Colloid Interface Sci.*, 1992, **148**, 80.
10 I. Lisiecki and M. P. Pileni, *J. Am. Chem. Soc.*, 1993, **115**, 3887.

Received in Cambridge, UK, 26th January 1998; 8/00676H