Development of a Novel Polymer–Metal Nanocomposite Obtained Through the Route of *In Situ* Reduction for Integral Capacitor Application

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ABSTRACT: Metal nanoparticles exhibit a number of interesting characteristics, including unique physical, chemical, optical, magnetic, and electric properties. Numerous investigations have exploited their properties in a readily usable form by incorporating them into polymers. The current focus of interest is the behavior of such polymer nanocomposites near the percolation loading levels of the metal nanoparticles. This material is particularly suitable for the new integral passive technology. Discrete capacitors are used in many applications, such as noise suppression, filtering, tuning, decoupling, bypassing, termination, and frequency determination, and they occupy a substantial amount of surface area on a substrate. Thus there are limitations in the number of capacitors that can be placed around the chip. Integral passive components are gradually replacing discrete components because of the inherent advantages of improved electrical performance, increased real estate on the printed wiring board, miniaturization of interconnect distance, reduced processing costs, and efficient electronics packaging. For integral capacitors, polymer composite material has emerged as a potential candidate because it meets the requirements of low processing temperature and reasonably high dielectric constant. Yang and Wong, whose patent was filed in 2001, demonstrated novel integral passive component materials with extraordinarily high dielectric constants ($K > 1000$) and high reliability performance. These materials are characterized by high dielectric constant based on the mechanism of interfacial polarization, although they need precision filler concentration control. The current study overcomes this drawback and produces the composite through an *in situ* reduction in an epoxy matrix. Material characterization was done through TEM, SEM, X-ray analysis, and energy-dispersive analysis for X rays. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1531–1538, 2004

Key words: nanocomposites; dielectric properties; integral passive technology; TEM; *in situ* reduction

INTRODUCTION

Nanoparticles exhibit a number of quantum-size effects that determine specific electrophysical performance.[1] Nanoscale metal particles, for example, exhibit an enhancement of some properties, including magnetic and optical polarizability,[2] Raman scattering,[3] and chemical reactivity.[4] In addition, nanocomposites in a readily processable form can be made with the incorporation of nanoparticles into polymers.[5–7] Polymeric matrices prevent both oxidation and coalescence of the nanoparticles and thereby help in long-time stability in the composites. It is known that the uniqueness of polymer-based nanocomposites, compared with other nanosize objects, lies in the influence of the matrix resin on composites' performance and matrix–nanoparticle interaction. Another distinctive feature of these systems is the cooperative behavior of interacting particles in the case of highly filled composites, which becomes observable at the so-called percolation threshold where certain continuous structures of fillers are formed.[8] The classic percolation theory or the nearest-neighbor model assumes a statistical distribution of the discontinuous phase in a continuous matrix. Usually decreasing filler size leads to a decreased percolation threshold because interparticle contacts increase with an increase in the amount of the particles.[9]

Most studies to date have focused on the characterization of such polymer composites. Although there has been some earlier work on incorporation of silver nanoparticles in an epoxy matrix,[10] the present study considers an *in situ* reduction approach. This study was conducted to explore possible use in embedded capacitor applications. The current trend in consumer applications is smaller, lighter, and cheaper products, and thus embedded passives have gradually been replacing discrete passives because of the inherent advantages of improved electrical performance, increased real estate on the printed wiring board (PWB), miniaturization of interconnect distance, reduced processing costs, and efficient electronics packaging. For integral capacitors, polymer composite material has emerged as a potential candidate because it meets the requirements of low processing temperature and rea-
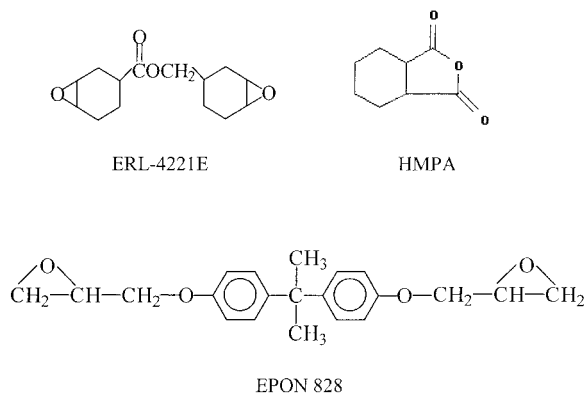
Figure 1 Epoxy resins and anhydride hardener used in this study.

sonably high dielectric constant. Yang and Wong (U.S. Patent filed 4/29/2001) demonstrated novel integral passive component materials with tremendously high dielectric constant ($K > 1000$) and high reliability performance. These materials have high dielectric constant based on the interfacial polarization mechanism, although they need precision filler concentration control. The current study overcomes this drawback by producing an epoxy–silver nanocomposite through an *in situ* nucleation approach. Reduction of metal salt is carried out in an epoxy matrix using a reducing agent. Characterization is performed to optimize the conditions for reproducible results.

EXPERIMENTAL

MATERIALS

Two types of epoxy resins were used in this study: bisphenol-A–type epoxy resin (EPON 828 from Shell

Chemicals, Houston, TX) and cycloaliphatic epoxy resin (ERL 4221E from Union Carbide, subsidiary of The Dow Chemical Co., Midland, MI). These two types of epoxy resins are commonly used in the field of underfill applications because of their low viscosity and low ion contamination. The epoxy equivalent weight (EEW) of ERL 4221 was 134 g/mol, and the EEWs of EPON 8281 and EPON 828 are 187 and 188 g/mol, respectively. The curing agent used in this study was hexahydro-4-methylphthalic anhydride (HMPA; Aldrich Chemical Co., Milwaukee, WI). The molecular weight of HMPA was 168.2 g/mol and its purity was more than 97%. The chemical structures of the epoxy resins in study and HMPA are shown in Figure 1.

Catalysts or accelerators that were chosen in this case were imidazole (2E4MZ-CN) and dimethylbenzylamine (DMBA) because, from earlier studies, it was found that the curing peak temperatures are around 150°C. The current approach is by chemical reduction, specifically, reduction of silver nitrate with hydroquinone. Acetonitrile was the solvent of choice because of its low boiling point (82°C) and because it can dissolve all the components.

In situ formation of metal nanoparticles in an epoxy matrix

Figure 2 shows the schematic of the formulation procedure. The basic procedure is as follows: epoxy resin and a hardener (HMPA), if added, were mixed in a 1:1 weight ratio in acetonitrile solvent using magnetic stirring. Then the reducing agent was dissolved in a weight equivalent to 1.2 times the stoichiometric requirement (each mole of silver nitrate requires a half mole of hydroquinone for reduction). Finally, silver
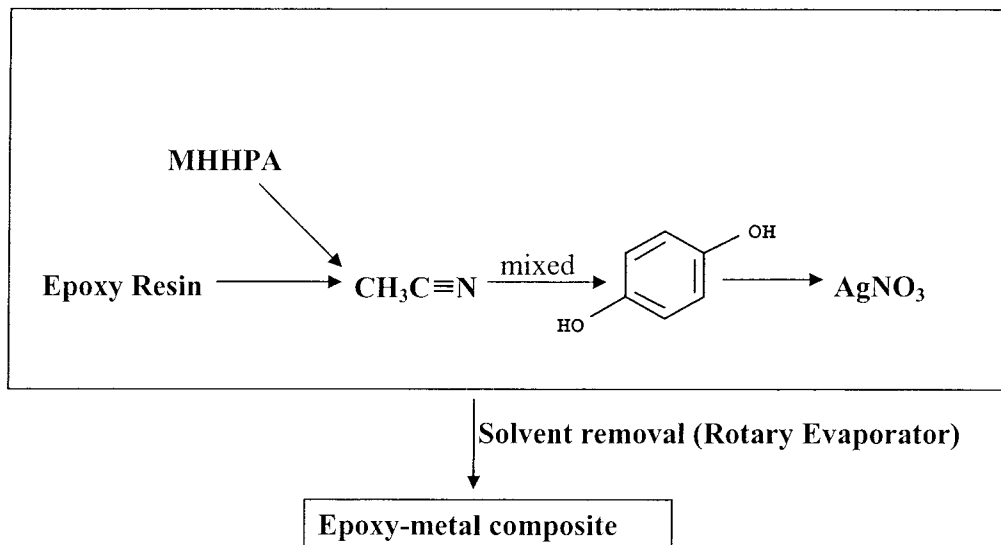

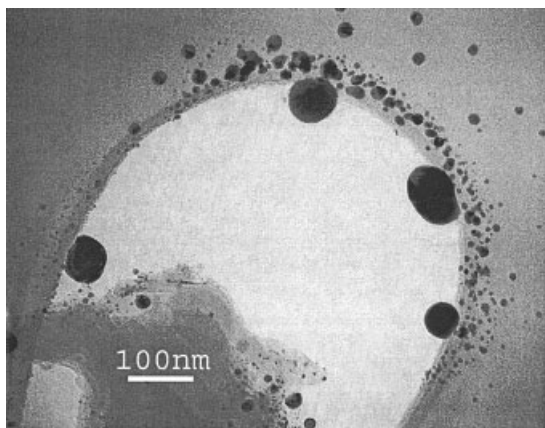**Figure 2** Schematic of the preparation of the polymer–metal composite.

Figure 3 Silver nanoparticles as formed by reduction of silver nitrate by hydroquinone in acetonitrile medium as it was evaporated.

Figure 5 Silver particles as formed *in situ* in EPON 828 polymer matrix in the presence of HMPA (30 phr silver nitrate with respect to epoxy).

nitrate was dissolved in a ratio measured with respect to the amount of epoxy used. If any other protecting agent or modifier is used, it is added before the silver nitrate addition step (final step). The formulation was mixed at each step using magnetic stirring. After this the solvent was evaporated for 30 min using a rotary evaporator while the water bath beneath was maintained at 40°C. At this point the formulation is free of solvent, and after being allowed to return to room temperature the catalyst is finally added.

All the formulations were stored in a freezer at −40°C after preparation. Before any characterization, the stored formulation was allowed to warm to room temperature.

Characterization

A JEOL 100C transmission electron microscope (TEM; JEOL, Tokyo, Japan) was used for observing the morphology of nanoparticles. Scanning electron microscopy was performed using a Hitachi S800 FEG scanning electron microscope (Hitachi, Osaka, Japan) to observe the size of nanoparticles in cured samples.
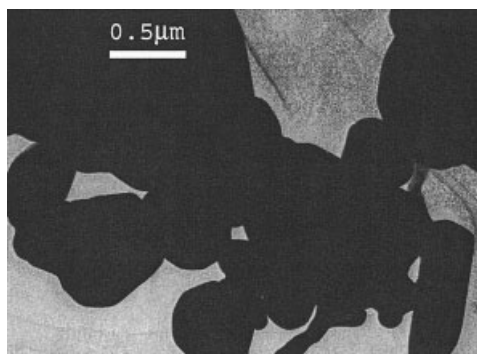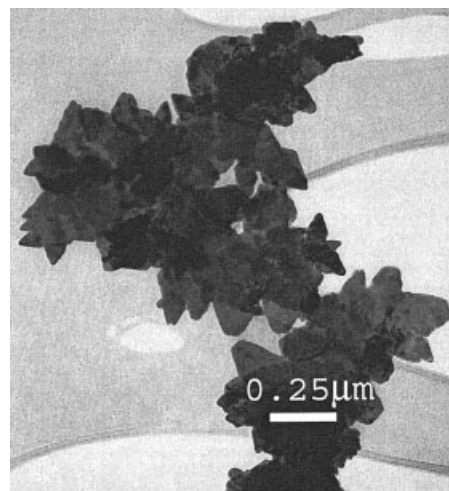
EDAX (energy-dispersive analysis for X rays) was used to confirm the presence of metal (attached to a Hitachi S800 SEM). A Philips (The Netherlands) automated powder diffractometer (PW 1800) was used for X-ray analysis. X-ray diffraction (XRD) was used to confirm the metallic phase and to confirm the size of particles by the Scherrer method.

RESULTS AND DISCUSSION

Reduction in the solvent medium

The metal precursor and the reducing agent are the only components mixed into the solvent. The solvent was evaporated at a temperature of 40°C in the rotary evaporator in all the studies that follow unless otherwise specified. The residue was observed in TEM by dispersing a small amount in the solvent. Figure 3 shows the silver nanoparticles so obtained. As can be seen there are few particles in the 50-nm range, some in the 20-nm range, and more particles in the 5-nm range. It can be speculated that the larger particles are
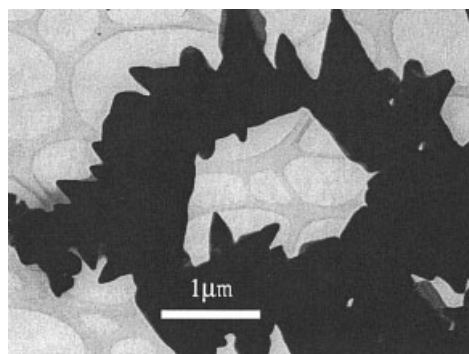

Figure 4 Silver nanoparticles as formed in an EPON 828 epoxy matrix (30 phr silver nitrate with respect to epoxy).

Figure 6 Silver particles as formed *in situ* in EPON 828 polymer matrix in the presence of imidazole catalyst.
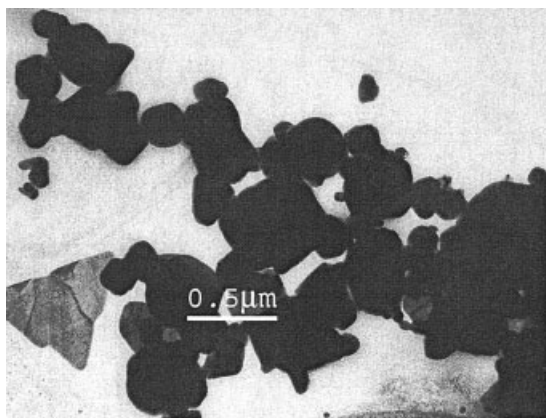
Figure 7 Silver nanoparticles as formed *in situ* in ERL 4221E epoxy matrix (30 phr silver nitrate with respect to epoxy).

those that formed in the beginning of the evaporation process, whereas the smaller ones are those nucleated toward the end of the evaporation process. The particle shape is mostly spherical, so hydroquinone was obtain lower particle sizes in the tens of nanometers. Further work would focus on how the presence of some components would affect this reduction process and the particle sizes obtained.

Reduction in the presence of epoxy EPON 828

The following study focuses on the effect of the presence of the bis-A–type epoxy resin EPON 828 and other components like hardener and catalyst during the reduction process.

Figure 4 shows the silver nanoparticles formed in the EPON 828 matrix in the absence of any other additives. As can be observed the particles are relatively large, in the micron range, and smaller particles
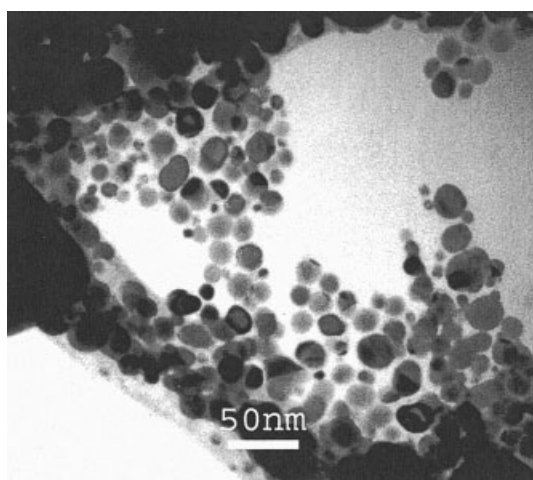

Figure 8 Silver nanoparticles as formed *in situ* in ERL 4221E epoxy matrix in the presence of the hardener HMPA (30 phr silver nitrate with respect to epoxy).
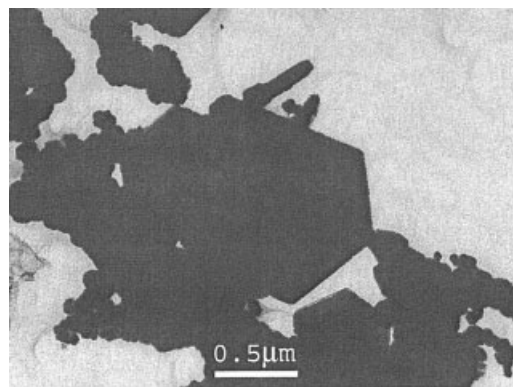

Figure 9 Silver nanoparticles as formed *in situ* in ERL 4221E epoxy matrix in the presence of DMBA catalyst (30 phr silver nitrate with respect to epoxy).

are in the range 0.5 μm, which shows that the epoxy matrix is not a good enough stabilizer, probably because there is no interaction between the silver ions and the epoxy chains. Further work would focus on the use of additives that would interact with the silver ions and so control the nucleation and growth processes.

Figure 5 shows silver nanoparticles as formed in an EPON 828 matrix in the presence of HMPA hardener. As can be seen the particles are smaller in size than those in the previous case, probably because of the interaction of the carboxylate groups with silver ions. The particles, in the 100–200 nm range, are faceted but seem to agglomerate. So from this sample it can be said that the presence of an additive that interacts with silver ions is beneficial because it stabilizes the silver ions and atoms thus formed.

Figure 6 shows silver nanoparticles formed in the EPON 828 matrix in the presence of imidazole catalyst. The particles are still faceted but there is extensive connectivity between the particles. The particles are still in a similar size range, although slightly on the higher side.
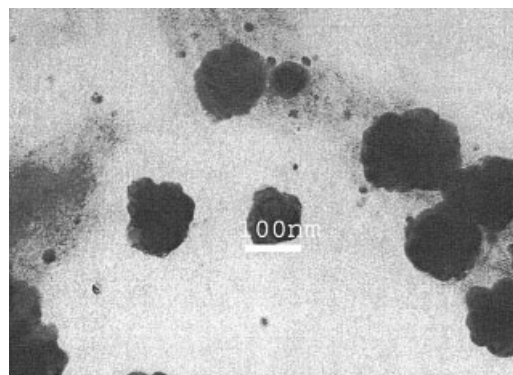

Figure 10 Silver nanoparticles as formed *in situ* in ERL 4221E epoxy matrix in the presence of the hardener HMPA and DMBA catalyst (30 phr silver nitrate with respect to epoxy).
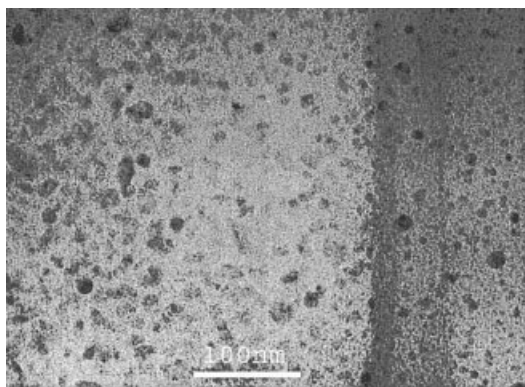
Figure 11 Silver nanoparticles as formed *in situ* in ERL 4221E epoxy matrix in the presence of the hardener HMPA (20 phr silver nitrate with respect to epoxy).

Figure 13 Silver nanoparticles as formed *in situ* in ERL 4221E epoxy matrix in the presence of the hardener HMPA (70 phr silver nitrate with respect to epoxy).
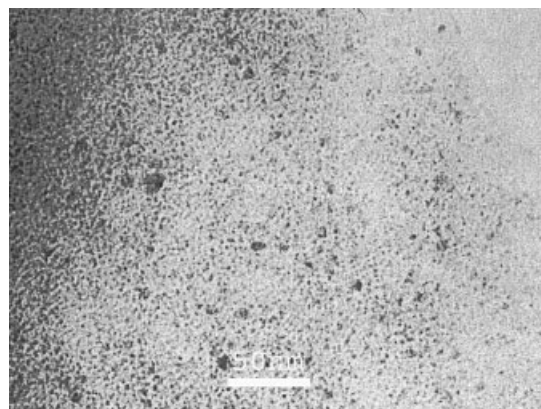
Reduction in the presence of epoxy ERL 4221E

The following studies focus on using a different epoxy, ERL 4221E, which is a cycloaliphatic epoxy with a carboxylate group that might affect the particle size. The same set of studies as for the EPON 828 was conducted and the results are compared.

Figure 7 shows the silver particles as formed in the ERL 4221E epoxy matrix, which seem to be smaller on average compared to those in EPON 828. The larger particles are in the 0.5-μm range, whereas the smaller ones are in the 100- to 200-nm range. It can thus be observed at this stage that if the epoxy matrix has groups that interact with the silver ions it has some beneficial effect with respect to the final particle size. Other additives were added to determine their effect.

Figure 8 shows silver particles as formed in the ERL 4221E matrix in the presence of the hardener HMPA. The particles are mostly in the 20-nm range and some particles are in the 10-nm range; thus the cumulative effect of HMPA and ERL 4221E seems to have a substantial effect on the particle sizes obtained. Both HMPA and ERL 4221E have carboxylate groups and

they seem to coordinate very favorably with silver ions.

Figure 9 shows silver particles as formed in the ERL 4221E matrix in the presence of the catalyst DMBA. Some large faceted particles can be observed, whereas the others are agglomerates of smaller 50-nm size particles. Amine groups in the curing agent might coordinate with silver ions and lead to agglomeration.

Figure 10 shows silver nanoparticles formed in the ERL 4221E matrix in the presence of both hardener and catalyst. There are large particles in the 100-nm range and small particles in the 20-nm range. Evidently, the amine groups have some strong coordination effect that leads to larger particle sizes. The smaller particles evidently show that the amount of amine used was insufficient to overcome the combined effect of ERL 4221E and HMPA.

In conclusion to this section it can be said that the optimum formulation among those considered is the ERL 4221E resin along with HMPA hardener mixed with the metal precursor and the reducing agent during the reduction process. Further work would focus
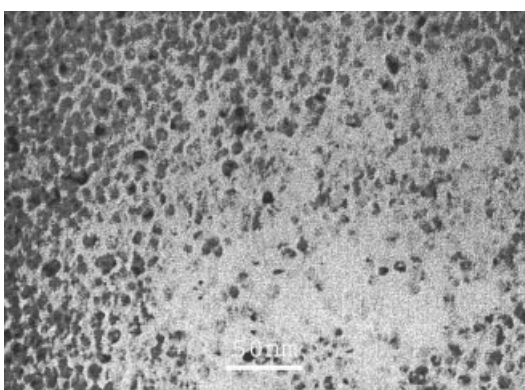

Figure 12 Silver nanoparticles as formed *in situ* in ERL 4221E epoxy matrix in the presence of the hardener HMPA (30 phr silver nitrate with respect to epoxy).

Figure 14 Silver nanoparticles as formed *in situ* in ERL 4221E epoxy matrix in the presence of the hardener HMPA (80 phr silver nitrate with respect to epoxy).
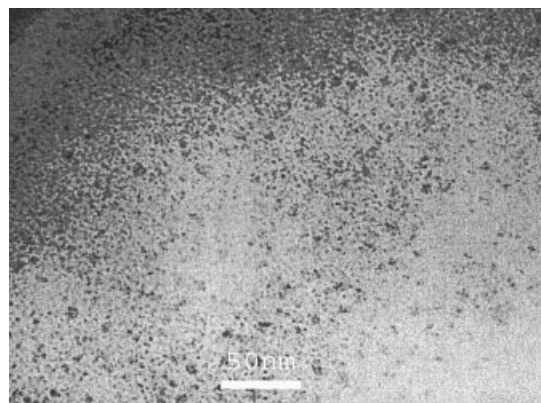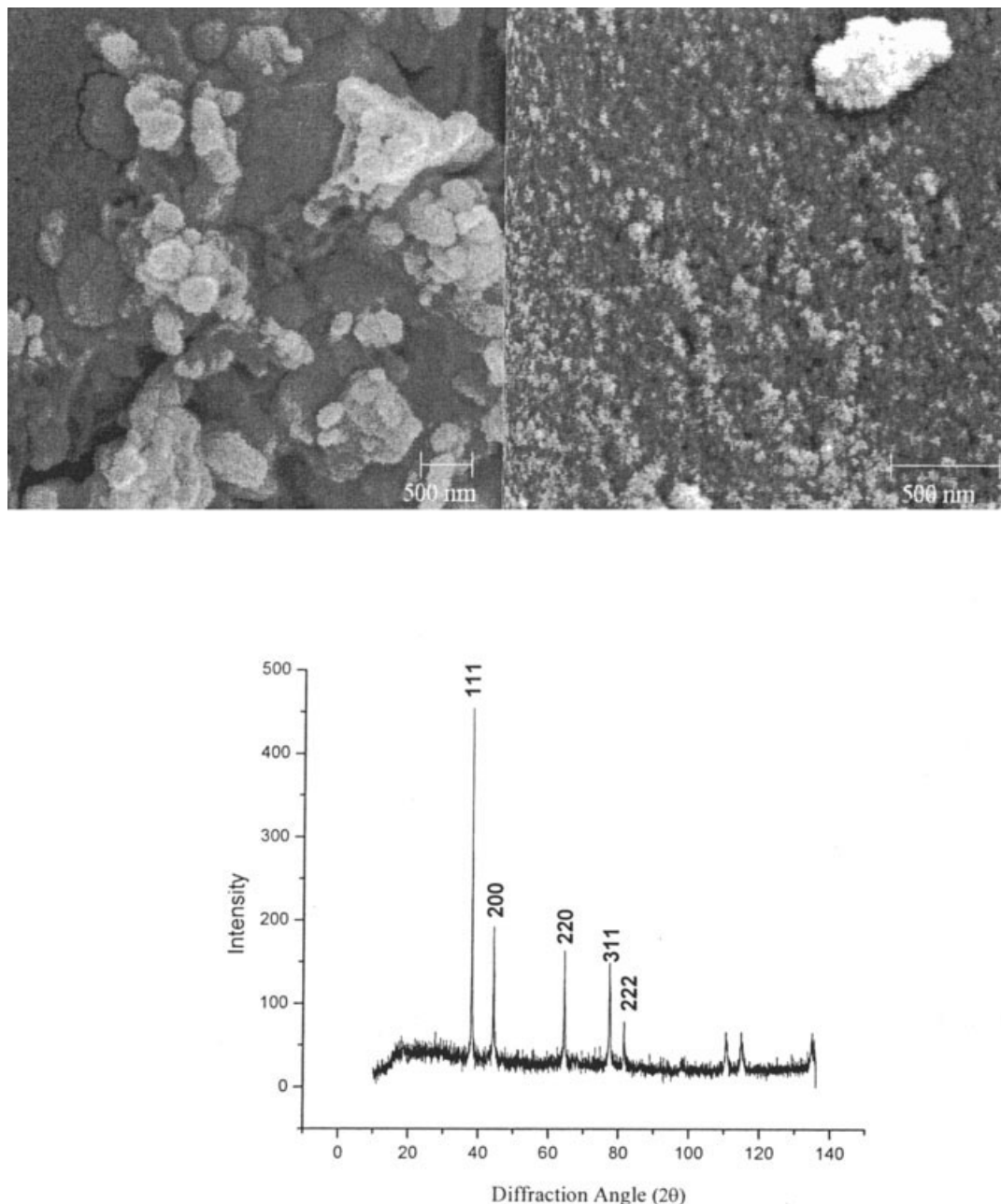
Figure 15 SEM images and XRD pattern showing the presence of silver nanoparticles in ERL 4221E epoxy matrix (originally HMPA and catalyst were absent during the course of the reduction reaction). Average particle size = 39 nm from XRD.

on only this system. Epoxy resin and the HMPA were mixed in the solvent acetonitrile using magnetic stirring. Hydroquinone was then added and mixed in 1.2 times the stoichiometric amount required with respect to silver nitrate. Finally, silver nitrate was mixed in a chosen ratio with respect to the amount of epoxy used. The following studies focus on variation of other parameters, like the temperature and amount of precursor, to observe the effect on the final particle size.

Effect of changing the silver nitrate concentration

The amount of silver nitrate present in the initial formulation can have an effect on the size of the particles so obtained. A study to find this influence was performed for a loading ranging from 10 to 80 phr silver nitrate. The TEM images for a few of these formulations are shown in Figures 11–14.

As can be seen the particle sizes are in two ranges, 20 and 4 nm. As stated earlier this might be attributed to the fact that the particles initially formed might be larger in size because the diffusion effects might be greater. The smaller particles may be formed toward the end of the process when the diffusion effects are weak. Also it can be seen that as the loading increases the fraction of the smaller particles seems to be greater. This supports the earlier statement by the fact that a greater degree of reduction occurs after the
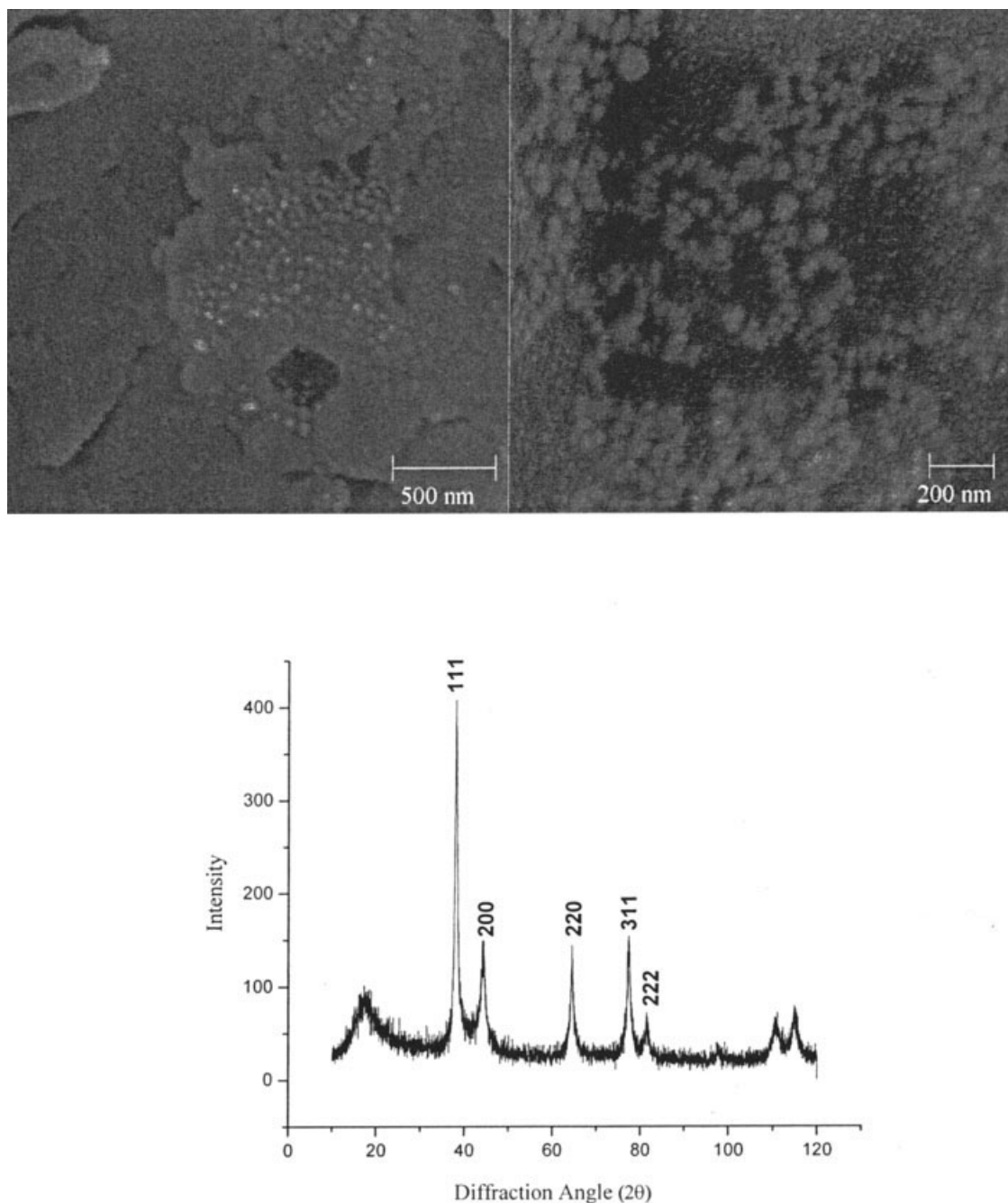
Figure 16 SEM images and XRD pattern showing the presence of silver nanoparticles in ERL 4221E epoxy matrix (HMPA was present during the course of the reduction reaction). Average particle size = 13 nm from XRD.

solvent evaporation than before. Thus there are more of the smaller particles in the case of higher loading level formulations.

Effect of curing on the nanoparticles

To use a polymer composite for any application it must be cured beforehand. The curing process involves heating to temperatures of 150°C for a period of around 1 h, so this temperature might cause the particles to agglomerate, thus changing the particle size. For this reason, the samples' cross section and surface were observed after curing with SEM. XRD was performed on the cured sample and the particle size was calculated according to the Scherrer formula. The results show similar particle sizes as from TEM. The very small particles that can be seen in Figures 15 and 16 are the particles in the 20-nm range, so curing does not actually affect the nanoparticle size and the nanoparticles are well protected by the epoxy resin and the hardener, respectively, during the curing process.

The particle sizes calculated from XRD also show a size difference when HMPA hardener was present during reduction. From an average size of 39 nm for the sample made in the absence of hardener during reduction, the average size in the presence of hardener was nearly 13 nm. This again confirms the fact that the hardener together with the epoxy resin have a substantial effect on the particle stability, during both formation and curing.

CONCLUSIONS

A polymer–metal composite was successfully produced by the route of *in situ* reduction. The various additives present in the formulation have a substantial effect on the final properties of the composite. Compounds like HMPA that have a carboxylate group to coordinate with silver ions and epoxy resins, which also can interact with silver ions, were found to be beneficial. The temperature of reaction had a strong influence on the particle sizes obtained. The amount of silver nitrate in the initial formulation had no effect on the particle sizes obtained. The optimum particle sizes obtained were particles in the 20- and 4-nm range for a formulation having HMPA during the course of the reaction in ERL 4221E epoxy matrix. The curing of the composite does not seem to affect the particle sizes, as observed from SEM. The epoxy matrix and HMPA act as good stabilizers for the nanoparticles so obtained. The XRD results show that the phase is indeed silver and the average particle sizes obtained from the Scherrer formula matched with those observed through TEM. Further work would focus on characterizing the dielectric properties and optimizing the dielectric constant near the percolation threshold.

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