

전기전도성 다공질 나일론 6 필름

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Electroconductive Porous Nylon 6 Film

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요약: 나일론 6필름의 부피 및 표면 전도도를 향상시키기 위하여 다공질 나일론 6필름을 제조하여 P형 반도체로 알려진 Cu_xS 로 처리하였다. Cu_xS 로 처리한 다공질 나일론 6필름의 표면 및 부피 전도도는 각각 10^{10} 과 10^8 정도 증가함을 알 수 있었다. 또한 Cu_xS 로 처리한 다공질 나일론 6필름의 전도도의 온도의존성, I-V 특성 및 시간의존성을 조사한 결과 전도 기구는 모상인 나일론 6에는 의존하지 않고 Cu_xS 결정에 의존하며 전도는 주로 전자전도임을 확인하였다.

Abstract: To improve the volume and surface conductivity of the nylon 6 films, porous nylon 6 film was prepared and then treated with copper sulfide, which is known as the p-type semiconductor. Optimum conditions for the treating of Cu_xS were studied. As a result, the amount of the copper compound, the reducing agent and the sulfur containing compound should influence on the amount of absorbed copper sulfide. The surface and volume conductivity of the Cu_xS -treated porous nylon 6 film were found to be higher by order of 10^{10} and 10^8 , respectively than those of the original nylon 6 film. The morphology of surface and fracture of the Cu_xS -treated porous nylon 6 films was investigated with scanning electron microscope(SEM). Temperature dependence of conductivity of the Cu_xS -treated porous nylon 6 film was investigated. The I-V (Current-Voltage) characteristics and time dependence of samples were observed. Electrical conduction mechanism of Cu_xS -treated porous nylon 6 films was not dependent on matrix polymer but dependent on the 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 previous papers,¹⁻³ it was shown that electroconductive PET and nylon 6 films were obtained by grafting (AM and 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 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°C - 100°C) and γ -phase (below 100°C).^{8,9}

The purpose of this paper is to improve volume conductivity as well as surface conductivity of the Cu_xS -treated porous nylon 6 films, and to pursue the conduction mechanism of the Cu_xS -treated porous nylon 6 films by considering I-V characteristics and time dependence of conductivity.

EXPERIMENTAL DETAILS

Material

Original nylon 6 film with thickness of $15\mu\text{m}$ was supplied by Sam Young Chemical Co., Ltd. The film was Soxhlet extracted with petroleum ether for 8 hrs and dried in vacuum. CaCl_2 (Shin Yang Chemical Co., Ltd.), cupric sulfate (Shinyo Pure Chemical Co., Ltd.), hydroxylamine sulfate (Junsei Chemical Co., Ltd.), and sodium thiosulfate (Hayashi Pure Chemical Co., Ltd.) were used without further purification.

Preparation of Porous Nylon 6 Film

This process can be divided into two stages as follows.^{10,11} (a) The nylon 6 film was dissolved in the solution of MeOH containing 20wt% CaCl_2 and this solution was cast by doctor-knife. (b) The cast film was immersed in water at 50°C for 1 hr and porous nylon 6 film with thickness of $35\mu\text{m}$ was obtained.

Introduction of Cu_xS

Introduction of Cu_xS was carried out according to our previous papers.¹⁻³ The porous nylon 6 film was immersed in a bath with an aqueous solution comprising cupric sulfate (CuSO_4) and hydroxylamine sulfate [$(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$] and was heated at room temperature up to 90°C for adsorption of the monovalent copper ions sufficiently

on it. Then sodium thiosulfate was added to the bath. After heat treatment, the films were rinsed well in cold water and were vacuum dried. Effect of pH of the aqueous solution, concentration of each reaction reagents and reaction time on the introducing of Cu_xS were studied.

Measurement of Surface Resistance and Volume Conductivity

Surface resistance of Cu_xS -treated samples was measured using Multimeter (Keithley 179A) with two probes separated by 10mm. Volume conductivity was measured by two probes d.c. technique with an electrometer. Silver paste was deposited on the both surface of the specimens. Diameter of the electrode was 1 cm.

Temperature Dependence of Conductivity

Surface and volume conductivities σ of original and Cu_xS -treated porous nylon 6 films were measured by four line method with Electrometer (Keithley 6 films were measured by four line method with Electrometer (Keithley 617) and TRMS Multimeter (Keithley 179A). Fig. 1 shows the schematic diagram of the apparatus. The distance of each line, which was made from copper, was 3mm. The measurement of temperature dependence of conductivity have been made in the temperature region between 20°C and 200°C . A heating rate of $1^\circ\text{C}/\text{min}$ was used. If the distance of each line was equal, the conductivity was calculated by the following equation :

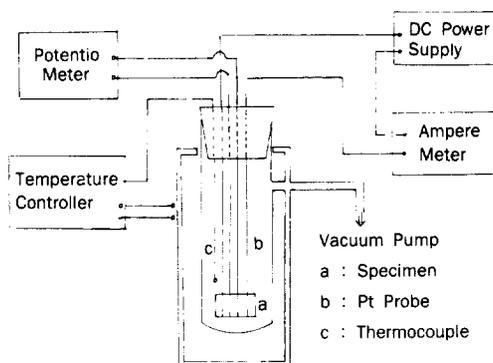


Fig. 1. Schematic diagram of measurement apparatus for electronic conductivity.

$$\sigma = \frac{I}{2\pi S} \cdot \frac{I}{V}$$

where σ is electrical conductivity, I and V are current and voltage, respectively and S is the interprobe spacing.

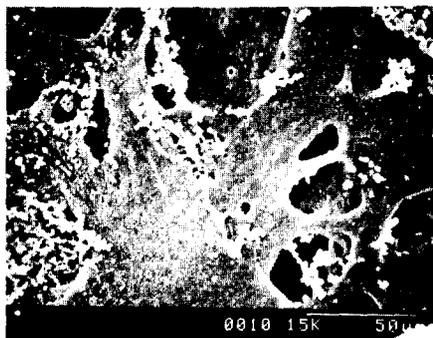
I-V Characteristics and Time Dependence of Conductivity

I-V characteristics were measured at given temperature by applying d.c. voltage from 50 mV to 500mV. Time dependence of conductivity was investigated at given temperatures under the applied voltage of 200 mV up to 60 min.

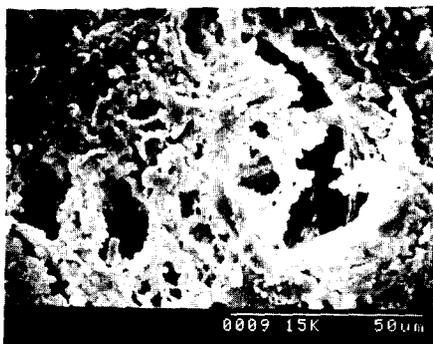
RESULT AND DISCUSSION

Identification of Porous Structure

Fig. 2 shows SEM for surface of the casting



(A) ($\times 600$)



(B) ($\times 1000$)

Fig. 2. SEM for surface of the cast nylon 6 film.

nylon 6 film. The surface structure as shown in Fig. 2 for the casting nylon 6 film can be proved the porous structure. But the porosity can not be calculated because the shape and size of the pore are irregular.

Effect of Reaction Conditions on the Introduction of Cu_xS

The effect of pH of the aqueous solution on the introducing of Cu_xS onto porous nylon 6 film was studied as shown in Fig. 3, since it has been reported¹⁻³ that the pH plays an important role in the absorption of cuprous ion. The resistance falls with increase of the pH up to pH5 and then increases up to pH7. The volume conductivity becomes high with increase of the pH up to pH5 and then becomes low up to pH7. The CuSO_4 concentration dependence of the surface resistance and volume conductivity is shown in Fig. 4. The resistance of the films decreases steadily with an increase of CuSO_4 concentration up to 0.2 M/l, and further decrease was not found. The volume conductivity increases steadily with an increase of CuSO_4 concentration up to 0.2M/l, and then decreases at further concentration. The effect of concentration of hydroxylamine sulfate as a reducing agent on the resistance and volume conductivity is shown in Fig. 5. It can be seen that the resistance of films decreases

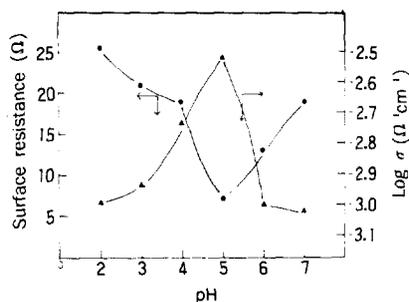


Fig. 3. Volume conductivity and surface resistance at various pH values.

CuSO_4 : 0.2M, reaction temp. : 90°C
 $[(\text{NH}_2\text{OH})_2\text{H}_2\text{SO}_4]$: 0.2M, reduction time : 2 hrs, $\text{Na}_2\text{S}_2\text{O}_3$: 0.2M, total reaction time : 4 hrs, liquor ratio : 1 : 1500

with increasing hydroxylamine sulfate concentration up to 0.2M /l, and then increases upon further increase in hydroxylamine sulfate concentration. The volume conductivity of films increases with increasing hydroxylamine sulfate concentration up to 0.2M /l, and then decreases upon further increase in hydroxylamine sulfate concentration. This means that, beyond this concentration, hydroxylamine sulfate can not act as a reducing agent any more. Fig. 6 shows the sodium thiosulfate concentration dependence of resistance and volume conductivity. it appears that the resistance and

volume conductivity of films are optimum condition at concentration 0.2M /l. This leads to the conclusion that the amounts of the copper compound, the reducing agent, and the sulfur compound should influence the amount of absorbed copper sulfide. Fig. 7 shows $\text{Na}_2\text{S}_2\text{O}_3$ reaction time dependence of resistance and volume conductivity. The resistance and volume conductivity of films were almost independent of $\text{Na}_2\text{S}_2\text{O}_3$ reaction time at reaction time more than three hours.

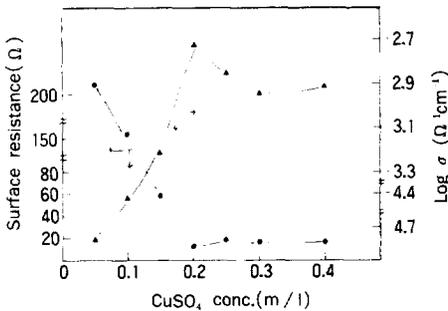


Fig. 4. Volume conductivity and surface resistance at various CuSO_4 concentration. $[(\text{NH}_2\text{OH})_2\text{H}_2\text{SO}_4] : 0.2\text{M} / \text{l}$, reaction temp. : 90°C , $\text{Na}_2\text{S}_2\text{O}_3 : 0.2\text{M} / \text{l}$, reduction time : 2 hrs, liquor ratio : 1 : 1500, total reaction time : 4 hrs, pH : 5.

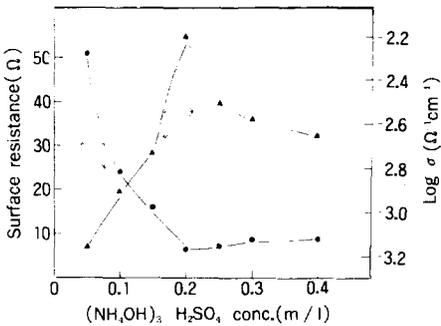


Fig. 5. Volume conductivity and surface resistance at various $[(\text{NH}_2\text{OH})_2\text{H}_2\text{SO}_4]$ concentration. $\text{Cu}_2\text{SO}_4 : 0.2\text{ M}$, reaction temp. : 90°C , $\text{Na}_2\text{S}_2\text{O}_3 : 0.2\text{ M}$, reduction time : 2 hrs, liquor ratio : 1 : 1500, total reaction time : 4 hrs, pH : 5.

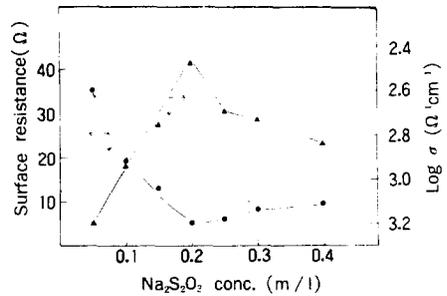


Fig. 6. Volume conductivity and surface resistance at various $\text{Na}_2\text{S}_2\text{O}_3$ concentration. $\text{CuSO}_4 : 0.2\text{ M}$, reaction temp. : 90°C , $[(\text{NH}_2\text{OH})_2\text{H}_2\text{SO}_4] : 0.2\text{ M}$, reduction time : 2 hrs, liquor ratio : 1 : 1500, total reaction time : 4 hrs, pH : 5.

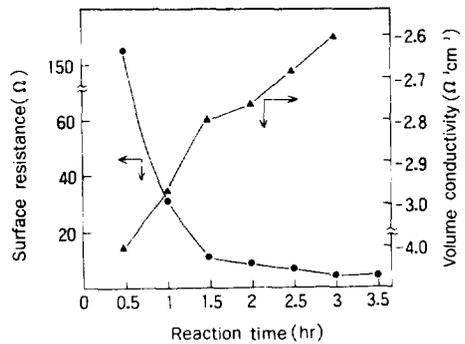


Fig. 7. Volume conductivity and surface resistance at various $\text{Na}_2\text{S}_2\text{O}_3$ reaction time. $\text{CuSO}_4 : 0.2\text{ M}$, reaction temp. : 90°C , $[(\text{NH}_2\text{OH})_2\text{H}_2\text{SO}_4] : 0.2\text{ M}$, reduction time : 2 hrs, liquor ratio : 1 : 1500, $\text{Na}_2\text{S}_2\text{O}_3 : 0.2\text{ M}$, pH : 5.

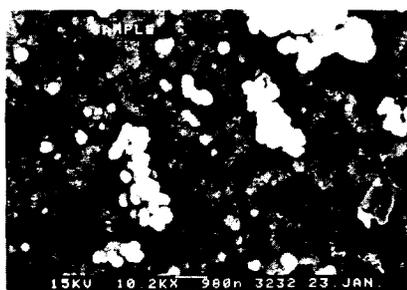
Identification of Cu_xS Introducing of Porous Nylon 6 Films

Fig. 8 shows the SEM for surface (A) and fracture (B) of Cu_xS -treated porous nylon 6 film. In Fig. 8 (A), Cu_xS -treated porous nylon 6 film exhibits many needle-like or whisker-like crystal and porous structure was also shown in the surface of the film. In Fig. 8 (B), we also found the porous structure and it was shown that Cu_xS was introduced into the inner part of the film deeply.

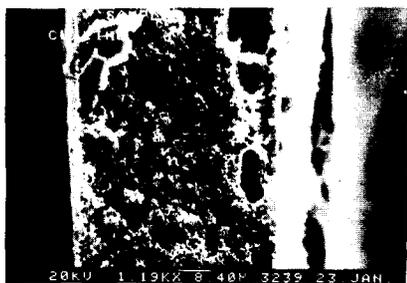
Temperature Dependence of Conductivity

Fig. 9 shows the temperature dependence on the surface conductivity of Cu_xS -treated porous nylon 6 film. It was found that the conductivity of sample was increased in accordance with increasing temperature. In the temperature region between 110°C and 116°C, conductivity of sample is constant. Such a behavior is usually referred⁶ to a phase transition of the material in the temperature region at about 100°C and 180°C. It is reported that the change in conductivity curve at about 100°C is assigned to the transition from γ -phase

to β -phase of Cu_xS . It must be note⁶ that transition temperature of Cu_xS from γ to β -phase certainly varied as the deviation from stoichiometry and temperature dependence of nonstoichiometric copper sulfide changes as a function of deviation from stiochoimetry "x" in the form Cu_xS .⁶ Thus, it should be reasonable to consider β -phase of the Cu_xS -treated films is established at about 180°C and is attributed to the character of a meta-stable structure of the specimen. This behavior is very similar to the characteristics of electrical behavior on Cu_xS crystal. From these results, it is found that electrical property of the Cu_xS -treated porous nylon 6 film does not depend on the matrix polymers but on the cuprous sulfide crystal. Fig. 10 shows the temperature dependence of the volume conductivity for porous Nylon



(A)



(B)

Fig. 8. SEM for surface and fracture of Cu_xS -treated porous nylon 6 film.

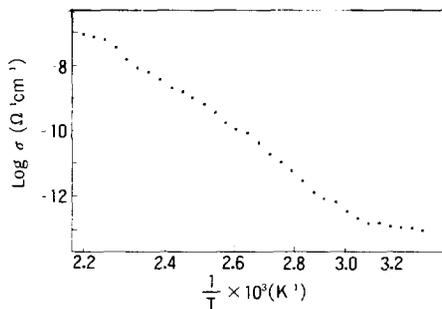


Fig. 9. Temperature dependence of volume conductivity for the cast nylon 6 film.

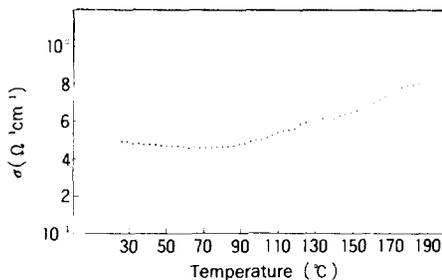


Fig. 10. Temperature dependence of surface conductivity for Cu_xS -treated porous nylon 6 film.

6 film.

In Fig. 10, $\log \sigma$ is plotted at different temperature. The plot of $\log \sigma$ versus $1/T$ was a continuous sigmoid curve through which straight lines were drawn in certain temperature ranges. The curve is similar in nature to that of nylon 66 curve proposed by Seanor.¹² Fig. 11 shows temperature dependence of volume conductivity for Cu_xS -treated porous nylon 6 film. In Fig. 11, $\log \sigma$ is plotted at different temperatures. This behavior is very similar to the characteristics of the surface conduction. The activation energy E_a for motion of copper vacancies was calculated to be 0.12 eV between 25°C and 180°C. The activation E_a for motion of copper vacancies was calculated to be 0.12 eV between 25°C and 180°C. The activation E_a was calculated by following equation :

$$\sigma = \sigma_0 \exp(-E_a / kT)$$

where σ_0 and σ are electrical conductivity at 25°C and 180°C, respectively, E_a is the activation energy of conduction, k is Boltzmann constant and T is the temperature.

Conduction Mechanism

In order to estimate the conduction mechanism, the electric current was measured as a function of time under the constant voltage. If the ionic conduction is dominant, the current would decrease with the applied time, as the ionic carriers are eventually purged from the system. It is also known that, for ionic conductions, Ohm's law

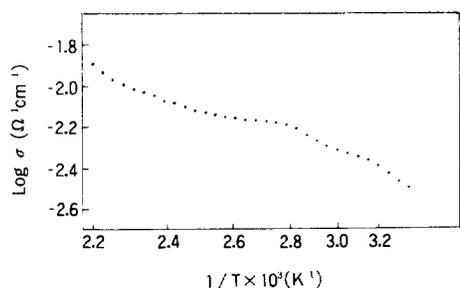


Fig. 11. Temperature dependence of volume conductivity for Cu_xS -treated porous nylon 6 film.

does not hold but the sine-hyperbolic law becomes valid.¹³ Fig. 12 shows the time dependence of conductivity for Cu_xS -treated porous nylon 6 film under given temperature. The conductivity under the applied voltage of 200mV is almost constant up to 60 min. According to many articles,^{6,5} ionic current of cuprous sulfide was observed in β -phase but not in α -phase 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

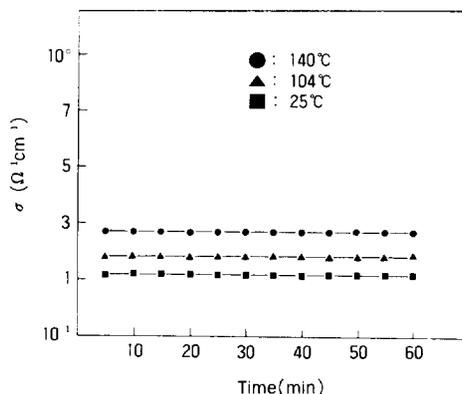


Fig. 12. Time dependence of surface conductivity for Cu_xS -treated porous nylon 6 film.

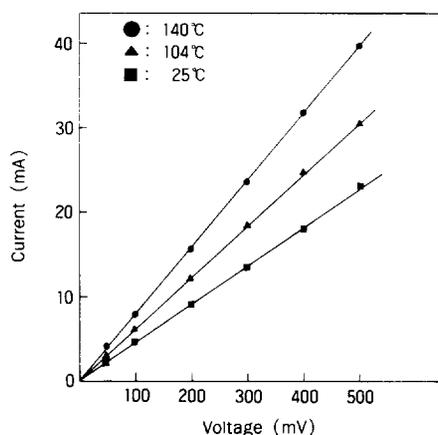


Fig. 13. Dependence of current on applied potential for Cu_xS -treated porous nylon 6 film at various temperature.

conductivity at below 200°C, its total electronic conduction (electronic and ionic) will be approximately of electronic nature. Since the melting point (T_m) of the PET nylon 6 samples used was in the vicinity of 200°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 25°C and 180°C. Therefore, as is seen in Fig. 12, the electronic conduction is the main process in the Cu_xS -treated porous nylon 6 films. In order to support this fact, I-V characteristics was observed. Fig. 13 shows the I-V characteristics of Cu_xS porous nylon 6 film under given temperature. It was found that the current was proportional to the applied voltage. That is, the conduction is approximately ohmic. These strongly suggest that the electronic conduction is the main process in the Cu_xS -treated porous nylon 6 films.

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