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Preparation and structure of copper nanoparticle/poly(acrylic acid) composite films

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Composite films consisting of metallic Cu nanoparticles dispersed in poly(acrylic acid) (PAA) have been prepared by reduction of Cu^{2+} from the copper salt of PAA above 220 °C under a H_2 atmosphere. Optical absorption properties and structures have also been investigated by UV/VIS, WAXD, TEM and IR. Spherical Cu particles were found to be homogeneously dispersed in the PAA and the diameters of the particles were in the range 10–16 nm. The composite films exhibited an optical absorption peak centered at *ca.* 570 nm, which was attributed to surface plasmon resonance of Cu nanoparticles. The composite film made by heat treatment at 220 °C was less stable because Cu particles in the film were oxidized to Cu^{2+} ions within several weeks, while the composite films prepared by heating above 230 °C were stable and the Cu particles in their films were not oxidized. The stability of the Cu nanoparticles in PAA is suggested to be related to the formation of ketone groups by condensation reactions between carboxylic acids of PAA above 230 °C.

Introduction

Recently, numerous studies have been carried out on composite materials consisting of glasses or polymers doped with metal and semiconductor nanoparticles because of the attraction of their optical properties, *e.g.*, nonlinear optical and laser amplification properties.[1–5] For metal particles in composites of organic polymers, most of the investigations have dealt with noble metals such as Au and Ag, because these nanoparticles are known to exhibit characteristic optical absorption caused by surface plasmon resonance (SPR) originated from collective oscillation of free electrons.[6] Various methods to prepare metal-doped polymer films have been developed and the characteristics of these films have been studied in detail by many researchers.[1–4] For materials to be utilized in future applications, it is important to ensure chemical and thermal stability of the composites and to control the size and concentration of the dispersed metal particles to give the desired properties for the obtained materials. One of the present authors has previously prepared polymer thin films containing noble metal nanoparticles by a thermal relaxation technique, and the relationship between the properties and the film microstructure has been investigated.[7–11]

In contrast to noble metal nanoparticles, few studies have so far been carried out on polymer composites doped with nanoparticles of non-noble metals such as Cu. Cu nanoparticles exhibit SPR absorption as well as Au and Ag, and there are many reports on the preparation of Cu particles embedded in inorganic glass matrices and their optical properties.[12–16] In general, nanoparticles in inorganic glasses have been prepared by heating at relatively high temperatures. Since high temperature annealing generally causes the thermal degradation of organic polymers, it is difficult to prepare Cu nanoparticles in organic polymer matrices by heating at high temperatures. In this study we report on a new procedure for the preparation of Cu metal nanoparticle/polymer composite films by heat treatment. Namely, composite films consisting of Cu nanoparticles and poly(acrylic acid) (PAA) have been prepared by the reduction of Cu^{2+} from the copper salt of PAA over 200 °C under H_2, and the optical absorption properties and structures of the prepared composites have also been investigated.

Experimental

Materials

A 25 wt% PAA aqueous solution was purchased from Wako Pure Chemical Industries and was used without any purification. The viscosity-average molecular weight of the PAA was *ca.* 150 000. Anhydrous copper(II) acetate was obtained from Yoneyama Chemical Industries and was used without any purification.

Preparation of Cu nanoparticle/PAA composites

The PAA aqueous solution was smeared on a glass plate which was then immersed in a 5 wt% copper(II) acetate aqueous solution at room temperature for 5 min. A gel film was immediately formed, which was blue-green and insoluble in water. This indicates that the PAA was cross-linked by coordination of the carboxylic acids of PAA to Cu^{2+}. When 50 mg of the PAA aqueous solution was smeared on a glass plate measuring 26 × 55 mm in area, a gel film of *ca.* 10 μm thickness was obtained. PAA (1 g) reacted with 0.19 g Cu^{2+} under the present preparation conditions. After drying, the PAA–Cu^{2+} films were heated at various temperatures above 200 °C for 30 min under a H_2 atmosphere so as to obtain Cu nanoparticle/PAA composites. In this case H_2 was used as a reducing agent of Cu^{2+}.

Measurements

Infrared spectroscopy (IR) measurements were performed with a Perkin-Elmer FT-IR spectrometer 1640. Measurement conditions were 64 scans and a resolution of 2 cm^{-1}. Electron spin resonance (ESR) measurements were carried out with a JEOL X-band ESR spectrometer TE200 at 23 °C. Ultraviolet-visible (UV/VIS) absorption spectra were measured using a Hitachi UV/VIS/NIR spectrophotometer U-3500. Wide angle X-ray diffraction (WAXD) experiments were performed on a Rigaku Geigerflex 2028 diffractometer with CuKα radiation. The voltage and current of the X-ray source were 40 kV and 150 mA, respectively. Crystallite sizes were calculated from the Cu(111) diffraction line using Scherrer's equation, $L=\lambda/(\beta\cdot\cos\theta)$, where L is the mean dimension of the crystallites, β is the integral width of the diffraction peak, θ is the diffraction angle, and λ is the wavelength of the CuKα_1 radiation (0.1540 nm). The observed integral width of each diffraction peak was corrected for both the CuKα doublet broadening and the instrumental broadening. Transmission electron microscopy (TEM) observation was performed with a JEOL JEM-2000 transmission electron microscope operated at 200 kV. Thin sections (*ca.* 100 nm in thickness) for TEM observation were obtained by the conventional microtome technique. Thermal mechanical analysis (TMA) was carried out with a SEIKO SS-10 at a heating rate of 1 °C min^{-1} under a H_2 flow.

Results and discussion

Complexation between PAA and Cu^{2+}

In order to confirm the formation of the PAA copper salt and investigate the coordination state of Cu^{2+} in the specimen, IR and ESR measurements were carried out. Fig. 1 shows the IR spectra of the PAA and the PAA–Cu^{2+} films. The carbonyl asymmetric stretching band [ν(C=O)] of unneutralized –CO$_2$H is found at 1700 cm^{-1} in the spectrum of PAA. On the other hand, for the PAA–Cu^{2+} film the ν(C=O) of unneutralized –CO$_2$H is considerably weakened and three peaks appeared around 1500–1600 cm^{-1}. Because shifts to lower wavenumbers are generally observed upon complexation,[17] these peaks can be assigned to the ν(C=O) band complexed with Cu^{2+}, and the peaks suggest that there are some different coordination states coexisting within the Cu^{2+} complexes.

Fig. 2 shows the ESR spectrum of PAA–Cu^{2+}. Two bands are observed around 310 mT and 455 mT, indicating that two coordination states of Cu^{2+} coexist. According to the g-values of the two bands, the former is an anisotropic band with hyperfine structure and can be assigned to mononuclear Cu^{2+} complexes with four-oxygen ligation.[18,19] The latter, isotropic, band is assigned to a binuclear complex of the dimeric copper(II) acetate monohydrate type.[19,20] It is considered that most of the Cu^{2+} in PAA–Cu^{2+} is in the state of mononuclear Cu^{2+} type, because the relative intensity of the band at 310 mT is somewhat larger than that at 455 mT.

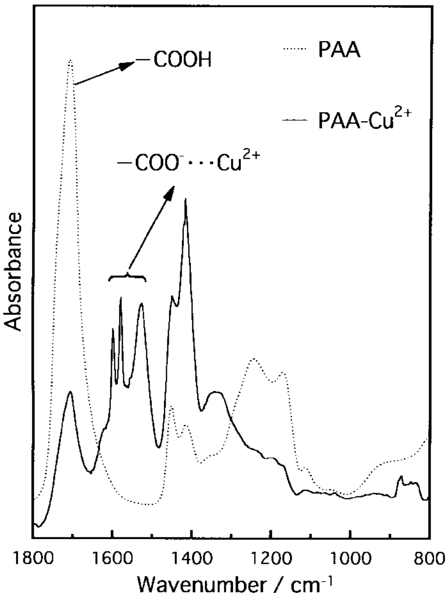


Fig. 1 FT-IR spectra of PAA and PAA–Cu^{2+} prepared by the reaction of PAA with copper(II) ion in the treatment solution.

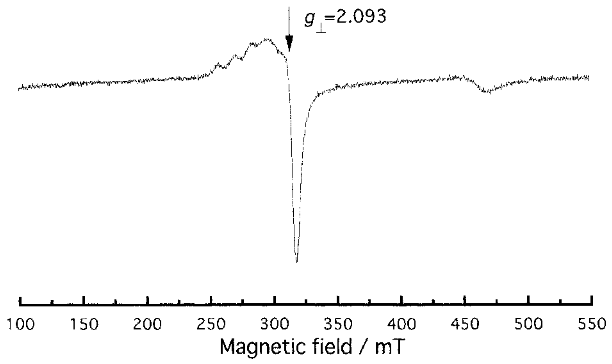


Fig. 2 ESR spectrum of PAA–Cu^{2+}, measured at 23 °C.

Formation of Cu particles in PAA

Fig. 3 shows the UV/VIS spectra of the PAA–Cu^{2+} films heated under an H_2 atmosphere at various temperatures. For the as-prepared PAA–Cu^{2+} film, the colour of the film was blue-green, and the UV/VIS spectrum shows an absorption peak centered at 690 nm, which is originated from the d–d transition of the 3d orbital in Cu^{2+}.[21] During heat treatment below 210 °C the colour of the PAA–Cu^{2+} films did not change, remaining blue-green similar to the as-prepared film. This indicates that Cu^{2+} ions in the films are not reduced by the heat treatment below 210 °C. The colour of the films significantly changed upon heating above 215 °C. The film heated at 215 °C became colourless and the spectrum showed no absorption in the visible region, indicating the absence of the d–d transition of the Cu^{2+} 3d orbital. This is attributed to the reduction of Cu^{2+} to Cu^{+} by H_2. Consequently, the Cu^{+} 3d orbital is filled with 10 electrons and the d–d transition does not occur. The absorption edge around 360 nm is probably caused by charge transfer between –CO$_2^-$ and Cu^{+}. After heat treatment above 220 °C, the films changed to deep red and the spectrum shows an absorption peak at 565 nm. It is well known that metallic nanoparticles exhibit characteristic optical properties due to SPR absorption, which results in an absorption peak in the UV/VIS region.[2,4,6,21–23] In the present study the absorption peak at 565 nm is approximately

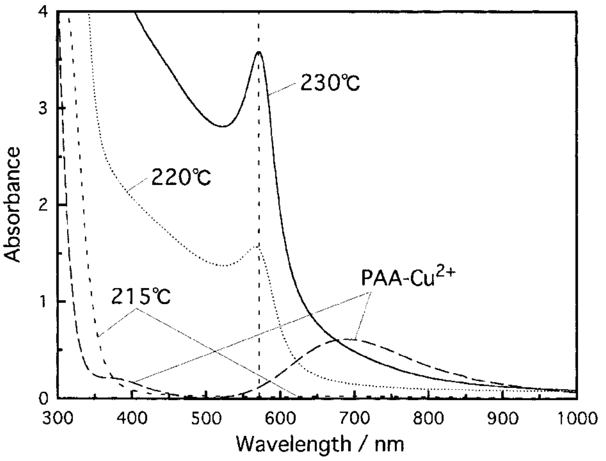


Fig. 3 UV/VIS spectra of the PAA–Cu^{2+} films heated at various temperatures under a H_2 atmosphere for 30 min.

coincident with the SPR wavelength of Cu nanoparticles reported by different authors.[11–15,24,25] Therefore, it is considered that Cu nanoparticles were formed in the films by heat treatment above 220 °C. Upon heat treatment at 230 °C, an absorption peak is observed at 570 nm, the intensity is enhanced, and the position shifts slightly to longer wavelength in comparison with the PAA–Cu^{2+} film heated at 220 °C. This suggests that the number of Cu particles formed in the matrix increases as the heat treatment temperature increases.[7]

From the results of UV/VIS the following reduction mechanism of Cu^{2+} is proposed.

$$-CO_2^- \cdots Cu^{2+} \cdots {}^-O_2C- + 1/2H_2 \xrightarrow{215\,^\circ C} -CO_2^- \cdots Cu^+ + -CO_2H$$

$$-CO_2^- \cdots Cu^{2+} + 1/2H_2 \xrightarrow{220\,^\circ C} -CO^0 + -CO_2H$$

$$n(Cu^0) \rightarrow nCu^0$$

Fig. 4 shows the WAXD patterns of the films heat-treated at various temperatures under an H_2 atmosphere. PAA homopolymer is amorphous and exhibits a broad scattering pattern with a peak maximum at $2\theta = ca.\ 17°$.[26] In Fig. 4, after complexation between Cu^{2+} and PAA (as-prepared sample), the peak maximum shifts to *ca.* 20°. The WAXD pattern of the PAA–Cu^{2+} heated below 210 °C is almost identical in shape to that of the as-prepared film and shows no diffraction peaks attributable to metallic Cu. This indicates that the Cu^{2+} is not reduced by the heat treatment below 210 °C, and PAA–Cu^{2+} remains unchanged. Upon heat treatment at 215 °C, the amorphous pattern is found to change although no diffraction peaks of metallic Cu are observed, *i.e.*, the peak maximum of the amorphous scattering shifted from 20° to 23°. This change indicates a conformational change of the PAA molecular chains. This heat treatment temperature of 215 °C corresponds to that at which the reduction of Cu^{2+} to Cu^+ occurs, as shown in Fig. 3. Therefore, the reduction to Cu^+ causes the changes in the conformation of the PAA molecules as well as the coordination state of copper ions. Upon heat treatment above 220 °C, a diffraction peak is observed at 43.3°, which is assigned to the (111) reflection of metallic Cu. Heat treatment at 230 °C results in an increase of the intensity of the diffraction peak for Cu metal and the line width is sharpened as compared to the film heated at 220 °C. In addition, the peak maximum of the scattering for PAA shifts to 17°, which is consistent with that of PAA homopolymer. These results indicate that most of Cu^{2+} in the film is reduced to metallic Cu at 230 °C, which is in good agreement with the results of the UV/VIS measurement (Fig. 3). The crystallite size of the Cu particles in each composite film was calculated from the width of the Cu(111) diffraction line at 43.3°. Fig. 5 shows the dependence of crystallite size of the Cu particles on the heat treatment temperature. Each crystallite size is in the range of *ca.* 10–16 nm and small enough to exhibit SPR absorption of Cu particles.[24,25] The crystallite size increases with increasing heat treatment temperature up to 230 °C and is about 16 nm in the 230–240 °C range, and then slightly decreases again above 240 °C.

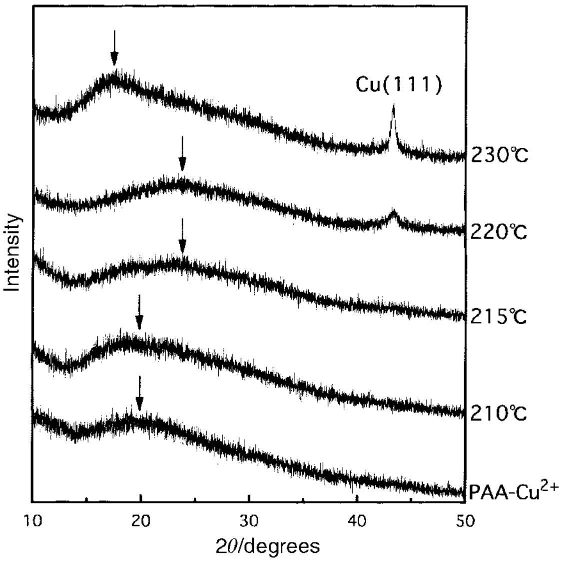


Fig. 4 WAXD patterns of the PAA–Cu^{2+} films heated at various temperatures under a H_2 atmosphere for 30 min.

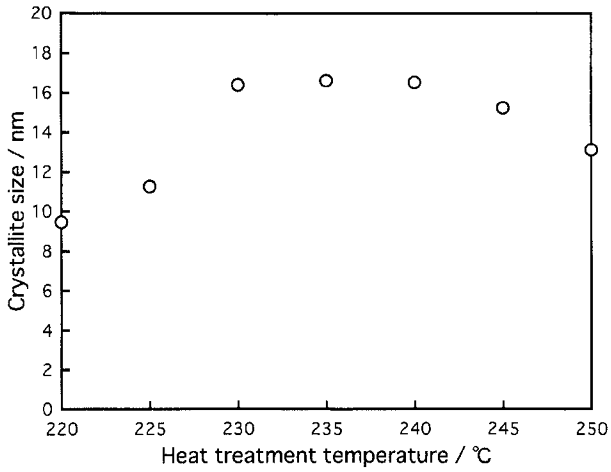


Fig. 5 Dependence of the crystallite sizes of Cu particles in PAA films on the heat treatment temperature.

We observed directly the dispersion state of Cu particles in the film by TEM observation. Fig. 6 shows the TEM image of the cross-section for the film heat-treated at 230 °C. Spherical Cu particles are homogeneously dispersed in PAA; the particle diameter is 15–20 nm, which is nearly coincident with the crystallite size estimated by WAXD ($L = 16.4$ nm). We also attempted to prepare a thin section of the film heated at 220 °C for TEM observation, but this was unsuccessful. In preparing the ultrathin cross-sections for TEM observation with a microtome, distilled water is necessary to float them. However, the specimen was softened by swelling with distilled water and could not be cut into an ultrathin film. Furthermore, the colour of the film heated at 220 °C changed from red to blue-green within several weeks. This implies that Cu metal particles were oxidized and changed again to Cu^{2+} in the film, *i.e.*, the

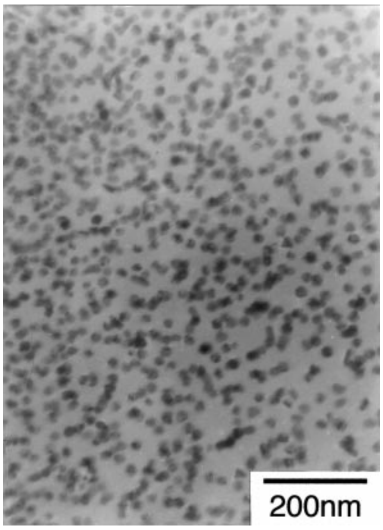


Fig. 6 Cross-sectional TEM image of Cu–PAA film heated at 230 °C under a H_2 atmosphere for 30 min.

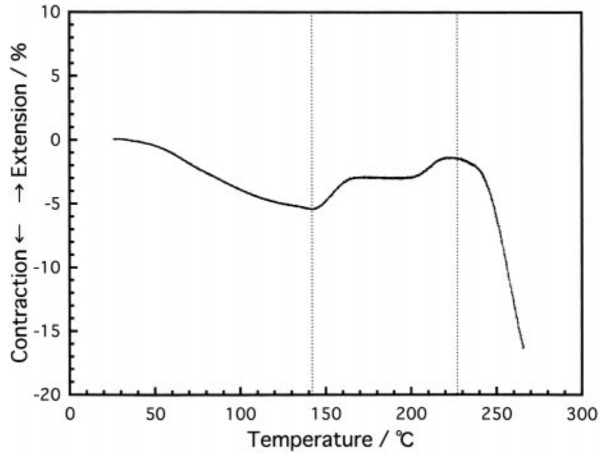


Fig. 7 TMA thermogram of PAA–Cu^{2+} films under a H_2 flow.

composite film prepared by heat treatment at 220 °C is less stable. On the other hand, the films heat-treated above 230 °C hardly swelled in distilled water and the colour of the composites remained unchanged. Judging from these results, the intermolecular crosslinking between PAA chains is probably formed by heat treatment at 230 °C and the Cu particles can be stabilized in the matrix.

In order to investigate the formation of crosslinking in the specimens, TMA measurements were carried out. Fig. 7 shows the TMA curve of the as-prepared PAA–Cu^{2+} film. Below 140 °C, the PAA–Cu^{2+} film is observed to be gradually contracted with increasing temperature due to the elimination of water contained in the film, and then the film is extended stepwise up to 225 °C. This extension may be caused by softening of the matrix due to the glass transition temperature of PAA (*ca.* 103 °C[27]). The specimen considerably contracts again above 230 °C. It seems likely that this second contraction is attributed to a stiffening of the matrix, originated by the formation of intermolecular crosslinking between the PAA chains. Therefore, the film heated at 230 °C does not swell when the film is immersed in distilled water.

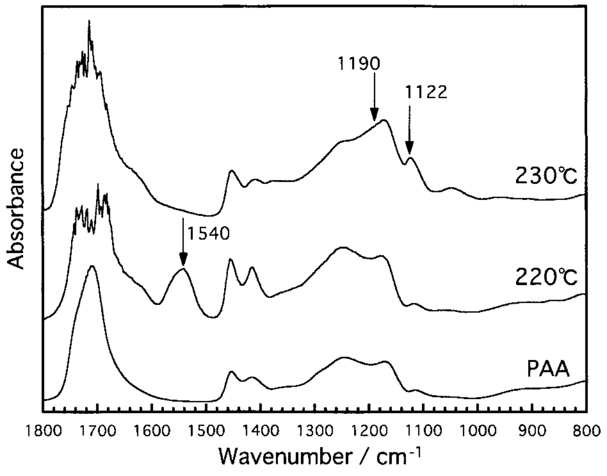
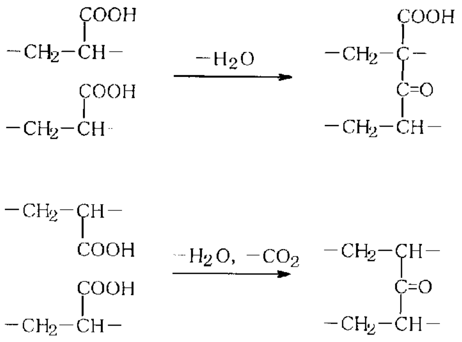


Fig. 8 IR spectra of PAA and PAA–Cu^{2+} films heated at various temperatures.

IR measurements were carried out to elucidate the binding formula of the intermolecular crosslinking between PAA chains in the film. Fig. 8 shows the IR spectra of the PAA and the PAA–Cu^{2+} films heated at 220 °C and 230 °C, respectively. For the film heated at 220 °C, an absorption band which presumably may be assigned to the ν(C=O) band of $-CO_2^{-}\cdots Cu^{+}$ is observed at 1540 cm^{-1}. Thus, it is reasonable that all the Cu ions are not reduced by the heat treatment at 220 °C, as concluded from the results of UV/VIS and WAXD measurements. During heating of PAA above 150 °C crosslinking reaction between the molecular chains occurs.[28] It is well known that acid anhydride is formed by dehydration between $-CO_2H$ groups as a type of crosslinking.[26,28] For the film heated at 230 °C, the absorption band assigned to acid anhydride is not observed in the spectrum because of the absence of any absorption peak at *ca.* 1800 cm^{-1}. Instead, two new absorption peaks are observed around 1100–1200 cm^{-1}, which can be assigned to C–C stretching bands of C–C=O of ketone groups. The ketone groups are probably generated by condensation reaction between $-CO_2H$ groups of the PAA and bring about the crosslinking of PAA molecules. The possible condensation reaction routes for the formation of the ketone groups are expressed in the following equations.



As a result, the number of ketone groups instead of carbonyl groups increases and crosslinking between the PAA chains proceeds. The ketone does not react with Cu metal, therefore Cu nanoparticles are stable in the matrix. However, the PAA–Cu^{2+} film heated at 220 °C exhibited no absorption bands of ketone groups, indicating that the carboxyl groups of PAA remain in the film. Consequently, the carboxyl groups react with Cu nanoparticles which lead to the formation of a $-CO_2^{-}-Cu^{2+}$ complex, and, therefore, the colour of the film heated at 220 °C changes from red to blue-green as mentioned above. These results demonstrate that the formation of the crosslinking between PAA chains plays an important role in the stabilization of Cu nanoparticles in the matrix.

Conclusion

Cu nanoparticle/PAA composite films have been prepared by the reduction of Cu^{2+} from the copper salt of PAA at high temperature under H_2. Upon thermal treatment, Cu^{2+} in PAA–Cu^{2+} was reduced by H_2 as follows.

$$Cu^{2+} \xrightarrow{215\,^{\circ}C} Cu^{+} \xrightarrow{220\,^{\circ}C} \text{metallic Cu particle}$$

The colour of the PAA–Cu^{2+} films heated above 220 °C changed from blue-green to deep red and an optical absorption at *ca.* 570 nm was observed, caused by SPR absorption of Cu nanoparticles. Cu particles dispersed homogeneously in the films and the diameters were in the range 10–16 nm. The stability of the Cu particles in the composite films obtained above 230 °C was higher than that obtained at 220 °C. The difference of the stability of the Cu nanoparticles can be related to the formation of ketone groups by condensation reaction between the carboxylic acid groups of PAA above 230 °C. Namely, $-CO_2H$ groups in PAA–Cu^{2+} remained when heated at 220 °C and reacted with Cu particles. Consequently, $-CO_2^{-}-Cu^{2+}$ formed again and the colour of the composite reverted to blue-green. On heating above 230 °C ketone groups were generated in the composites by condensation reaction between –CO_2H groups, which are responsible for the stabilization of the Cu nanoparticles.

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