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# Effect of Cold-drawing on the Carbonization of Polyimide Films

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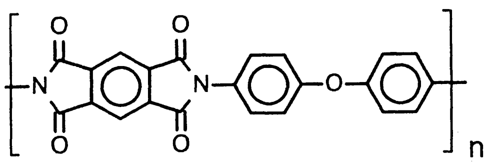
Kapton-type polyimide films that were cold-drawn at the stage of polyamic acids were carbonized. Electrical conductivity of the carbonized films increased proportionally with the draw ratio from 70 S/cm for the undrawn films up to almost 200 S/cm for the 70 % drawn films.

Polyimide films are attracting much attention as a precursor of graphite films because they give highly crystalline graphite films maintaining their original shapes.[1-8] It was revealed that such factors as the chemical structure of polyimide and the orientation of polymer chain along the film surface have remarkable influence on the graphitizability of the resulting carbon films.[3-7] It has been well studied that stretching of polymer films induces higher orientation along the film surface. Stretching of the polyimide film precursor, polyamic acid film, is expected to be effective to obtain polyimide films that are highly oriented along the film surface. It has been preliminary revealed by the present authors that constraint during imidization improves the graphitizability of the resulting carbon films.[8] However, the effect of drawing of the precursor films on the carbonization and graphitization has not been clearly examined yet. In the present work, the effect of drawing of polyimide films on the electrical properties of carbonized films was studied.



Kapton-type polyimide films were prepared from pyromellitic dianhydride and diaminodiphenyl ether. Cold-drawing of the polyamic acid films followed by thermal imidization gives stretched polyimide films that are highly oriented along the drawing direction.[9] The imidized films were then heated up to 1000 °C at the rate of 400 °C/h, and then maintained at the temperature under nitrogen atmosphere for carbonization. The carbon films thus obtained were black and somewhat brittle. Electrical conductivity of the carbon films was measured by a four-terminal method at room temperature.

The effect of exposure time at 1000 °C was examined first. As shown in Fig. 1, the prolonged heating induced higher electrical conductivity of the resulting carbon films, suggesting the formation of higher ordered structure. As a standard experimental condition, precursor films were exposed at 1000 °C for 1 h throughout the following study.

The effect of drawing was examined using polyimide films with various draw ratios. Draw ratio is the ratio of stretching at the stage of polyamic acid. As clearly demonstrated in Fig. 2, the conductivity of the films enhanced proportionally with the draw ratio from around 70 S/cm for the undrawn films up to almost 200 S/cm for the 70 % drawn films. This enhanced electrical conductivity is reasonably attributed to the increase

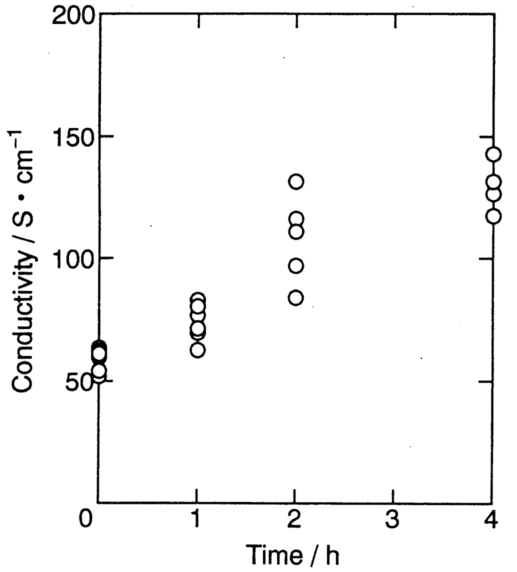



Fig. 1. Conductivity of polyimide films pyrolyzed at 1000 °C for various time period.

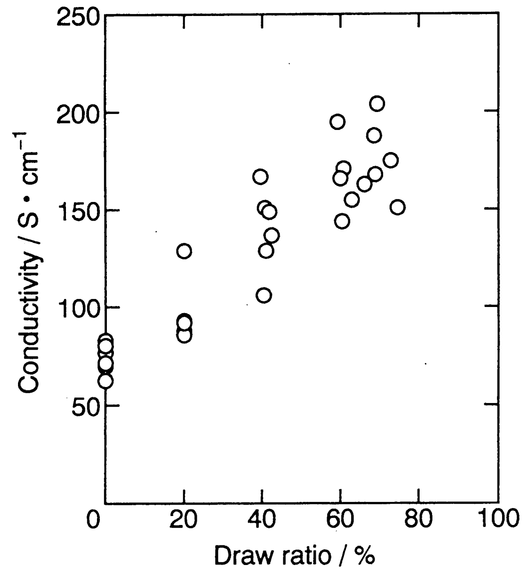



Fig. 2. Conductivity of cold-drawn polyimide films pyrolyzed at 1000 °C for 1 h.

of preferred orientation of hexagonal carbon layers along the film surface which resulted from the orientation of polyimide molecules in the film by cold-drawing.

In the case of rigid-rod polyimide, cold-drawing of polyamic acid followed by imidization is known to increase modulus due to increased orientation.[9,10] On the other hand, little increase of modulus has been observed for flexible polyimides such as Kapton-type polyimide. Relaxation of the orientation during imidization is considered for the little increase of modulus. Our experimental results mentioned above indicate that orientation is retained to considerable extent even after the carbonization of flexible Kapton-type polyimide. Since the effect of drawing on modulus is remarkable and orientation is considered to be higher in the case of rigid-rod polyimide, we are currently examining the pyrolysis of rigid-rod polyimide from which higher effect of drawing on electrical conductivity is expected.

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