Carbonization of Polyimide Films: Effect of Cold-Drawing and Chemical Structure

TSUTOMU TAKEICHI,[1,*] HIDEHIRO TAKENOSHITA,[1] SATOSHI OGURA,[1] and MICHIO INAGAKI[2]

[1]Materials Science, Toyohashi University of Technology, Toyohashi 441, Japan; and [2]Faculty of Engineering, Hokkaido University, Kita-ku, Sapporo 060, Japan

SYNOPSIS

Polyimides of various chemical structures were prepared from pyromellitic dianhydride (PMDA), biphenyltetracarboxylic dianhydride (BPDA), oxydianiline (ODA), and *p*-phenylenediamine (PDA). The cold-drawn polyimide films were prepared and carbonized. The electrical conductivity of the carbonized films enhanced linearly with the draw ratio. The effect of cold-drawing on the electrical conductivity is more remarkable with the rigid polyimides such as PMDA/PDA and BPDA/PDA than the flexible polyimides such as PMDA/ODA and BPDA/ODA. The tendency is well in accord with the effect of cold-drawing on the improvement of modulus of polyimides. With the rigid polyimides, the higher alignment of polymer chain is supposed to be achieved by the cold-drawing. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The pyrolysis of polyimide films is attracting much attention because they give carbon and then high quality graphite films maintaining their original film shapes.[1-8] Polyimides having various chemical structures can be easily prepared from appropriate dianhydrides and diamines, which helps to make clear the factors that determine the graphitizability of polyimide films. From the extensive works in this context, it was proposed[4,5] that graphitizability of polyimide films is determined by such factors as the chemical structure of polyimide, and the orientation of polymer chain along the film surface. Stretching of films of polyimide precursor, polyamic acid, is expected to be effective to obtain polyimide films that are highly oriented along the film surface.[9,10] We have already shown clearly that carbonization of stretched films of Kapton-type polyimide gave carbon films with greatly enhanced electrical conductivity.[11]

It is understood that alignment of polymer chains is much more effective with the rigid polyimide than the flexible polyimide, as is shown from the improvement of modulus.[10] It is expected that the effect of drawing on the graphitizability is much more remarkable with the rigid polyimide than the flexible Kapton-type polyimide we have previously studied.[11] Here, we would like to report the effect of chemical structure on the carbonization of polyimide films with cold-drawing.

EXPERIMENTAL

Reagents

Diamine monomers, *p*-phenylenediamine (PDA) and oxydianiline (ODA), and dianhydride monomers, pyromellitic dianhydride (PMDA), and biphenyltetracarboxylic dianhydride (BPDA), were purified by recrystalization and sublimation. *N*-Methylpyrrolidone (NMP) and *N,N*-dimethylacetamide (DMAc) were purified by distillation.

Preparation of Polyimides

From diamine monomers, PDA and ODA, and dianhydride monomers, PMDA and BPDA, four kinds of polyimide, PMDA/ODA, PMDA/PDA, BPDA/ODA, and BPDA/PDA were prepared. The chemical structures are shown in Figure 1.

* To whom correspondence should be addressed.

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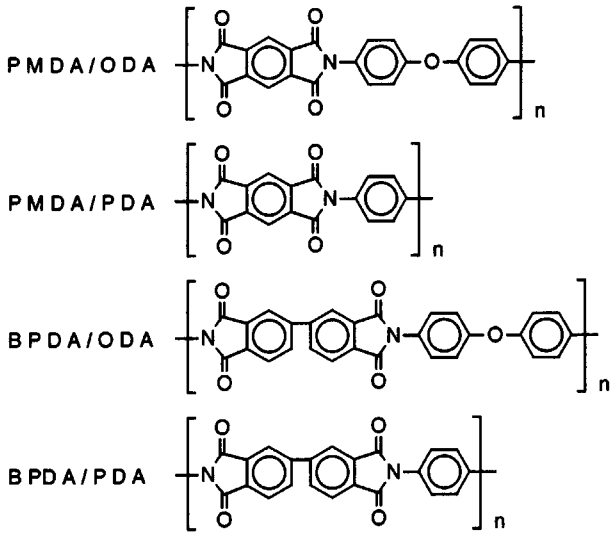

Figure 1 The chemical structure of polyimides.

The following procedures were used for the preparation of polyimide films.[12-14] Into the solution of diamine in NMP or DMAc was added dianhydride at room temperature under nitrogen atmosphere. The mixture was stirred for several hours. The viscous solution was cast on a glass plate and dried at 50°C in vacuo. The polyamic acid films were peeled off the glass plate and heated step-wise up to 300°C for imidization.

Preparation of Cold-Drawn Polyimide Films

Cold-drawn polyimide films were obtained by stretching polyamic acid films at room temperature (r.t.) using IMADA Seisaku-sho Model SV-51-E, followed by thermal imidization as fixed with a frame.

Carbonization of Polyimide Films

The polyimide films were heated to 1000°C at the heating rate of 400°C/h, and then maintained at the temperature for 1 h under N_2. Black-colored carbon films with luster were obtained.

Measurements

The electrical conductivity of carbon films was measured by a four-terminal method at r.t. Viscosities of polyamic acids were measured at 30°C with a Ubbelohde viscometer with 0.5% solutions in NMP or DMAc. Tensile properties of the polyimide films were investigated at r.t. using an IMADA Seisaku-sho Model SV-3 at a rate of 1 mm/min. Dynamic viscoelastic properties of the polyimide films were measured with ORIENTEC Automatic Dynamic Viscoelastometer RHEOVIBRON Model DDV-01FP at 35 Hz at a heating rate of 4°C/min.

RESULTS AND DISCUSSION

Four kinds of polyimides were prepared. Intrinsic viscosities of polyamic acids were above 1.0 dL/g, and molecular weights of the resulting polyimides were high enough to form tough and flexible polyimide films. The polyimide films were carbonized by heating up to 1,000°C, and the electrical conductivity of carbonized films were measured.

First of all, effect of drawing was examined with the Kapton-type polyimide, PMDA/ODA, one of the best known and representative polyimide. As shown in Figure 2, the electrical conductivity of the carbonized films enhanced linearly 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 of preferred orientation of hexagonal carbon layers along the film surface that resulted from the orientation of polyimide molecules in the films by cold-drawing.

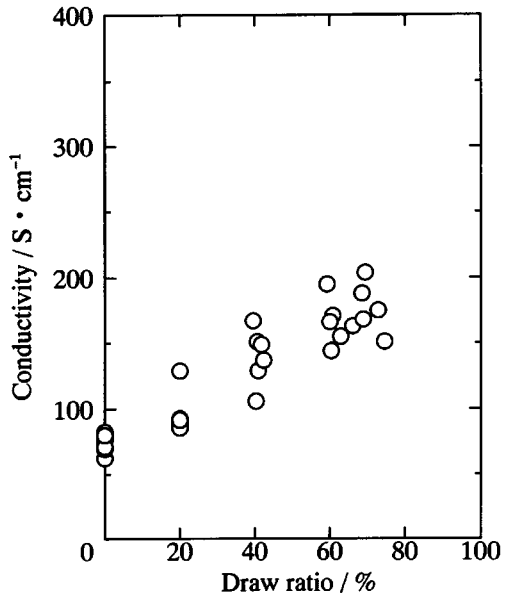

Figure 2 Electrical conductivity of PMDA/ODA films pyrolyzed at 1000°C for 1 h.

In the case of flexible polyimide such as Kapton-type polyimide, little increase of modulus has been observed for the cold-drawn films (Fig. 3). Relaxation of the orientation during imidization is considered for the little increase of modulus.[10] Our experimental results mentioned above indicate that orientation is retained to considerable extent even after the carbonization of flexible Kapton-type polyimide. So, we suppose that the little increase of modulus for the Kapton-type polyimide is due to the partial relaxation of orientation and also due to the intrinsic low value of theoretical modulus because of the flexible ether linkage. On the other hand, conductivity of carbonized films from Kapton-type polyimide is supposed to enhance by cold-drawing because of the retained orientation.

For the rigid polyimide such as PMDA/PDA and BPDA/PDA, the effect of drawing on modulus is much more remarkable and orientation is considered to be higher than that for the flexible polyimides such as PMDA/ODA and BPDA/ODA, as shown in Figure 3. Therefore, we tried to examine the pyrolysis of rigid polyimide, PMDA/PDA, from which higher effect of drawing on electrical conductivity is expected. The electrical conductivity of the carbonized films revealed, as expected, that the effect of drawing is more remarkable than the flexible polyimide, PMDA/ODA. As shown in Figure 4, the

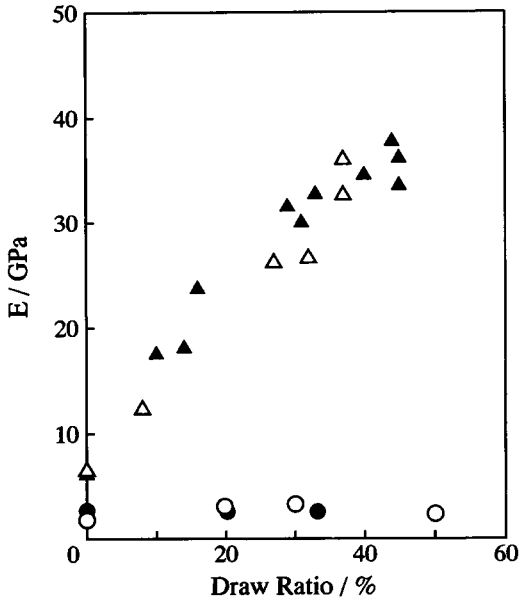

Figure 3 Tensile modulus of various kind of cold-drawn polyimide films. ○; PMDA/ODA, △; PMDA/PDA, ●; BPDA/ODA, ▲; BPDA/PDA.

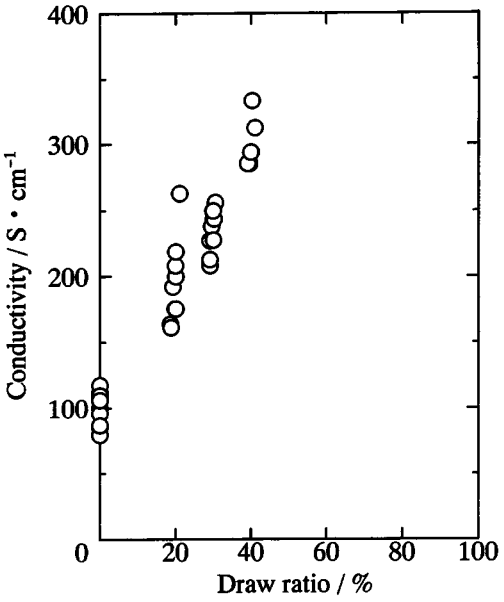

Figure 4 Electrical conductivity of PMDA/PDA films pyrolyzed at 1000°C for 1 h.

conductivity were around 100 s/cm for the undrawn films and around 300 s/cm for the 40% drawn films.

The effect of drawing on carbonization was also examined with the polyimides prepared from BPDA as one component. Electrical conductivity of the carbonized films also increased with drawing. In this case also, effect of drawing was remarkable with the rigid polyimide, BPDA/PDA (Fig. 5), than the flexible polyimide, BPDA/ODA (Fig. 6).

The values in the Figures 2 and 4–6 look scattered to some extent. As a possible reason for the scattering of the conductivity value, ununiformity of the elongation even in a film at the drawing is considered. So, average values of conductivity was replotted for each polyimide in Figure 7. It is clearly seen that the electrical conductivity increases with draw ratio, and that the effect is more remarkable in the rigid polyimide than in the flexible polyimide.

We notice in Figure 7 that, at very low draw ratio, BPDA-based polyimides (BPDA/PDA and BPDA/ODA) give more conductive carbon films than their PMDA counterparts (PMDA/PDA and PMDA/ODA, respectively). The reason can be explained from the glass transition temperature (T_g) and the decomposition temperature (T_d) of the polyimides. BPDA-based polyimides have considerably lower T_g than the PMDA counterparts, but there is little difference in T_d. This makes the BPDA-based polyimides to be exposed longer in the temperature range

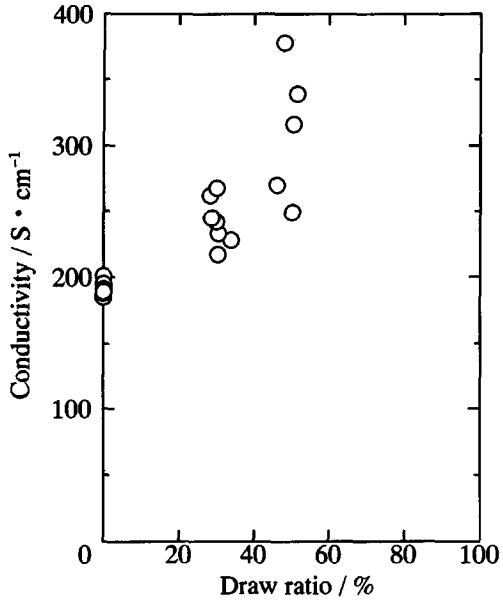

Figure 5 Electrical conductivity of BPDA/PDA films pyrolyzed at 1000°C for 1 h.

between T_g and T_d at the pyrolysis, which helps them to align and orient more than the PMDA counterparts.

The enhancement of conductivity with drawing is, on the contrary, more effective with the PMDA-based polyimides than the BPDA counterparts. This

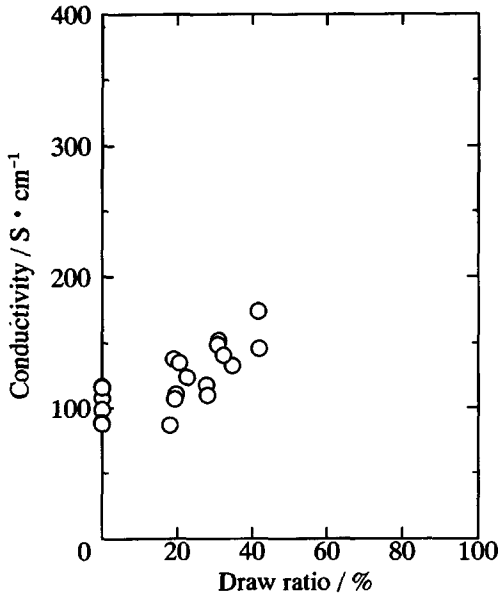

Figure 6 Electrical conductivity of BPDA/ODA films pyrolyzed at 1000°C for 1 h.

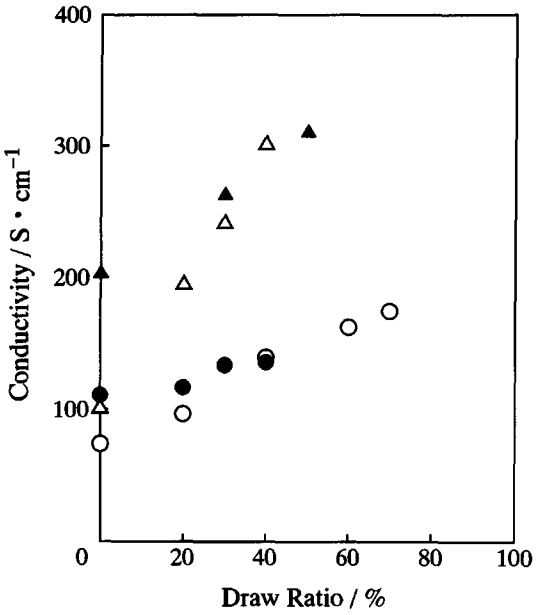

Figure 7 Electrical conductivity of various polyimide films pyrolyzed at 1000°C for 1 h. ○; PMDA/ODA, △; PMDA/PDA, ●; BPDA/ODA, ▲; BPDA/PDA.

is explained by the rigidity of the polyimides. It is understood that the more rigid polymer is more easily align and orient than the less rigid polymer. Apparantly, PMDA-based polyimides are more rigid than the BPDA counterparts, making the effect of cold-drawing more remarkable.

In conclusion, it was clearly demonstrated that higher alignment of polymer chains by cold-drawing was achieved with the rigid polyimides giving carbon films with much enhanced electrical conductivity. Even with the flexible polyimides, alignment of polymer chains was confirmed, though smaller than the rigid polyimides.

We are currently working on the clarification of the nature of alignment of polymer chains and the graphitizability of the aligned polyimide films.

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REFERENCES

1. A. Buerger, E. Fitzer, M. Heym, and B. Terwiesch, *Carbon*, **13**, 149 (1975).
2. Y. Hishiyama, S. Yasuda, A. Yoshida, and M. Inagaki, *J. Mater. Sci.*, **23**, 3272 (1988).

3. M. Inagaki, K. Sakamoto, and Y. Hishiyama, *J. Mater. Res.*, **6,** 1108 (1991).
4. M. Inagaki, L.-J. Meng, T. Ibuki, M. Sakai, and Y. Hishiyama, *Carbon,* **29,** 1239 (1991).
5. M. Inagaki, T. Ibuki, and T. Takeichi, *J. Appl. Polym. Sci.,* **44,** 521 (1992).
6. M. Inagaki and Y. Hishiyama, *J. Mater. Res.,* **7,** 1174 (1992).
7. Y. Hishiyama, A. Yoshida, Y. Kaburagi, and M. Inagaki, *Carbon,* **30,** 333 (1992).
8. M. Inagaki, M. Sato, T. Takeichi, A. Yoshida, and Y. Hishiyama, *Carbon,* **30,** 903 (1992).
9. M. Kochi, T. Uruji, T. Iizuka, and R. Yokota, *J. Polym. Sci.: Part C: Polym. Lett.,* **25,** 441 (1987).
10. M. Kochi, R. Yokota, T. Iizuka, and I. Mita, *J. Polym. Sci.: Part B: Polym. Phys.,* **28,** 2463 (1990).
11. T. Takeichi, H. Takenoshita, S. Ogura, and M. Inagaki, *Chem. Lett.,* **1993,** 657.
12. T. Takeichi, H. Date, and Y. Takayama, *J. Polym. Sci.: Part A: Polym. Chem.,* **28,** 1989 (1990)
13. T. Takeichi, H. Date, and Y. Takayama, *J. Polym. Sci.: Part A: Polym. Chem.,* **28,** 3377 (1990)
14. T. Takeichi, N. Takahashi, and R. Yokota, *J. Polym. Sci.: Part A: Polym. Chem.,* **32,** 167 (1994).

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