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# Synthesis of silver nanoparticles and their self-organization behavior in epoxy resin

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## Abstract

Silver nanoparticles were chemically synthesized by means of microemulsions techniques. Their self-organization behavior, including detailed description of the mechanism, the process and the resultant structure changes, was investigated by examining the electrically conductive characteristics of silver nanoparticles/solvent suspension, silver nanoparticles/epoxy resin mixture and its cured version, respectively. For silver nanoparticles suspension, higher particle concentration was found to be unfavorable to the formation of conducting paths owing to particles aggregation. For silver/epoxy mixture, transition-like changes in conductivity as a function of temperature were observed, manifesting two-stage self-organization of the nanoparticles: one related to the formation of some texture and the other related to melting and growth of the particles. As a result, conductive networks can be established by freezing the nanoparticles aggregation at the first stage under a particle loading even lower than the percolation threshold estimated conventionally. Accordingly, curing reaction of epoxy resin should be so designed as to adequately match the self-organization process. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* Silver nanoparticles; Epoxy resin; Self-organization

## 1. Introduction

Nanoparticles are provided with a number of quantum-size effects that determine specific electrophysical performance [1]. Nano-scale 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]. Preventing from both oxidation and coalescence by polymeric matrices, nanoparticles possess long-time stability in the composites. It is known that the peculiarity of polymer based nanocomposites in comparison with other nano-size objects lies in the influence of matrix resin on composites performance and matrix/nanoparticles 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 a rise in the amount of the particles [9]. It should be mentioned, nevertheless, that the distribution of nanoparticles in polymer matrix is not completely random. Synthesis induced ordering of particle's location and aggregation often take place. The high energy input necessary for preparing multiphase polymer systems pushes these systems far from thermodynamic equilibrium. A self-organization process may occur in the form of structural change or of phase transition at a supercritical value, where the energy input and the entropy export are so far above their critical values [10].

However, the self-organization behavior of nanoparticles, which might result in significant changes in properties of nanocomposites, have not been studied in detail yet with respect to either the mechanism involved or the structural characteristics. At present, most investigations focus on the description of the structure formed in heterogeneous polymer systems and the sudden changes in structure and properties resulting from the specific composition and manufacturing histories, while the self-organization process, including the critical composition and synthesis conditions, has not been understood. Therefore, the present work aims at a careful description of the self-organization process of silver nanoparticles in epoxy resin and the

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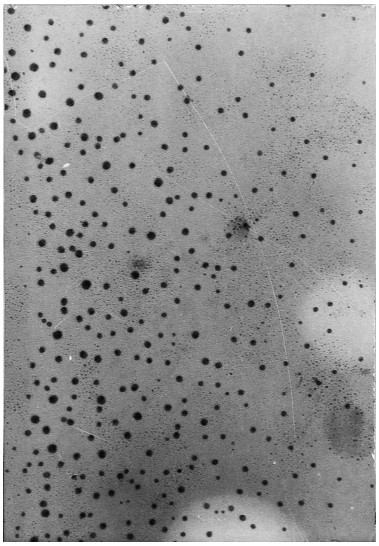

Fig. 1. Typical TEM micrographs of uncapped Ag particles prepared by reduction in microemulsion with $r_w = 0.6$ (magnification: $6 \times 10^4$).

resultant structure by means of an examination of the electrically conductive behavior of the composite systems basing on the possible relationship between the structure formed through self-organization and the conduction performance. The interaction between silver particles and matrix is elucidated through curing kinetics investigation. For the convenience of discussion, different dispersing matrices are used successively in this order of priorities: solvent, epoxy resin without curing agent and epoxy resin with curing agent. Each of the former system is relatively simpler than the latter and thus allows itself to serve as a reference for the latter.

## 2. Experimental

### 2.1. Synthesis of silver nanoparticles

Chemical synthesis of silver nanoparticles were carried out by reduction of aqueous silver salt solution in a W/O microemulsion [11,12]. The aqueous silver salt micelles in cyclohexane were stabilized by the non-ionic surfactant and the same micelles of $NaBH_4$ solution were used for the reduction, keeping identical droplet size and concentration in both sets. The salt concentration in the aqueous phase were 0.1 M in $AgNO_3$ and 0.05 M in $NaBH_4$, respectively, and the molar ratio of reductant to silver ions is held constant for all experiments, i.e. $[H^{-1}]/[Ag^{+}] = 2$. Colloidal silver particles were prepared by mixing two sets of W/O microemulsion under thorough stirring for 30 min at room temperature (RT). After a few days the particles were precipitated from the solution and then isolated by centrifugation. To achieve different sizes of colloidal particles, a group of samples were prepared by changing the weight ratio of water to surfactant ($r_w$) at a constant weight fraction $c_w$ of the samples ($c_w = (w_w + w_s)/(w_w + w_s + w_o)$, where $w_w$, $w_s$ and $w_o$ denote the weight fraction of water, surfactant and oil, respectively). The surfactant and other residual materials were then removed by threefold washing with acetone and by recentrifugation of the solution.

Materials were used as their commercially available purity. The cyclohexane was supplied by Guangdong Shantou Xinning Chemical Co. The surfactant, polyoxyethylene nonyl phenyl ether (OP-10), was a product of Shanghai Xiangde Fine Chemical Engineering Co. Dodecanethiol was provided by Guangzhou Chemical Solvent and Glass Co. The 1-hexanol, produced by Shanghai Xingzhi Chemical Engineering Co. was used as assistant surfactant (OP-10/$C_6H_{13}OH = 2/3$). $AgNO_3$ was provided by Guangzhou Lixin Chemical Co., and $NaBH_4$ was produced from Acros Chemica N. V. (Belgium).

### 2.2. Preparation of silver nanoparticles/solvent suspension and silver nanoparticles/epoxy composites

The prepared silver nanoparticles could be readily redispersed to obtain a homogeneous suspension in chloroform and acetone aided by sonication.

The silver suspension in chloroform were mixed with epoxy resin by stirring and sonication. After evaporation of the solvent at room temperature through vacuum drying process, a viscous mixture was obtained. By using TEOA (triethoxylamine) as curing agent, a solid composite comprised of silver nanoparticles/epoxy can be made through the following curing process: temperature was increased from RT to 100°C at a rate of 5°C/min (step of temperature increasing), and then kept until the system is cured (constant temperature step). Usually 3 h were needed for complete curing. Accompanying the curing process, the resistivities of composites were measured by an electrometer.

### 2.3. Characterization

Transmission electron microscopic (TEM) observation was performed with a HITACHI HU-12 on the sample prepared from cyclohexane dispersion of the particles, which were deposited on copper grid with a carbon film in advance. Ultraviolet (UV)/visible spectra of a suspension ($1.85 \times 10^{-4}$ g particles/ml cyclohexane) were collected by a 756MC UV/visible spectrophotometer from 190 to 900 nm with pure cyclohexane as the reference. Melting points of silver nanoparticles were determined by Perkin–Elmer DSC II differential scanning calorimeter (DSC) and Perkin–Elmer DTA-1700 differential thermal analyzer (DTA) at a heating rate of 10°C/min, respectively. Curing kinetics of epoxy based composites was also monitored by the earlier Perkin–Elmer DSC II at heating rates of 5°C/min, 10°C/min and 15°C/min. Wide angle X-ray scattering (WAXS) spectra of the nanoparticles were obtained by a Rigaku D/max-3A X-ray diffraction unit.

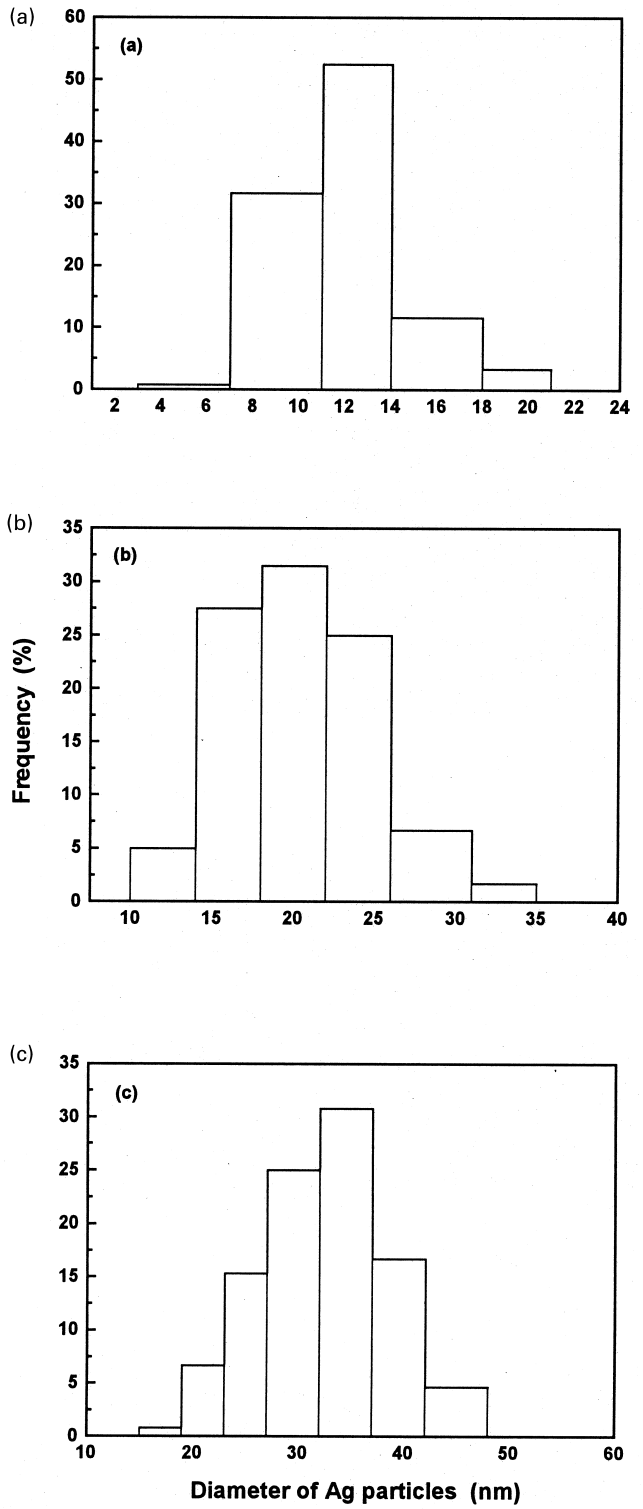

Fig. 2. Uncapped Ag particles diameter distribution determined from TEM observation, (a) $r_w = 0.2$; (b) $r_w = 0.4$; (c) $r_w = 0.6$.

## 3. Results and discussion

### 3.1. Characterization of silver nanoparticles

Direct evidence of uncapped silver particles' morphology, size and size distribution estimated from TEM observation are illustrated in Figs. 1 and 2. Moreover, the mean particle size, $d_{\mathrm{mean}}$, the most probable diameter, $d_{\mathrm{most}}$, as well as the standard derivation, (SD), are calculated accordingly and listed in Table 1. It is seen that both $d_{\mathrm{mean}}$ and $d_{\mathrm{most}}$ increase proportionally to $r_w$, reflecting the size of colloidal silver particles was successfully controlled by varying $r_w$.

UV/visible absorption spectrum of the silver particles shows a peak position, $\lambda_{\mathrm{max}}$, of ca. 400 nm (Fig. 3), which agrees with previous study of nano-scale silver [13,14]. Hereinafter the particles prepared by microemulsion are referred to as primary particles so as to be distinguished from the agglomeration formed in composites.

The measurement by means of DSC gives a melting point of 129°C for Ag nanoparticles (~40 nm), which is much lower than the value of conventional Ag crystal. When the same sample cooled down to RT from 300°C is re-scanned, however, there is no longer endotherm in the range of 40–300°C and a melting peak appears at 953°C. This is indicative of a transformation of nanoparticles into conventional Ag crystal during the first heating process. Further works demonstrated that the nanoparticles of different diameters (~10 and ~20 nm) also have similar melting points at around 129°C for the first heating scan. Thus, the nanoparticles ~40 nm in diameter was randomly chosen to mix with solvent or with epoxy resin for studying the aggregation behavior.

In order to reveal whether particle size is changed after heat treatment at a temperature over the earlier-mentioned melting point of the nanoparticles, WAXS diffractogram of original particles is compared with that of the particles treated at 150°C for 30 min (Table 2). It is surprising that the nanoparticles still fall in the nano-size range after heat treatment. In general, nanoparticle size determined from the full widths at half maximum (FWHM) height of WAXS spectra is ascribed to the nanocrystal [15]. The treated particles reported here should not be nano-size primary particles, but agglomeration consisting of multi-nanocrystals. The existence of nanocrystals in the agglomeration manifests the melting process of primary silver nanoparticles at about 100°C is different from the conventional melting process of metal silver at about 1000°C, and more likely a sintering process.

### 3.2. Electric conductive behavior of Ag nanoparticles/solvent suspension

In general, it is difficult to describe the self-organization of silver particles in polymer matrix owing to the complexity of polymer system, which is far from thermodynamic equilibrium. Prior to a direct investigation, therefore, a simpler alternate should be used. As silver nanoparticles in solvent, by definition, are colloidal, and the electrical conductive behavior of the system can be investigated easily in terms of colloidal theories, study of the suspension of silver nanoparticles/solvent is an ideal starting point.

Table 1
Geometrical description of Ag nanoparticles measured by TEM

| $r_w$ | $d_{mean}$ (nm) | $d_{most}$ (nm) | SD (nm) |
|---|---|---|---|
| 0.2 | 10 | 11 | 12 |
| 0.4 | 20 | 20 | 22 |
| 0.6 | 40 | 32 | 29 |

Table 2
WAXS characterization of silver nanoparticles (~40 nm) as a function of different treatments

| Samples | $2\theta$ (deg) | | FWHM[a] (deg) | | $d$[b] (nm) | |
|---|---|---|---|---|---|---|
| Ag, RT[c] | 38.06 | 44.33 | 0.43 | 0.64 | 19.5 | 13.4 |
| Ag, 150°C[d] | 38.22 | 44.42 | 0.33 | 0.46 | 25.5 | 18.6 |

[a] Full widths at half maximum height.

[b] Particle diameter determined from: $d = k\lambda/\beta\cos\theta$.

[c] Particles before heat treatment.

[d] Particles heat-treated at 150°C for 30 min.

Moreover, silver nanoparticles/solvent suspension is able to serve as a reference for the mixture of nanoparticles/epoxy resin to be studied afterwards, even though the viscosity of polymer is much higher than solvent.

As shown in Fig. 4, resistivity of Ag nanoparticles/solvent suspensions exhibits some degree of conduction only if the concentration of particles gets close to the percolation threshold where the particles start to contact with one another through the aggregation of particles. In the range low concentration to moderate concentration, a drastic decrease in resistivity can be observed accompanying the percolation process, as is often the case of composites incorporated with conductive fillers [9]. However, the anomalous higher resistivity of the suspension at higher loading of particles is not consistent with percolation theory, under the framework of which a further decrease in resistivity is expected as filler loading exceeds the percolation threshold.

Aggregation is a basic feature of a colloidal system [16]. The natural aggregation of nanoparticles results from their higher surface energy and strong interfacial interaction. Moreover, the electrostatic stabilization of Ag nanoparticles arising from the solvent is responsible for deagglomeration of particles. The stabilization, however, is usually a dynamic equilibrium process. Therefore, the random walk model of Brown for micro particles in diluted solutions can be adopted to mimic the aggregation process of the present silver nanoparticles in suspension. This aggregation accounts for the construction of conductive networks. It can also be deduced that the lower resistivity of Ag/chloroform system than Ag/acetone results from their stronger electrostatic interaction which facilitates the dynamic equilibrium of particles in solvent and the formation of conductive networks by random walk as well.

At higher concentration of nanoparticles, however, the electrostatic stabilization of Ag nanoparticles arising from the solvent is not enough to keep the primary particles suspended in the solvent as the case at lower concentration. The increasing probability of aggregation leads to the formation of agglomerates characterized by larger size and lower specific surface area as compared with primary particles or aggregate. A new dynamic equilibrium will be established according to the interaction between the agglomerates of silver particles and solvent, but the conductive networks have to be less efficient, resulting in higher resistivity of the system. This behavior is related to the aggregating of primary particles, namely self-organization process, which can not be predicted by the percolation theory as discussed in the first paragraph of this section.

### 3.3. Self-organization behavior of silver nanoparticles in epoxy resin

Usually, the curing of epoxy resin is very fast so that it is difficult to study a structural development of particles in the resin. In order to reveal the manner in which the silver nanoparticles construct the conducting paths during curing,

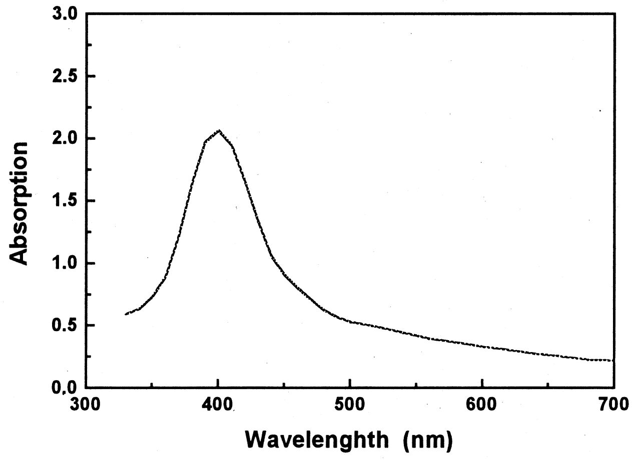

Fig. 3. UV/visible absorption spectrum of silver particles in cyclohexane ($r_w = 0.6$).

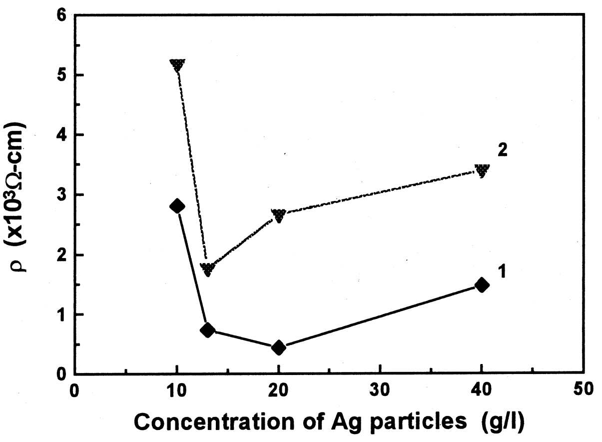

Fig. 4. Dependence of volume resistivity of Ag nanoparticles/solvent suspension on the concentration of particles: 1, chloroform; 2, acetone.

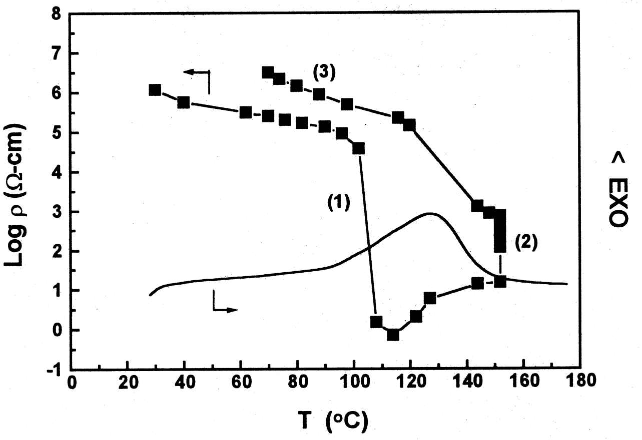

Fig. 5. Temperature dependence of volume resistivity of Ag nanoparticles (20 phr)/epoxy mixture and DSC heating trace of Ag nanoparticles.

the self-organization of particles in epoxy resin without curing agent should be understood in advance, which is the basis for the study of solidified nanocomposites consisting of Ag nanoparticles and epoxy resin.

At an elevated temperature, the viscosity of epoxy resin decreases to a critical level, and hence, similar to the earlier Ag/solvent system, silver primary particles can also be movable in such a highly flowable epoxy resin. Comparing with the Ag particles suspension, however, more complex self-organization process of the particles is expected, because the additional energy input pushes the system far away from the thermodynamic equilibrium.

Resistivity measurement for the Ag particles/epoxy resin mixture without curing agent includes heating and cooling processes in the following sequence (Fig. 5): (1) temperature is raised from RT to 150°C at a heating rate of 5°C/min and, (2) kept there for 10 min, and finally (3) temperature is decreased to RT with the same rate as heating. From Fig. 5, it can be seen that the room temperature resistivity of the system is quite high, which implies that the concentration of particles is below the percolation threshold even though it is much higher than the critical value of Ag nanoparticles/solvent suspension (Fig. 4). This phenomenon can be ascribed to the high viscosity of epoxy resin which prohibits the formation of conductive by means of random walk. With increasing temperature the viscosity of epoxy resin is gradually decreased and the self-organization of nanoparticles can take place, then the conductive behavior begins to be detected like the case of nanoparticles/solvent suspensions. At about 100°C the resistivity of the system has a drastic drop, which corresponds to a structural change or phase transition as a result of self-organization of the primary particles, i.e conductive networks are formed. With a further increase in temperature, there is an increasing tendency of the resistivity. Especially when the system is heated at 150°C for 10 min, the resistivity increases by two orders, implying a continuous destruction of the conductive networks. The DSC trace of these particles is also shown in Fig. 5, from which it can be observed that the destruction of the conductive network is somewhat related with the

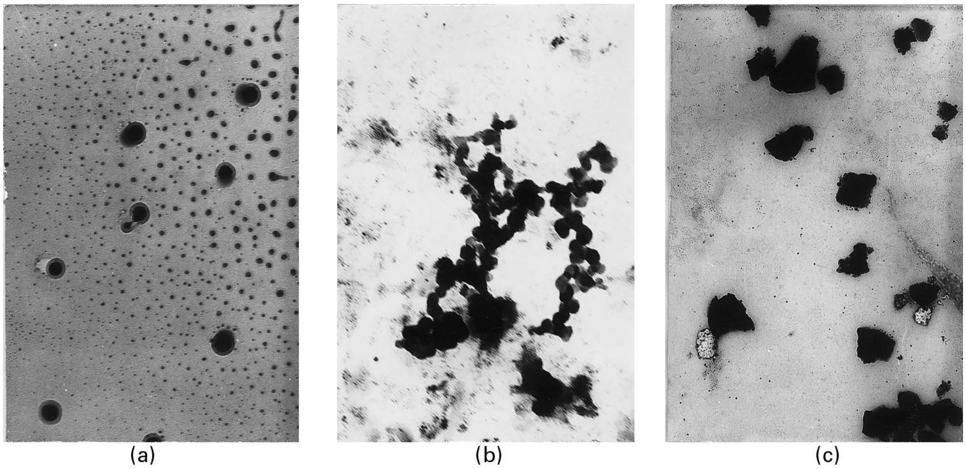
(a) (b) (c)

Fig. 6. TEM micrographs of Ag particles extracted from Ag nanoparticles (20 phr)/epoxy mixture: (a) starting blend at RT (magnification: $6 \times 10^4$); (b) treated at 90°C for a while (magnification: $3 \times 10^4$); (c) treated at 150°C for 10 min (magnification: $2 \times 10^4$).

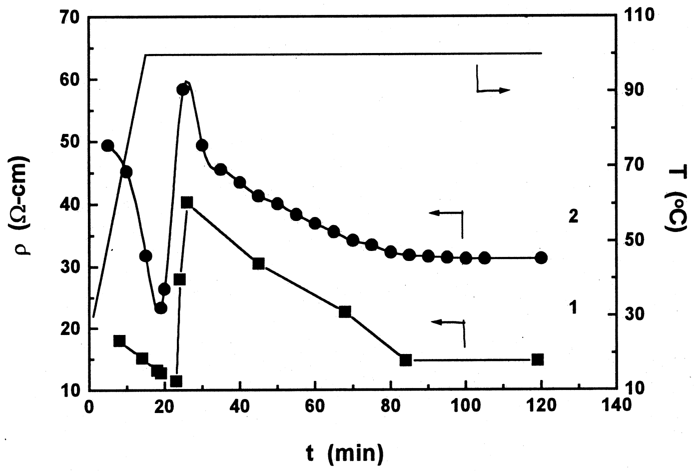

Fig. 7. Dependence of volume resistivity and curing temperature on curing time of Ag/epoxy/TEOA system. Ag content: curve 1 = 20 phr; curve 2 = 10 phr.

melting or grow of the particles (cf. the melting range on the DSC curve).

The structural development of particles at the critical temperatures revealed in Fig. 5 was observed by TEM for Ag(20 phr)/epoxy mixture, in hopes of finding out the direct evidence about the structural formation and destruction. The particles contained in the starting blend at RT shows the presence of a thin polymeric coating around them (see Fig. 6(a)). These suspended particles in epoxy resin have a homogeneous distribution and are hardly in contact with each other as a result of the higher viscosity of the system. When the system is kept at 90°C for a while, some kind of aggregation of particles can be observed (Fig. 6(b)). As temperature exceeds the melting point of Ag nanoparticles (129°C, determined by DSC, see Fig. 5), the particles begin to melt and grow to form larger secondary particles, as shown in Fig. 6(c). These larger particles disperse in epoxy resin with larger inter-particle spacing, and the conducting networks based on the particles texture exhibited in Fig. 6(b) were destroyed completely, which results in an increase of resistivity by three orders at the end of heat treatment process (2), see Fig. 5.

Therefore, it can be concluded that the aggregation process of silver particles in epoxy resin consists of two stages with increasing temperature: the first, self-organization of the particles corresponding to the establishment of conducting networks (process (1) in Fig. 5); and the second, formation of the secondary larger particles leading to destruction of the existing conducting networks (process (2) in Fig. 5). If the system is frozen at the first stage, a conducting network with lower percolation threshold will be obtained.

### 3.4. *Effect of curing process on the electric conductive behavior of Ag nanoparticles composite*

It is well-known that not only the viscosity, but also the molecular structure and physical properties (such as density, glass transition temperature, etc.) of epoxy resin change gradually in the course of curing, which would bring

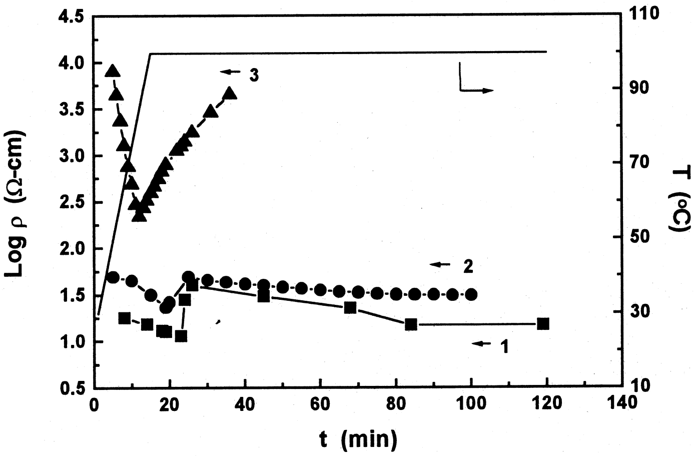

Fig. 8. Dependence of logarithmic volume resistivity and curing temperature on curing time of Ag/epoxy/TEOA system. Ag content: curve 1 = 20 phr; curve 2 = 10 phr; curve 3 = 5 phr.

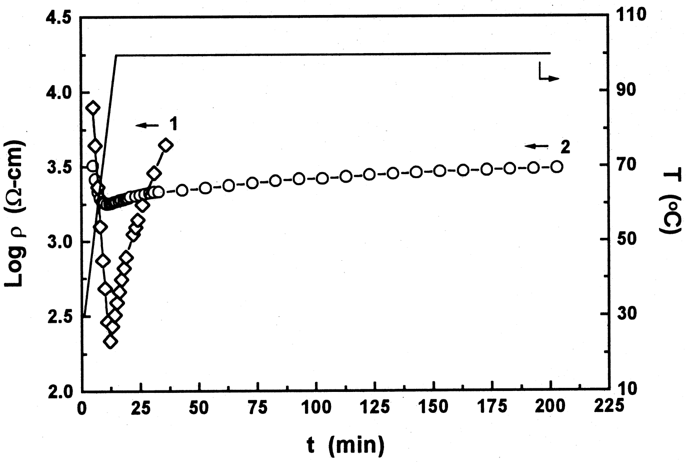

Fig. 9. Dependence of logarithmic volume resistivity and curing temperature on curing time. Curve 1: Ag(5 phr)/epoxy/TEOA; curve 2: Ag(2.5 phr)/carbon black(2.5 phr) /epoxy/TEOA.

about significant influence on the self-organization of the particles. According to the earlier investigation, the curing of Ag nanoparticles/epoxy resin should be controlled between the two stages, i.e., the self-organization and melting and growth of the particles. Thus, the curing agent, TEOA, and curing temperature (100°C, higher than the temperature corresponding to a drastic decrease in resistivity but lower than the melting point of Ag nanoparticles as shown in Fig. 5) were specially chosen so as to attain a low resistivity conductive composite. Changes in resistivity with curing process is shown in Fig. 7. It is seen that the systems with different nanoparticles contents have rather high resistivity at room temperature, but show some degree of conduction at elevated temperature of about 60°C. With the lapse of curing time, the resistivities of both the systems containing 10 and 20 phr particles exhibit a similar decreasing tendency (at the step of temperature increasing) and reach a minimum at about 100°C, and then go up sharply to some extent and decrease again gradually to the original conduction level (at the constant temperature step). In contrast to this, beyond the minimum on the time dependence of resistivity of the system containing 5 phr particles (Fig. 8), only a continuous increase in resistivity is observed at the constant temperature step.

The drop in resistivity at the step of temperature increasing can be attributed to the self-organization process similar to the silver/epoxy resin mixture. It is noticed that the system with lower content of particles shows a steeper decrease in resistivity and reaches the minimum at lower temperature (Figs. 7 and 8). As viscosity of epoxy resin is less raised by the addition of smaller amount of nanoparticles, the system of lower viscosity can exhibit self-organization phenomenon at lower temperature because the rate of particles motion in this temperature range is fast enough to allow the formation of the conduction networks.

Similarly, the increase and decrease of resistivities at the constant temperature step should also be related to the change in self-organization behavior caused by curing reaction (see curves 1 and 2 in Fig. 8). Prior to the gelation, the viscosity of the systems increases with the curing process, resulting in an rise in resistivity. As the gelation completes, the systems contract with the curing reaction, accounting for the secondary decrease in resistivity. A comparison between the final resistivities of the composites filled with 10 and 20 phr Ag nanoparticles reveals the value of the former is higher than that of the latter, suggesting that the percolation mechanism still take effect. With respect to the system containing 5 phr particles, particles fraction is too low to maintain stabilization of the conduction network when the viscosity is increased. Although the conduction networks are formed by self-organization process firstly at the step of temperature increasing, there is a kind of dynamic equilibrium for the network as a result of the motion of particles before the gelation of system, which is the key factor affecting the stabilization of the conduction networks. Nevertheless, if the particles content is high enough (10 and 20 phr, for example), the networks are relatively stable and can be readily solidified before being destroyed.

In order to further elucidate the self-organization behavior of silver nanoparticles, carbon black is added to the composite. The conduction performance of two sorts of composites with identical filler loading is compared in Fig. 9. It is found that the self-organization of the composite filled with both silver nanoparticles and carbon black is not pronounced enough, while the conduction network is stable. This difference in self-organization must be related to the feature of the particles and particles/matrix interaction. It was realized that the carbon black usually exists in the form of agglomeration, while the silver nanoparticles prepared in this work belong to the primary particles. Percolation mechanism predominates the conduction behavior of carbon black composites [17]. In the case of composite containing both carbon black and silver particles, carbon black is able

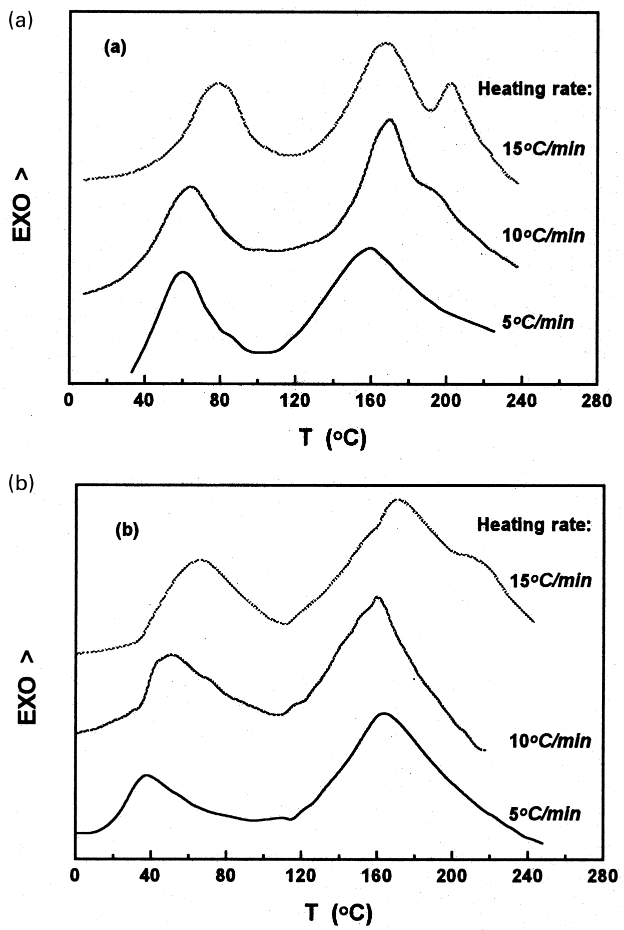

Fig. 10. DSC heating traces of (a) epoxy/TEOA and (b) Ag/epoxy/TEOA.

to build up relatively stable conduction networks, while silver nanoparticles contribute to the self-organization network, which is very weak because of the lower content of particles in comparison to the composites without carbon black. It should be noticed that there exist synergetic effects between the two kinds of particles, because the composites will possess very high resistivity when the composite is cured completely, where the silver particle cannot move.

### 3.5. *Effect of nanoparticles addition on the curing kinetics of epoxy resin*

The important influence of curing reaction on the self-organization of silver nanoparticles was noticed from earlier studies. The self-organization should be completed in a resin with lower viscosity (i.e. uncured version) and then the resultant structure should be fixed in terms of higher viscosity environment or even the gelation of the system (i.e. cured version). Accordingly, curing of the epoxy resin has to be carried out stage by stage. Therefore, it is necessary to study the kinetics of curing reaction in correlation to the self-organization process.

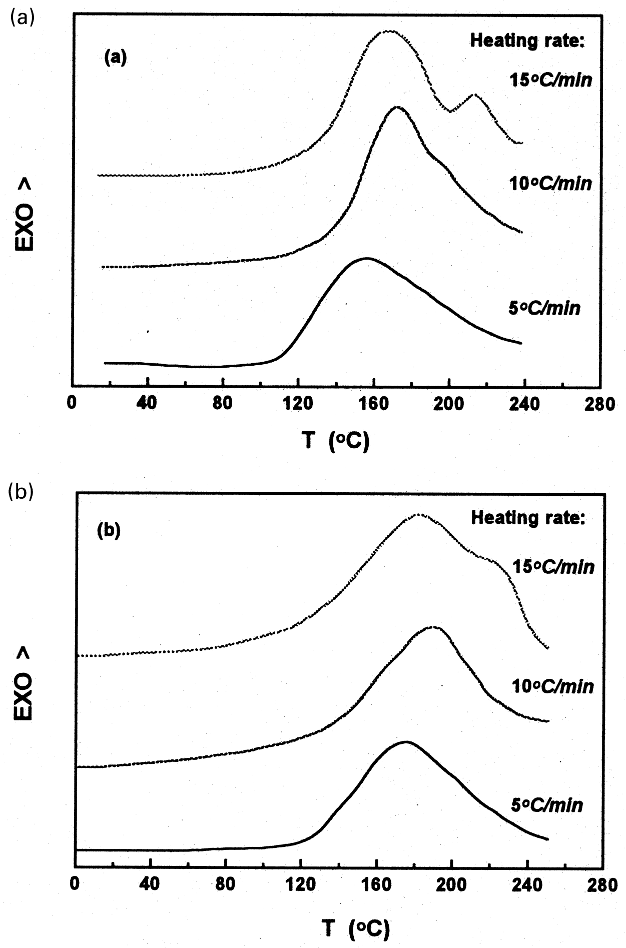

Fig. 11. DSC heating traces of (a) epoxy/TEOA and (b) Ag/epoxy/TEOA after preheating treatment at 100°C for 5 min.

With catalyzing of TEOA, the etherifying of epoxide groups occurs in the resin by several stages, leading to the appearance of 2–3 exotherms (Fig. 10). When the resin is cured under a lower heating rate (5°C/min), only two peaks are shown. With a rise in the heating rate, three peaks appear, which can be reasonably attributed to the heterogeneous curing in the primary curing stage. After the addition of the silver nanoparticles, however, the DSC traces of the composites only show two exothermic peaks in the current range of heating rates, indicating the interaction between epoxy resin and silver particles benefits the homogeneous primary curing.

In order to further testify the consideration that the progress of curing reaction by stages, the systems are preheated in the oven at 100°C for 5 min (corresponding to the resistivity increasing stage in Fig. 7), then the systems exhibit only one or two exothermic peaks on the DSC traces (Fig. 11). The first primary curing peak disappears, while other peaks remain and appear at the same temperatures as the system without preheating treatment, demonstrating again that the curing reaction takes place gradually stage by stage. In the meantime, the resistivity increase in Fig. 7 can be related with the primary curing stage.

The heating rate, $\phi$, peak exothermic temperature, $T_{p1}$

Table 3
Curing characteristics of neat epoxy resin and Ag particles/epoxy mixture catalyzed by TEOA

| Samples | $\phi$ (°C/min) | $T_{p1}$ (°C) | $T_{p2}$ (°C) | $E_1$ (kJ/mol) | $\Delta H_1$ (kJ/g) | $\Delta H_w$ (kJ/g) | $\Delta H$ (kJ/g) |
|---|---|---|---|---|---|---|---|
| | 5 | 60 | 160 | 30.5 | 71.8 | 311.1 | 382.8 |
| Epoxy | 10 | 70 | 180 | | 69.9 | 129.9 | 199.8 |
| | 15 | 80 | 170 | | 64.7 | 188.3 | 253.0 |
| | 5 | 80 | 205 | 52.7 | 97.6 | 258.1 | 355.7 |
| Ag (20 phr)/ Epoxy | 10 | 95 | 220 | | 64.6 | 126.3 | 190.9 |
| | 15 | 100 | 230 | | 37.1 | 100.3 | 137.4 |

and $T_{p2}$, heats of the first exotherm and of other exothermic peaks, $\Delta H_1$ and $\Delta H_w$, overall reaction heat, $\Delta H$, taken from Fig. 10, as well as activation energy of the first exothermic peak, $E_1$, calculated from Kissinger equation are presented in Table 3. The data reflect that the primary gelation of epoxy resin corresponding to the first exothermic peak, which is far from the completion of reaction, only contribute less than 50% of overall heat of fusion. Thus, the rise in resistivity in Fig. 7 is understandable because the system becomes more and more viscous with increasing curing time but is not yet cured completely. In addition, Table 3 indicates that the values of $T_{p1}$, $T_{p2}$ and $E_1$increase with the addition of Ag nanoparticles, suggesting the interaction between the Ag nanoparticles and epoxy resin is strong enough to hinder the curing reaction. It is can also be deduced that the good affinity of Ag particles to matrix results in an insulating layer that separates Ag particles from each other in the course of curing. Therefore, the so-called tunneling effect accounts for the conduction in composite materials, giving the similar conduction behavior but different level at different particles content (see Fig. 7).

## 4. Conclusion

The nano-size silver particles characterized with very lower melting point are chemically synthesized through microemulsions. The particles' diameter increases proportionally to the water/surfactant weight ratio. It is found that the entrap agent, dodecanethiol, has little effect in inhibiting aggregation of the particles, while the dodecanethiol bonded on the particles surface makes the particles electrically insulated.

Investigation of the electrically conductive behavior of silver nanoparticles filled solvent suspension, epoxy resin without curing agent, and epoxy resin with curing agent, can effectively describe the self-organization behavior of silver nanoparticles, including the mechanism involved, the process and the resultant structure changes. The loading dependence of resistivity of Ag particles/solvent suspension follows the percolation mechanism from low to moderate filler concentration. At high Ag fraction, the conductive networks become less efficient because of the aggregation of particles. In the case of Ag/epoxy resin mixture, a more complex self-organization process occurs, in which a conductive network can be formed even the content of particles is lower than the percolation threshold estimated conventionally. The addition of Ag particles thickens the resin, which in turn has important effect on the self-organization behavior of the particles. With increasing temperature, self-organization of particles helps to the formation of conducting networks throughout the matrix, which is destroyed as a result of melting and growth of the particles when temperature exceeds the melting point of the nanoparticles.

A composite capable of being electrically conductive was prepared by curing nano-sized Ag/epoxy resin with TEOA at lower particle fraction. The self-organization behavior of the particles accompanying the curing reaction is similar to the Ag/epoxy mixture without curing agent, except the additional successive increase and decrease in resistivity corresponding to the increase in viscosity and to the contraction of the system, respectively.

The curing kinetics investigation demonstrates that the curing reaction of the present epoxy resin matches the self-organization of particles, which provides a criterion for choosing proper curing system. Besides, the interaction between Ag nanoparticles and epoxy resin is proved to be very strong by the analysis of curing kinetics parameters.

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