

Bulk Conductive Polymers Prepared from Nylon-6/6,9 Copolymer/CuCl₂ Compounds

W. Jia,¹ R. Tchoudakov,¹ M. Narkis,¹ A. Siegmann²

¹Department of Chemical Engineering, Technion-I.I.T., Haifa 32000, Israel

²Department of Materials Engineering, Technion-I.I.T., Haifa 32000, Israel

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ABSTRACT: Semiconductive polymers were obtained by soaking nylon-6/6,9 particles in concentrated CuCl₂·2H₂O aqueous solutions, followed by reduction of the treated particles with sodium borohydride aqueous solutions. The reduced nylon-6/6,9/CuCl₂ particles were compression molded at a relatively low temperature (160°C). The bulk volume resistivity obtained is at an intermediate level, ~10⁵ ohm-cm. The compounds generated by reduction of the nylon-6/6,9/CuCl₂ particles were determined to consist of metallic copper by means of energy-dispersive X-ray microanalysis. The metallic copper is responsible for the electrical conductivity of the bulk samples. Samples stored at the ambient atmosphere gradually absorb oxygen and moisture, resulting in a decrease in the conductivity. The morphology

of nylon-6/6,9/CuCl₂ samples before and after reduction was studied by a scanning electron microscope and transmission electron microscope. A two-level hierarchy structure, submicrometer and nano-sized, of copper particles was observed, forming the conducting copper networks. Molded samples of reduced nylon-6/CuCl₂ and nylon-6,6/CuCl₂ particles, prepared by the same procedure as that of nylon-6/6,9/CuCl₂ particles, were insulating, whereas a reduced nylon-6/CuCl₂ film was moderately conductive. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1367–1373, 2004

Key words: conducting polymers; metal–polymer complexes; polyamides

INTRODUCTION

The conventional method to impart electrical conductivity to common insulating polymers uses incorporation of conductive fillers such as carbon blacks, carbon fibers, metallic powders or flakes, and intrinsically conducting polymers. Conductive polymer/filler composite materials are widely used in such areas as the automotive, aerospace, optical, medicals, and electronics industries. The electrical conductivity of the composites can be tailored for a given application by correctly selecting conductive fillers and loading levels.

In addition to the aforementioned conventional method, the doping of insulating polymers with dissolved metal salts or metal complexes for the purpose of imparting electrical conductivity has also received considerable attention.^{1–11} Polymer metal chelate films were prepared by solution casting. The solution was usually prepared by dissolving metal salts and polymers containing functional groups, such as poly(vinyl alcohol),^{4,6} polyamide,^{5,8} polyamide-imides,⁷ polyamide-hydrazide,^{10,11} and polyurethane,⁶ in a common solvent. Subsequently, these polymer metal chelate films were reduced to form metallized polymer

films. Low surface resistivities were thus obtained at about 10⁻¹–10² ohm/cm², depending mainly on the type of polymer and metal salt used.

Inspired by the metallized polymer film processing method, in this study a different approach to impart polymer electrical conductivity to polymer particles was investigated. Nylon-6/6,9 particles/CuCl₂ salt was prepared by a soaking method, followed by reduction with sodium borohydride (NaBH₄) aqueous solution. Intermediate volume resistivity levels of the bulk polymer compound were obtained at about 10⁵ ohm-cm. Other types of nylon particles and films, i.e., nylon-6 and nylon-6,6 particles, and nylon-6 films were also studied for comparison.

EXPERIMENTAL

Materials

Nylon-6/6,9, copolyamide-6/6,9 with an approximately 1:1 comonomer ratio was obtained from EMS-Chemie AG (Domat/EMS, Switzerland); nylon-6 from Polyram, PN60 LS9 (Israel); nylon-6,6 from Polynil, P-36/4 (Nilit, Israel); and nylon-6 film, Ultramid B35 PA6, from BASF (Germany). All chemicals used were of analytical grade.

Preparations of nylon/CuCl₂ salt compound

Nylon-6/6,9 and nylon-6 pellets were first ground in a Wiley mill using a 2-mm sieve. A certain amount of

Correspondence to: M. Narkis (narkis@tx.technion.ac.il).

nylon-6/6,9 particles (same as nylon-6 and nylon-6,6 particles) was soaked in 50 mL of a given concentration of aqueous $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution. The mixture was first magnetically stirred for a few minutes and then placed in an oven at selected temperatures for selected durations. Finally the treated particles with a yellow color were washed several times with deionized water and dried at 80°C for 2 h.

Preparation of bulk samples from reduced nylon/ CuCl_2 particles

Nylon-6/6,9/ CuCl_2 particles (~ 5 g) were reduced by 25 mL of a 2 wt% sodium borohydride aqueous solution at about 45°C for 10 min. The reduced particles (dark brown) were washed several times with methanol and dried in a vacuum oven at 60°C for 30 min. The dried reduced particles were then compression molded at 160°C to form a rectangular specimen ($\sim 1.2 \times 2.0$ cm) 2–3 mm thick. Nylon-6/ CuCl_2 and nylon-6,6/ CuCl_2 were prepared and reduced by the procedure described above. Reduced nylon-6/ CuCl_2 particles were molded at 240°C and nylon-6,6/ CuCl_2 particles at 280°C . Nylon-6/ CuCl_2 film was also prepared, starting with a nylon film, and reduced in the same way, but without the need for a molding stage.

Characterization

Electrical resistance measurements of the bulk samples (shortly after preparation) were conducted using a Keithley 240A high voltage supply and a Keithley 6514 electrometer. A DC voltage of 1 V was applied across the sample thickness. The surface resistivity of the film sample was measured using Surface Resistance Checker SRM-100 (Arrowquint Co., UK). The range of the surface measurement is 10^3 – 10^{12} ohm/sq; above 10^{12} ohm/sq the instrument shows "insulating."

A scanning electron microscope (SEM), Philips XL20 Model D816, was used to observe the morphology of the compression molded nylon-6/6,9/ CuCl_2 samples before and after reduction. The samples were freeze-fractured in liquid nitrogen.

A transmission electron microscope (TEM), JEOL, JEM-2000FX, was used to observe the morphology of the freshly reduced, compression molded nylon-6/6,9/ CuCl_2 sample. Thin samples (~ 50 nm) were cut using an ultramicrotome at -12°C .

SEM, Philips XL30, coupled with an energy-dispersive X-ray microanalysis, EDS, Model 6650 (Oxford Microanalysis Group, England), was used to study the surface elemental composition of the reduced nylon-6/6,9/ CuCl_2 particles shortly after reduction and 2 weeks after reduction. The accelerating voltage was 5 kV, and the corresponding interaction depth was

about 200 nm. All samples were sputtered with a thin carbon layer prior to analysis.

Photoacoustic Fourier transform infrared spectroscopy (PA FTIR), Model 300 (Equinox 55, Bruker), was used to record the absorbance spectra of the compression molded neat nylon-6/6,9 and nylon-6/6,9/ CuCl_2 compound.

Thermal analysis of the nylon-6/6,9/ CuCl_2 particles before and after reduction was performed using a Mettler DSC30 differential scanning calorimeter under nitrogen purge. The sample was placed in a DSC cell and heated from 25 to 250°C at a rate of $10^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Electrical resistivity of nylon/ CuCl_2 particles reduced by NaBH_4

The color of nylon-6/6,9/ CuCl_2 varies from yellow to orange, depending on the concentration of the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution and the soaking time. However, the electrical resistivities of nylon-6/6,9/ CuCl_2 are all at the same resistivity level, $\sim 10^{10}$ ohm-cm, two orders of magnitude lower than that of neat nylon-6/6,9 ($\sim 10^{12}$ ohm-cm).

During reduction by the NaBH_4 solution, the color of nylon-6/6,9/ CuCl_2 changes rapidly from yellow or orange to dark brown. The same phenomenon was observed with nylon-6/ CuCl_2 and nylon-6,6/ CuCl_2 .

Sterlyadkina et al. studied the reaction of copper chloride with sodium borohydride¹² in aqueous solutions. Accordingly, the reduced products can be Cu, CuH, and/or CuCl, depending on the molar ratio of CuCl_2 and NaBH_4 . In our case, most likely the reduced products are a combination of metallic copper and copper hydride (brown substance). This was supported by EDS analysis, which will be discussed below. The generation of metallic copper is responsible for the conductivity of the reduced nylon-6/6,9/ CuCl_2 samples.

The volume electrical resistivities of compression molded nylon-6/6,9/ CuCl_2 , nylon-6/ CuCl_2 and nylon-6,6/ CuCl_2 particles and the surface electrical resistivity of the nylon-6/ CuCl_2 film, all after NaBH_4 reduction, including the soaking conditions, are summarized in Table I. It is noted that when the concentration of the salt solution is 30% or more, the electrical resistivity of nylon-6/6,9/ CuCl_2 after reduction reaches the lowest value, $\sim 10^5$ ohm-cm. The soaking temperatures ranging from room temperature to 50°C yield similar resistivity levels; however, at 70°C the resistivity increases. It is also noteworthy that the increase of soaking time (from 1 day to 1 week) does not affect the resistivity of the reduced bulk nylon-6/6,9/ CuCl_2 sample. This indicates that the absorption of CuCl_2 salt in the nylon-6/6,9 particles is practically completed in 1 day or less, or that the reduction is limited to the surfaces.

TABLE I
Electrical Resistivity of Compression Molded Nylon/CuCl₂ Particles Reduced by NaBH₄

Type of polymer	CuCl ₂ · 2H ₂ O aqueous concentration (%)	Soaking conditions		Molding temperature (°C)	Volume resistivity after reduction (ohm-cm)
		Duration	Temperature (°C)		
Nylon-6/6,9 particles	15	1 day	50	160	9.3 × 10 ⁶
		3 days	25		2.3 × 10 ⁵
	30	1 day	50		3.5 × 10 ⁵
		1 week	50		5.4 × 10 ⁵
		1 day	50		1.6 × 10 ⁵
Nylon-6,6 particles	30	1 day	70	240	4.8 × 10 ⁶
		1 week	50		~10 ¹¹
	50	1 week	50		~10 ¹²
Nylon-6 particles	30	1 day	50	280	~10 ¹²
		1 day	70		~10 ¹⁰
	50	1 week	50		~10 ¹¹
Nylon-6 film	50	1 week	50	-	Surface resistivity after reduction: 10 ⁵ ohm/sq

As seen in Table I, the molded nylon-6/CuCl₂ and nylon-6,6/CuCl₂ samples are insulating after the NaBH₄ reduction. This may be due to the required high compression molding temperatures: 240°C for nylon-6/CuCl₂ and 280°C for nylon-6,6/CuCl₂. Upon heating to such high temperatures in the presence of air, metallic copper oxidizes to an insulating compound; thus the bulk samples are not conductive. Interestingly, the nylon-6/CuCl₂ film after reduction (absence of high temperature molding) exhibits a moderate conductivity level of 10⁵ ohm/sq. Nylon-6/6,9 is a copolymer with a relatively low melting temperature of 137°C.¹³ DSC studies show that the *T_m* of nylon-6/6,9/CuCl₂ particles decreases relative to the neat nylon copolymer by 10–20°C, depending on the amount of CuCl₂ salt absorbed. However, after reduction, the *T_m* increases to 140°C. The molding temperature of the reduced nylon-6/6,9/CuCl₂ particles was therefore 160°C, thus leading to no or very little oxidation, as proven by EDS results.

Morphology of nylon-6/6,9/CuCl₂ before and after reduction

Since nylon-6/6,9 copolymer was soaked in CuCl₂ solutions as solid particles rather than on a molecular scale by dissolving the copolymer in a common solvent with CuCl₂ salt, Cu²⁺ ions may essentially coordinate with surface amide groups of copolyamide-6/6,9 chains and owing to the low concentration cannot be detected by PA-FTIR results.

Figure 1a–d shows SEM micrographs of freeze-fractured compression molded nylon-6/6,9/CuCl₂ samples (nylon-6/6,9 particles were soaked in 30% CuCl₂·2H₂O solution at 50°C for 1 day) before and after reduction by NaBH₄ solution. It can be seen (Fig. 1a) that after soaking tiny CuCl₂ salt particles are

attached upon the nylon-6/6,9 particle surface. Since the sample shown in Figure 1a and b was not molded at a high enough temperature, remnant boundaries between nylon-6/6,9/CuCl₂ particles are seen, where most CuCl₂ salt particles are observed. This illustrates that the CuCl₂ salt was mostly adsorbed to and coating the surfaces, without significant penetration into the bulk of the nylon-6/6,9 particles. After reduction, larger particles consisting of certain structures are observed, as seen in Figure 1c and d. These particles consist of metallic copper, as shown by EDS (see below). The copper particles are distributed along the boundaries of nylon-6/6,9 particles; however, the distances between the discrete copper particles are too large to generate conductivity of the bulk sample. It was assumed that much finer copper particles, not observable by SEM, may exist, interconnecting the observable discrete copper particles and thus forming a conductive network. TEM micrographs indeed prove the existence of nanoscale copper particles (~20–50 nm), as shown in Figure 2. These copper nanoparticles can only be observed in certain areas, preferentially at the broken edge of the microtomed film. These copper nanoparticles are probably distributed also only along boundaries of the nylon particles, similar to the larger copper particles distribution observed in SEM. Hence, the overall conductivity of the bulk sample is a combination of a two-level hierarchy, namely, discrete submicrometer copper particles and nanoscale copper particles, which forms the electrically conducting networks.

EDS analysis of nylon-6/6,9/CuCl₂ particles after reduction

Freshly reduced nylon-6/6,9/CuCl₂ samples (particles and compression molded sample) and reduced

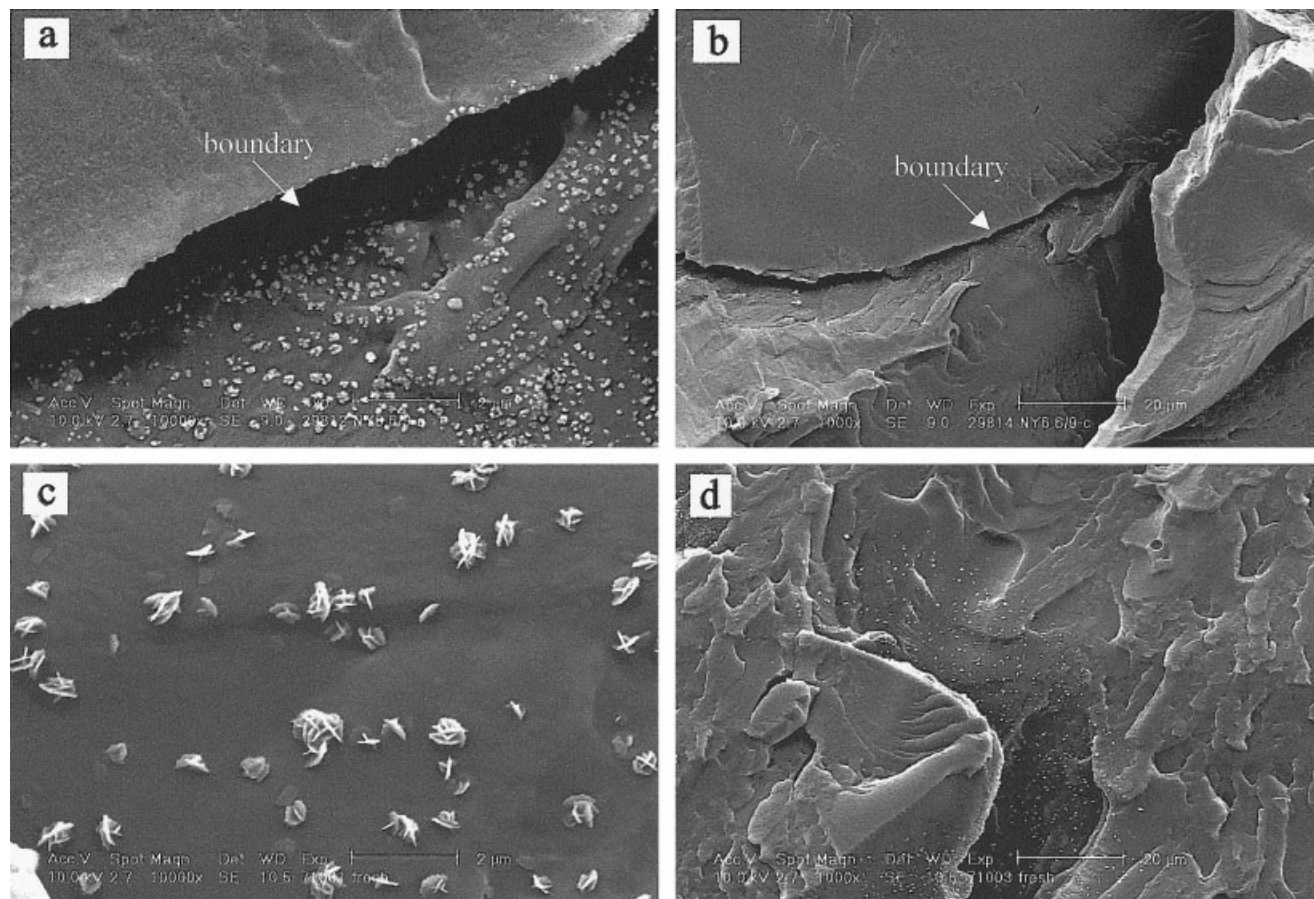


Figure 1 SEM micrographs of freeze-fractured compression molded nylon-6/6,9/CuCl₂ sample (nylon-6/6,9 particles were soaked in 30% CuCl₂·2H₂O solution at 50°C for 1 day) (a, b) before and (c, d) after reduction by NaBH₄.

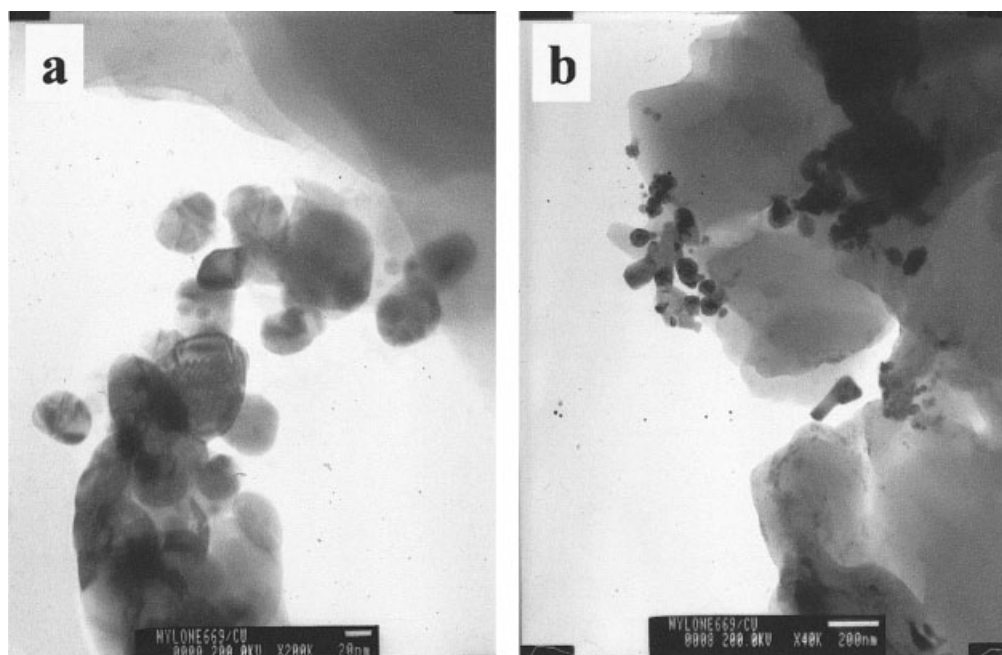


Figure 2 TEM micrographs of nylon-6/6,9/CuCl₂ sample (nylon-6/6,9 particles were soaked in 30% CuCl₂·2H₂O solution at 50°C for 1 day) after reduction by NaBH₄.

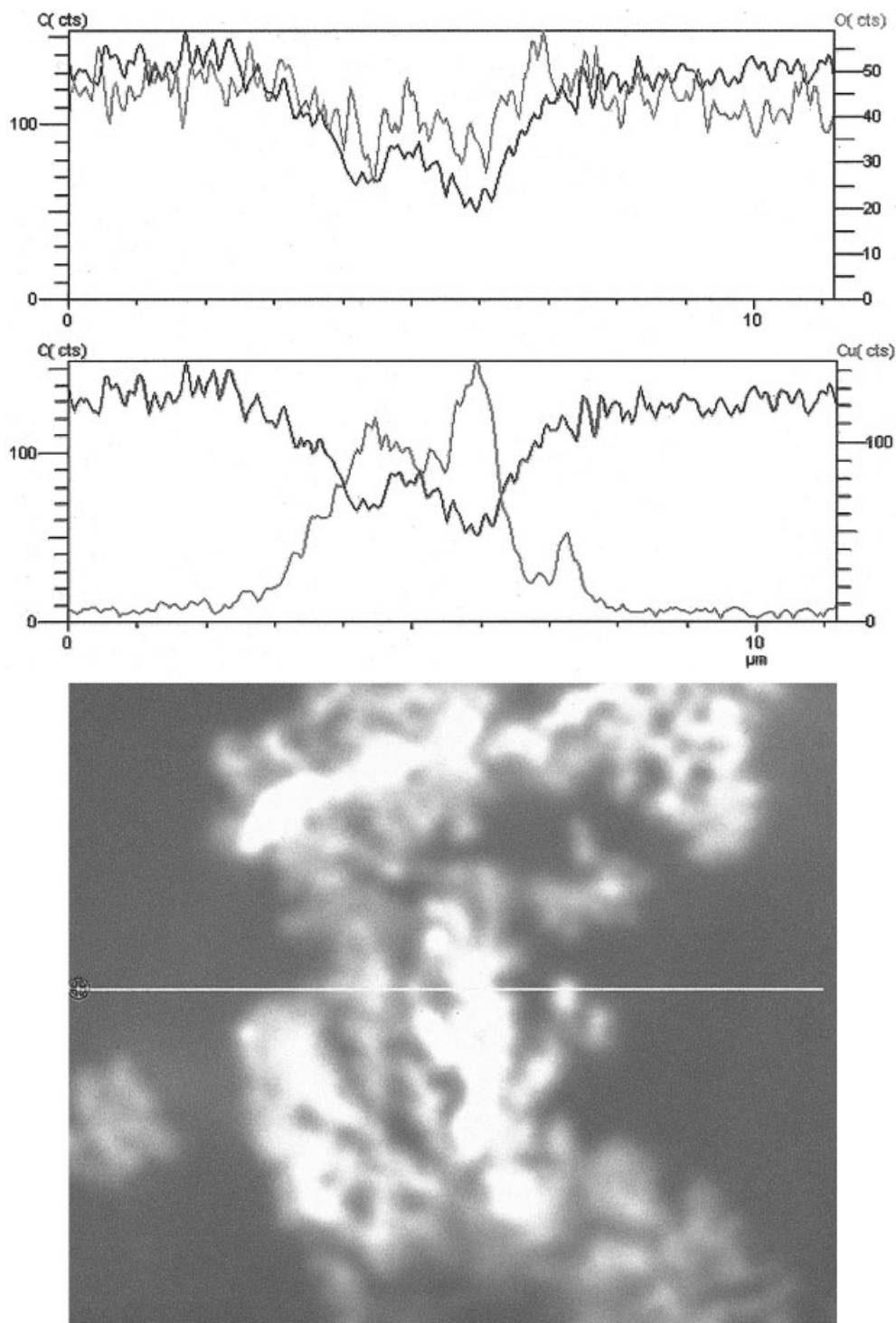


Figure 3 SEM micrograph (bottom) of freshly reduced nylon-6/6,9/ CuCl_2 particles, and EDS diagrams (top) of surface elemental composition distributions along the line shown in the micrograph.

nylon-6/6,9/ CuCl_2 samples (particles) after 2 weeks of storage at ambient environment were subjected to EDS analysis. The SEM micrograph in Figure 3 shows the selected analysis area of the freshly reduced nylon-6/6,9/ CuCl_2 particles. The top diagrams display the surface elemental composition distributions along the line shown in the micrograph. When the line passes

through the bright particles, the main element is copper, along with some carbon and oxygen. At locations other than the particles, there is no presence of copper element, but rather carbon, oxygen, and small amounts of nitrogen (not shown in the diagram). The distributions of carbon and oxygen are correlated to each other. Comparison of the surface elemental com-

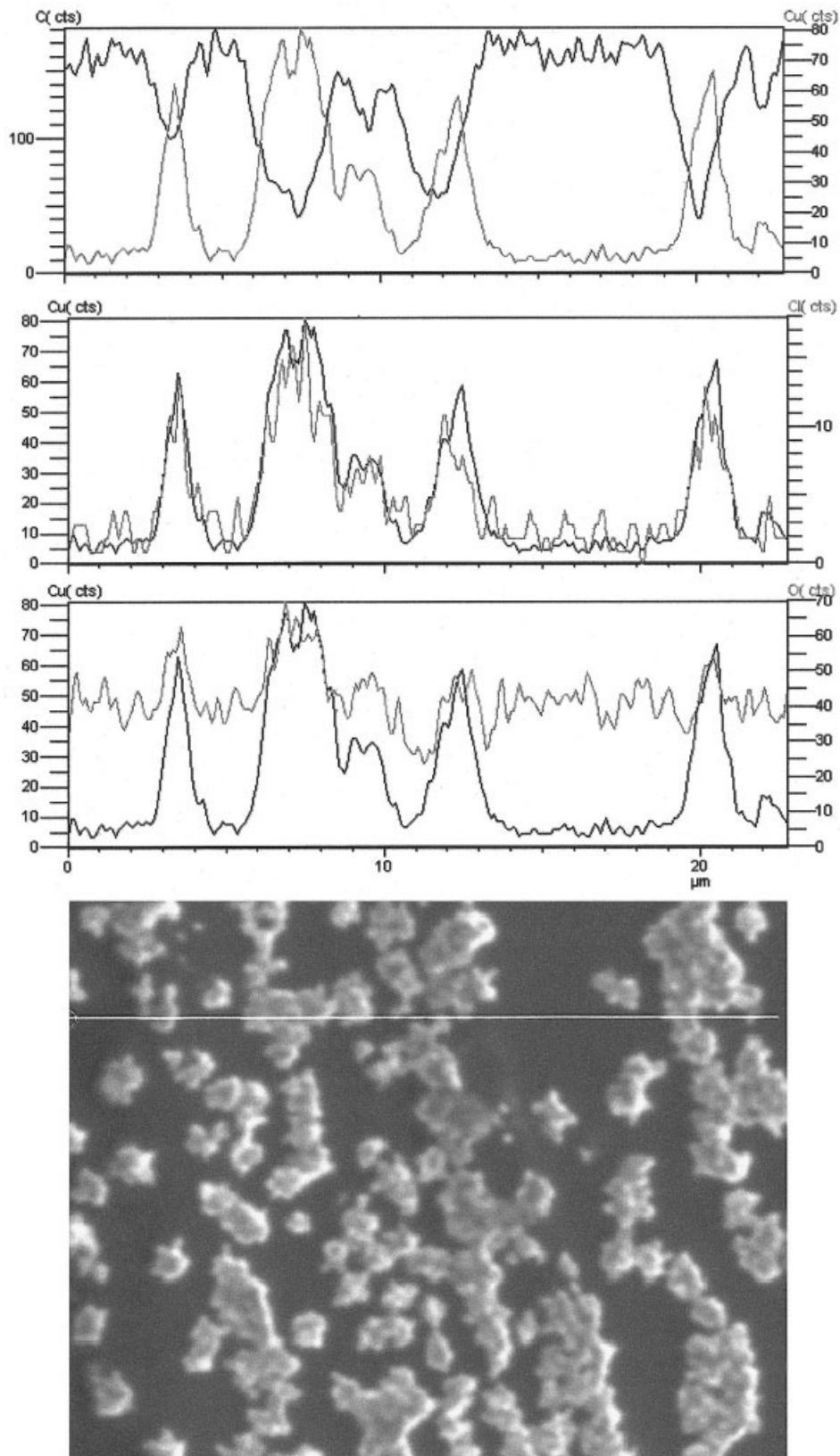


Figure 4 SEM micrograph (bottom) of reduced nylon-6/6,9/ CuCl_2 particles after storage at the ambient atmosphere for 2 weeks, and EDS diagrams (top) of surface elemental composition distributions along the line shown in the micrograph.

position spectra of the bright area and of the background polymer matrix surfaces shows that the oxygen content in both is similar. Hence, the oxygen content detected from the particle is actually from the surrounding polymer matrix; the particles themselves did not contain oxygen and therefore were not oxidized. It is thus concluded that the surface composition of the submicron particles distributed in the reduced sample, as seen in Figure 1c, is a combination of metallic copper and very likely copper hydride, a brown product of the Cu^{2+} reduction by borohydride.^{12,14,15}

Similar results were obtained for the freshly reduced compression molded sample, i.e., the oxygen content of the particle was similar to that of the polymer matrix, indicating that the particles themselves did not contain oxygen. This demonstrates that oxidation has not occurred during molding of the reduced nylon-6/6,9/CuCl₂ particles.

Figure 4 shows a SEM micrograph of reduced nylon-6/6,9/CuCl₂ particles after storage at ambient environment for 2 weeks. The diagrams display the surface elemental composition distributions along the line shown in the micrograph. In contrast to the freshly reduced sample, when the line passes through the particles, the elements found consist mainly of copper, chlorine, and oxygen. The distributions of chlorine and oxygen are correlated to copper, indicating the existence of a certain copper compound. At locations other than the particles, the elements are carbon, oxygen, and nitrogen (not shown in the diagram). Comparison of the surface elemental composition spectra of the particle and of the polymer matrix shows that the oxygen content in the particles is higher than in the surrounding polymer matrix, indicating that the particles have adsorbed large amounts of oxygen from air and probably moisture as well. Also, the appearance of chlorine element implies that some Cl^- ions have migrated from the inner layer to the surface of the particles. Therefore, a certain stable copper compound was formed during storage at ambient environment, resulting in a color change of the samples from brown to green, associated with a gradual conductivity decrease of the samples. Further studies are necessary to improve the chemical resistance and thus conductivity stability during storage.

CONCLUSION

Nylon-6/6,9 copolymer/CuCl₂ particles (<2 μm) were prepared by a soaking method and then reduced by NaBH₄ solution. The reduced particles were compression molded at 160°C, and the bulk volume resis-

tivity obtained was at an intermediate level, $\sim 10^5$ ohm-cm.

CuCl₂ salt coated and also adsorbed upon the surfaces of the nylon-6/6,9 particles. The reduction product, namely copper particles, is distributed along boundaries of the nylon-6/6,9 particles in the bulk compression molded sample in a two-level hierarchy: discrete submicrometer copper particles and nanoscale copper particles (~ 20 – 50 nm), as observed by SEM and TEM, forming a continuous conducting network. The surfaces of the reduced submicrometer particles contain metallic copper, as characterized by EDS. The existence of metallic copper contributes to the bulk conductivity of the samples. Samples stored at the ambient atmosphere gradually absorbed oxygen and moisture, resulting in a color change and a decrease in conductivity.

The reduced compression molded nylon-6/CuCl₂ and nylon-6,6/CuCl₂ particles were insulating, probably owing to the high molding temperatures needed (over 200°C), leading to severe copper oxidation. The nylon-6/CuCl₂ film after reduction is moderately conductive, i.e., 10^5 ohm/sq, because a high temperature molding stage was not necessary.

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