Electrical Conduction of Cu_xS-Treated Films

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Synopsis

Electrical conductivity measurements have been made on Cu_xS-treated PET and nylon 6 films in the temperature region between 20 and 200°C. Cu_xS-treated films have been observed to have two transition temperatures at about 100 and 180°C, respectively. It should be reasonable to consider that the conductivity behavior between 100 and 180°C is attributed to the character of a metastable structure of the cuprous sulfide. Temperature dependence of conductivity of the Cu_xS-treated PET and nylon 6 films was investigated and compared with that of original PET and nylon 6 films. The current–voltage characteristics and time dependence of conductivity of samples were investigated. Conduction mechanism of the Cu_xS-treated films was not dependent on matrix polymers but dependent on Cu_xS crystal, and the conduction is mainly electronic.

INTRODUCTION

During the last decade, much interest has been focused on improvement of electroconductivity of polymers. In the authors' papers,[1-3] it was shown that electroconductive PET and nylon 6 films were obtained by grafting acrylamide (AM) and acrylonitrile (AN) on the films and then introducing Cu_xS. In addition, the physical properties and morphological characteristics of the Cu_xS-treated films were investigated.[4,5]

Cuprous sulfides are produced naturally as "chalcocite," which are known to be brilliant, steel-gray crystallized minerals. The natural cuprous sulfide usually exists in the approximate composition Cu_xS and is a p-type semiconductor in which copper vacancies act as acceptors. Hence, the electrical conductivity of the natural cuprous sulfide depends strongly upon the deficit of copper atoms in the specimen.[6,7] It has been known that a stoichiometric compound Cu_xS has three polymorphic phases; i.e., α-phase (above 470°C), β-phase (470–100°C), and γ-phase (below 100°C).[8,9]

The purpose of this paper is to investigate the electrical properties of the Cu_xS-treated films, since this work has not been studied so far. Another purpose is to estimate the conduction mechanism of the Cu_xS-treated films by considering I–V (current–voltage) characteristics and time dependence of conductivity.

EXPERIMENTAL

Material

Original PET film of 250 μm thickness, supplied by Sunkyung Chem. Co. was used in this work, and nylon 6 chips (Kolon Inc. RV = 2.6–2.8) were dried for 2 h at 105°C in a vacuum oven and a film thickness of 0.3 mm was made of the dried nylon 6 chips using a heat press.[3] Graft polymerization and intro-
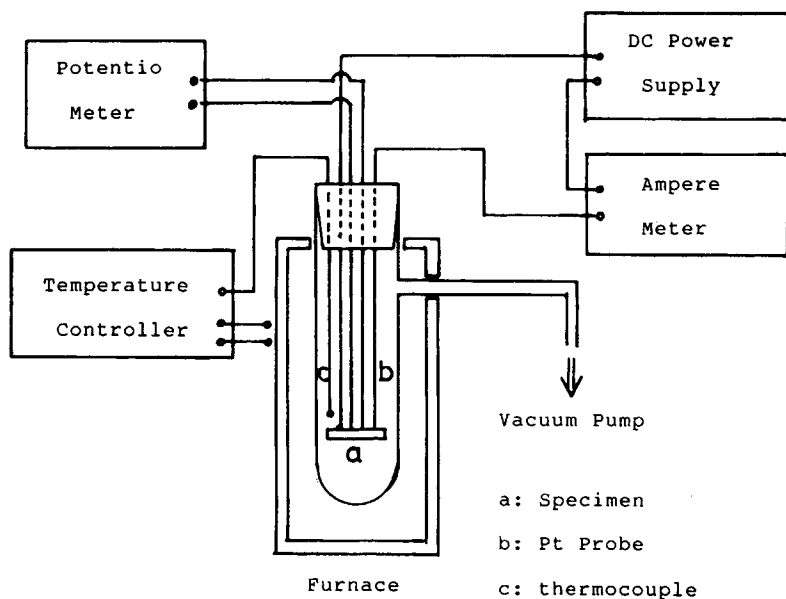
Fig. 1. Schematic diagram of measurement apparatus for electronic conductivity.

ducing of Cu_xS were described in detail in previous papers.[1-3] In the case of PET films, graft yields of AM-g-PET and AN-g-PET were 9.62 and 12.14%, respectively. In the case of nylon films, graft yield of AM-g-nylon and AN-g-nylon were 11.80 and 12.40%, respectively. And when the mole ratio of $CuSO_4$ and $Na_2S_2O_3$ was 1:1, high conductive Cu_xS-treated films were obtained. Each sample was heat treated for 2 h at 105°C and vacuum dried for 24 h.

Temperature Dependence of Conductivity

Electrical conductivity σ of original and grafted films was measured by two probe dc technique in a glass vessel regulated with thermostated silicone oil bath with an electrometer (Keithley 616). Electrical conductivity of the Cu_xS-treated films was measured on 20 × 40 mm samples by the four probe method. The schematic diagram of the apparatus is shown in Figure 1. A given voltage was applied to the two outer contacts, and then the electric current of the circuit and the potential difference between the two inner contacts were individually measured by a Keithley 616 electrometer as an ammeter and by a Keithley 619 electrometer as a potentiometer.

I–V Characteristics

Current–voltage (I–V) characteristics were measured at given temperature by applying dc voltage for 30 min. The conduction current was measured with Keithley 616 electrometer and the dc voltage was supplied with a stabilized dc power supply (ED 245 B). Given temperatures were 20°C (room temperature), 80°C (about glass transition temperature), 105°C (about phase transition

temperature), and 140°C (temperature between two phase transition temperatures).

Time Dependence of Conductivity

Time dependence of conductivity was investigated at given temperature under the applied voltage of 200 mV up to 60 min. All experiments were carried out in a vacuum of 10^{-1} Torr to avoid artificial effects such as partial discharges.

Hall Effect

The electrical conduction type, carrier density and mobility of the Cu$_x$S-treated films were obtained through Hall measurement at room temperature using a van der Pauw method. Cu$_x$S-treated films were cut to sizes of 4 × 4 mm. Fine copper wires were used as the measuring probes of Hall potentials and resistance, which contact with the platinum spots sputtered on the rectangular specimen.

RESULTS AND DISCUSSION

Temperature dependence of conductivity

Figure 2 shows the temperature dependence of the conductivity of original PET, AM-g-PET, and AN-g-PET. It was found that the conductivity of all samples was sharply increased in the vicinity of glass transition temperature (T_g).[10] The sharp increase of conductivity above T_g is the evidence for ionic conduction due to thermal activation.[10] The activation energy of original PET, AM-g-PET, and AN-g-PET was 2.38, 1.44, and 1.33 eV, respectively. On
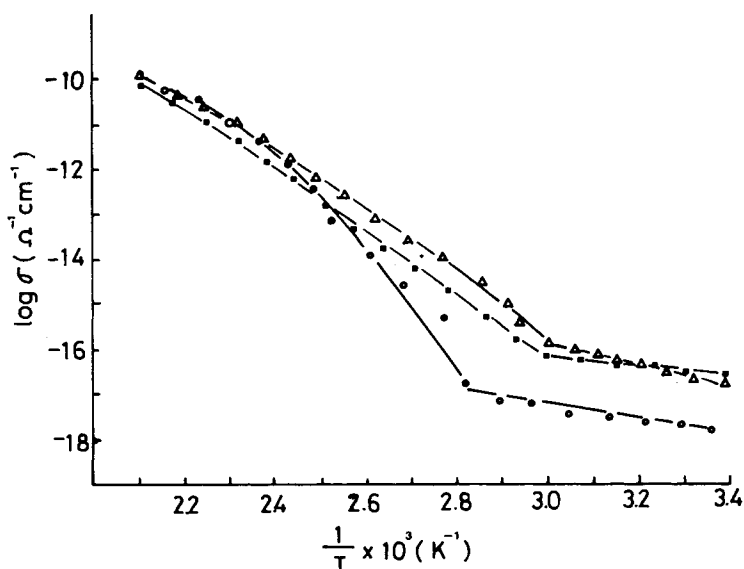
Fig. 2. Temperature dependence of conductivity of original PET (○), AM-g-PET (△), and AN-g-PET (■).
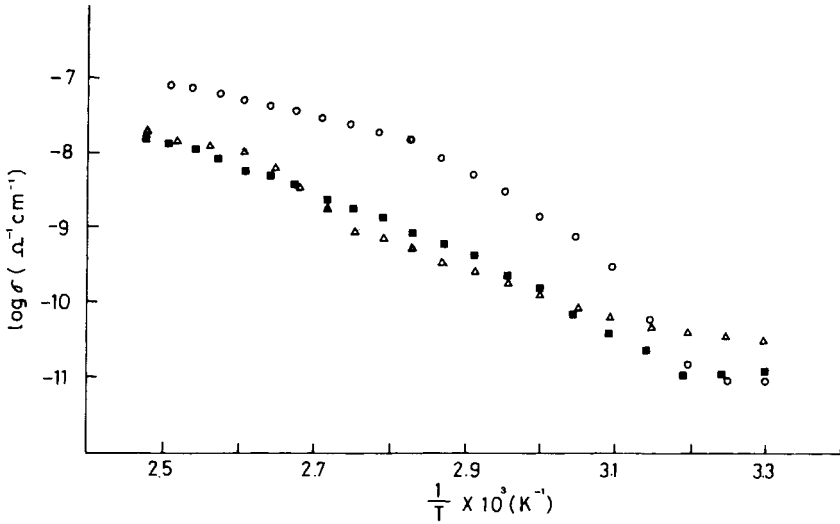
Fig. 3. Temperature dependence of conductivity of original nylon (○), AM-*g*-nylon (△), and AN-*g*-nylon (■).

the other hand, the T_g of the grafted films was decreased slightly and the decrease of T_g is caused by the branching effect due to grafting. This result coincides with DSC data reported by Im et al.[3,4]

Figure 3 shows the effect of temperature dependence on the conductivity of original nylon, AM-*g*-nylon and AN-*g*-nylon. In Figure 3, log σ is plotted at different temperatures. The plot of log σ versus $1/T$ was a continuous
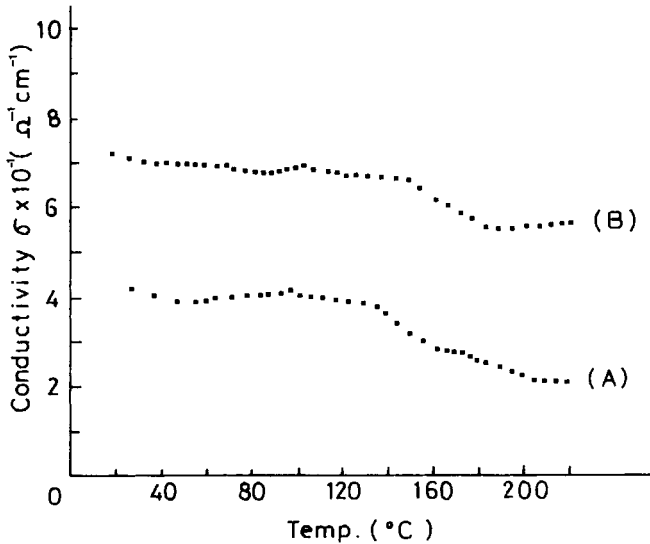

Fig. 4. Temperature dependence of conductivity of Cu$_x$S–AM-*g*-PET (A) and Cu$_x$S–AN-*g*-PET (B).
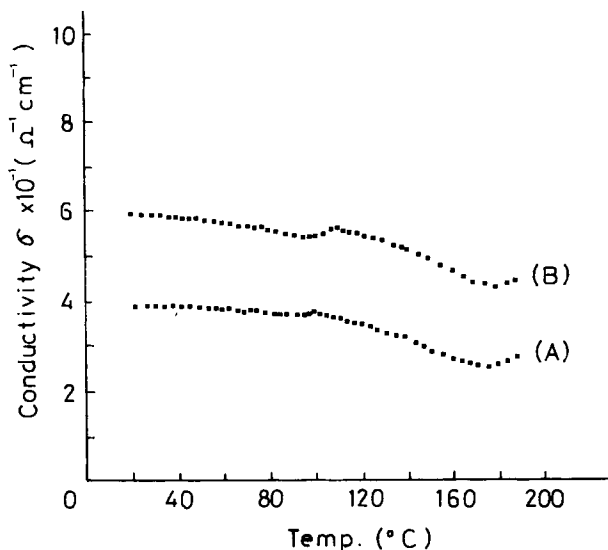
Fig. 5. Temperature dependence of conductivity of Cu$_x$S–AM-*g*-nylon (A) and Cu$_x$S–AN-*g*-nylon (B).

sigmoid curve through which straight lines were drawn in certain temperature ranges. This curve is similar in nature to that of nylon 66 curve proposed by Seanor.[11] The difference of conductivity curves between original nylon and grafted films is considered to change the degree of graft polymerization.

The temperature dependences of conductivity for Cu$_x$S-treated PET and nylon 6 films are shown in Figures 4 and 5, respectively. It is significant that a marked thermal hysteresis occurs in the conductivity curves of each specimen. Such a behavior is usually referred to a phase transition of the material in the temperature region at about 100 and 180°C. It is reported[6] that an abrupt change in conductivity curve at about 100°C is assigned to the transition from γ-phase to β-phase of Cu$_x$S. It must be noted[6] that the transition temperature of Cu$_x$S from γ- to β-phase certainly varied as the deviation from stoichiometry.

In Figures 4 and 5, it was expected from the curve that there was phase transition at about 100°C and there is another change in crystal structure of this compound at about 180°C. Thus, it should be reasonable to consider that the β-phase of the Cu$_x$S-treated films is established at about 180°C and the conductivity behavior between 100 and 180°C is attributed to the character of a metastable structure of the specimen. This behavior is very similar to the characteristic of electrical behavior on the Cu$_x$S crystal. From these results, it is found that the electrical property of the Cu$_x$S-treated films does not depend on the matrix polymers but on the cuprous sulfide crystal.

Conduction Mechanism

In order to estimate the conduction mechanism, the electric current was measured as a function of time under constant voltage. If the ionic conduction
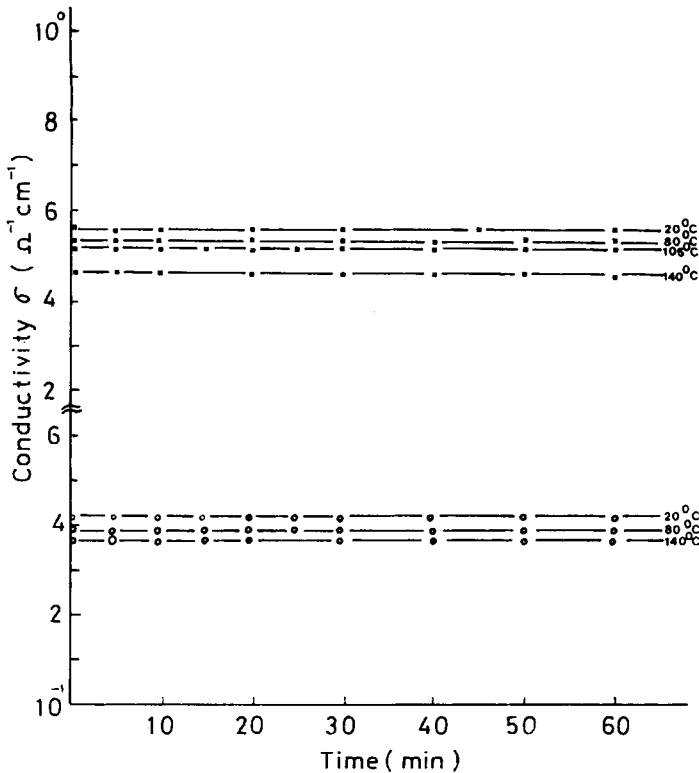
Fig. 6. Time dependence of conductivity for Cu$_x$S–AM-g-PET (■) and Cu$_x$S–AN-g-PET (○) under constant applied voltage (200 mV) at various temperatures.

is dominant, the current would decrease with applied time, as the ionic carriers are eventually purged from the system. It is also known that, for ionic conductions, Ohm's law does not hold but the sine-hyperbolic law becomes valid.[12]

Figure 6 shows the time dependence of conductivity for Cu$_x$S–AM-g-PET and Cu$_x$S–AN-g-PET. The conductivity under the applied voltage of 200 mV is almost constant up to 60 min. The time dependence of the conductivity for Cu$_x$S–AM-g-nylon and Cu$_x$S–AN-g-nylon is shown in Figure 7. The time dependence of conductivity for Cu$_x$S-treated nylon films was similar to that of Cu$_x$S-treated films.

According to many articles,[6-9] ionic current of cuprous sulfide was observed in β-phase but not in α- and γ-phase, and cuprous sulfide was found experimentally to have ionic conductivity with adding an electronic one at the limited range of temperature. Due to the small ratio of ionic conductivity/ electronic conductivity at below 200°C, its total electric conduction (electronic and ionic) will be approximately of electronic nature.

Since the melting points of the PET and nylon samples used were in the vicinity of 240°C, the experiment at above 200°C was not carried out as well as the ionic conduction could not be observed in the temperature range between 20 and 200°C.
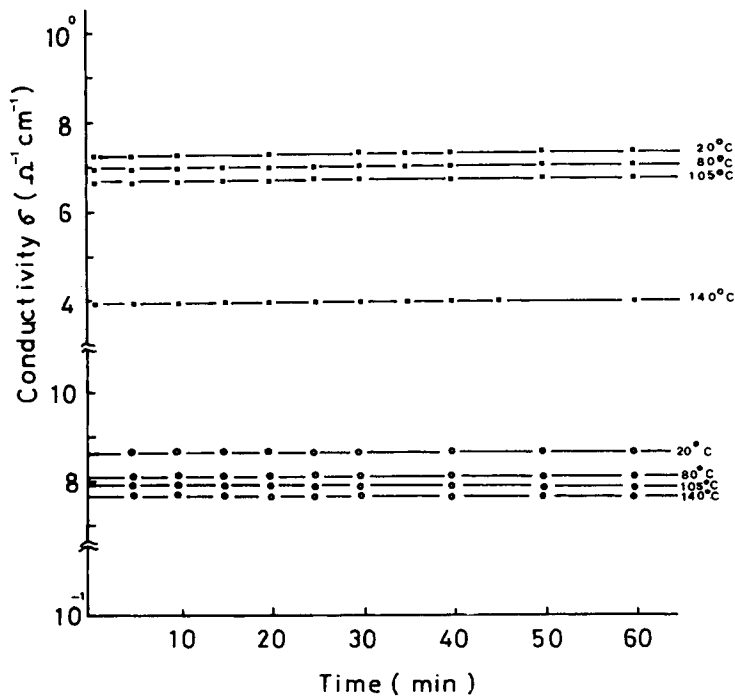
Fig. 7. Time dependence of conductivity for Cu$_x$S–AM-g-nylon (■) and Cu$_x$S–AN-g-nylon (○) under constant applied voltage (200 mV) at various temperatures.
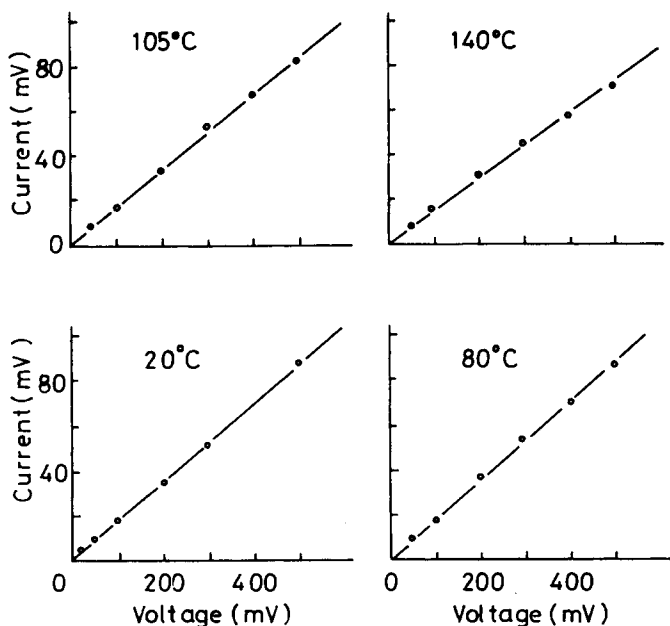

Fig. 8. Dependence of current on applied potential for Cu$_x$S–AM-g-PET at various temperatures.

TABLE I
Hall Effect of Cu_xS-Treated Films

Sample	Transport parameters AVG RHO[a] ($\times 10^{-2}$ Ω cm)	σ_0 ($\times 10^{-1}$ Ω^{-1} cm^{-1})	R_H ($\times 10^{-1}$ cm^3/A s)	μ_H (cm^2/V s)	n ($\times 10^{+19}$ cm^3)	Conductive type
Cu_xS–AM-g-PET	5.892	1.697	3.010	5.11	2.074	p
Cu_xS–AN-g-PET	5.831	1.715	1.253	2.15	4.980	p
Cu_xS–AM-g-nylon	1.073	9.319	2.659	24.79	2.347	p
Cu_xS–AN-g-nylon	2.687	3.722	4.230	15.75	1.475	p

[a]Average resistivity.

Therefore, as is seen in Figures 6 and 7, the electronic conduction is the main process in the Cu_xS-treated films.

In order to support this fact, I–V characteristics were examined. Figure 8 shows that I–V characteristics of Cu_xS–AM-g-PET under given temperatures. It was found that the current was proportional to the applied voltage. That is, the conduction is approximately ohmic. These results strongly suggest that the electronic conduction is the main process in the Cu_xS-treated PET films. For the samples of Cu_xS–AN-g-PET, Cu_xS–AM-g-nylon and Cu_xS–AN-g-nylon, the current is approximately ohmic and electronic conduction is dominant. In Figure 8, the slight decrease of the slope at 140°C may be attributed to the decrease of the current, i.e., the decrease of the conductivity. These results coincide with the decrease of conductivity in β-phase due to the character of a metastable structure of the cuprous sulfide.

The electrical conducting property of the Cu_xS-treated PET and nylon 6 films is considered to be due to a Cu_xS network on the surface of the film. However, the detailed mechanism of the electrical conduction is still unknown, since only a thin layer of Cu_xS–PET or nylon composite is formed on the surface of the PET or Nylon films.

Hall Effect

Table I shows the conductivity type, Hall coefficient R_H, carrier mobility μ_H, and carrier concentration n of the Cu_xS-treated PET and the Cu_xS-treated nylon films. R_H is the Hall coefficient, its sign is positive for p-type semiconductors, negative for n-type semiconductors. The Cu_xS-treated films were p-type semiconductors, and their conductivity was caused by the behavior of electron holes. In the Cu_xS-treated films, carrier mobility μ_H and concentration n were about 2–20 (cm^2/V s), 1–5 $\times$ 10^{19} (cm^{-3}), respectively. These values of μ_H, n, σ_0 are similar to those of the Cu_xS crystals reported by Hirahara.[7]

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