Alumina Fibers from Poly[((3-Ethoxypropanoyl)oxy)aloxane]

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Synopsis

Alumina fibers were obtained from the poly[((3-ethoxypropanoyl)oxy)aloxane] (P-3EPA) by using a polymeric precursor technology. The rheological properties of the concentrated solution of P-3EPA related to the extrusion and spinning processes have been investigated to determine the processability into fine filaments. Thirty weight percent P-3EPA dissolved into toluene showed an excellent spinnability and fine filaments of 20–30 μm in diameter were easily obtained. The phase changes during the sintering of the fiber were studied with wide-angle X-ray diffraction and were shown to be strongly related to the mechanical properties of the fiber. Further the addition of the ethyl silicate (ES) as a sintering agent which prevent the crystal growth of Al_2O_3 was found to be effective to improve the mechanical properties of the alumina fiber.

INTRODUCTION

Ceramics fibers have been recently attracting interest because of their superior tensile and thermal properties. From the viewpoint of polymer science and engineering, the use of polymeric preceramic materials seems to be most interesting for preparing ceramics fibers. For instance, the pioneering work by Ezekiel and Spain[1] in 1967 had revealed this procedure to be fruitful in obtaining graphite fibers. Yajima's success[2] in 1978 has enhanced this polymeric precursor technology: He and his co-workers had demonstrated that polycarbosilanes and polyborosiloxanes could be utilized as the processable precursors for the fibers of silicone carbide. The inorganic polymers having the $-Al-O-$ backbone can be possibly converted into alumina by pyrolysis. Recently, the synthesis of a novel series of poly[(acyloxy)aloxane]s has been developed in our laboratory.[3-5] One of these is poly[((3-ethoxypropanoyl)oxy)aloxane] (P-3EPA) prepared by two or three stage reactions of triethyl aluminum with water and 3-ethoxypropanoic acid. This stable preceramic polymer is soluble in various common organic solvents so that it can be solution processable into fibers. The fibers can be pyrolyzed and sintered into ceramics.

In the solution spinning process, first of all, the polymer solution has to be extruded through a spinneret. The solution should be viscous that it can keep a cylindrical shape against the gravity, and less elastic to be extruded through a spinneret smoothly. However, the solution has to be elastic enough to be spun into fine filament continuously.[6] These factors are all related to the rheological properties of the solution.

Secondly, the preceramic fibers thus obtained must be pyrolyzed and sintered into ceramic fibers keeping their shape. The conditions of such heat treatment are known to affect the mechanical properties of the resultant ceramic fibers

obtained through the phase transitions. The addition of some sintering agents which prevent the resultant ceramics crystalline structure from overgrowth may be one of the important factors.

The prime object of this study is to investigate the rheological properties of the concentrated solution of P-3EPA which has inorganic backbone to determine the processability into fine filaments and to compare these properties with those of organic polymers. In addition, changes in the properties of the fibers during pyrolysis and sintering, and the effect of sintering agent will be discussed.
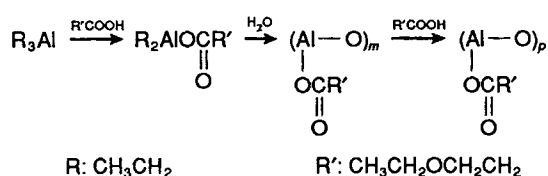
EXPERIMENTAL

Materials

Triethylaluminum (TEA) was provided by Toyo-Stoffer Chemical Corp. (Tokyo, Japan) and was used without further purification. Both tetrahydrofuran (THF) and toluene (TOL) were distilled over sodium metal under the nitrogen atmosphere. 3-Ethoxypropanoic acid (EPA) was supplied by Tokyo-Kasei Kogyo, Ltd. (Tokyo, Japan), and purified by distillation under a reduced pressure. Oligo-ethyl silicate (ES) was supplied by Colcoat Ltd. (Tokyo, Japan) and used as received.

Synthesis of Poly [((3-Ethoxypropanoyl)oxy)aloxane]

Poly[((3-ethoxypropanoyl)oxy)aloxane] (P-3EPA) was synthesized according to the procedure reported by one of the authors[4] through three-stage reaction of TEA with EPA and water

$$R_3Al \xrightarrow{R'COOH} R_2AlOCR' \xrightarrow{H_2O} (Al-O)_m \xrightarrow{R'COOH} (Al-O)_p$$

$$\underset{O}{\overset{\|}{}} \quad \underset{\underset{O}{\overset{\|}{OCR'}}}{|} \quad \underset{\underset{O}{\overset{\|}{OCR'}}}{|}$$

R: CH$_3$CH$_2$ R': CH$_3$CH$_2$OCH$_2$CH$_2$

Scheme 1

A solution of 23.6 g (0.2 mol) of EPA in 16.8 mL of TOL was added dropwise to the solution of an equimolar amount of TEA in 81 mL of TOL at −20°C. After the addition was over the solution was kept stirred at room temperature for 1 h, to complete the reaction. Then a solution of 3.6 g (0.2 mol) of H$_2$O in 36.4 mL of THF was added dropwise at −20°C. After the addition, the product was kept stirred for 2 h and then allowed to stand at room temperature overnight. To this solution, 11.8 g (0.1 mol) of EPA in 8.4 mL of THF was added and stirred thoroughly at 70°C. Again this solution was allowed to stand at room temperature overnight. The product was precipitated in a large excess of *n*-hexane, and then dried at 50°C under vacuum.

Preparation of Concentrated Solutions of P-3EPA in Toluene

Twenty to 50 wt % of P-3EPA were dissolved in toluene with 1 wt % of EPA. Twenty and 30 wt % solutions were prepared at 70°C and 40 and 50 wt % solutions were prepared at 100°C using an autoclave. Two solutions which contain some amount of ES as a sintering agent were also prepared. After being sintered into inorganic materials, these samples involve 10 and 20 wt % of Si relative to Al (denoted as 1/18 ES/P-3EPA and 1/8 ES/P-3EPA, respectively).

Measurements

All the experiments related to the rheological properties of the concd solution, linear viscoelasticity, and extrusion experiments were carried out mainly for the solutions which contain no sintering agent.

Linear Viscoelasticity

Linear viscoelasticity G', G'', and η^* of P-3EPA concd solutions in toluene were measured with a mechanical spectrometer (RMS-605, Rheometrics, U.S.A.) in a cone-plate mode at room temperature.

Extrusion Experiments

Equipment for the extrusion experiments consists of a cylinder of 15 mm in inner diameter, a piston of 15 mm in diameter, and a die of 1.0 mm in diameter and L/D of 8. This system was attached to the tensile testing machine (TOM-200D, Shinko Tsushin Kogyo, Japan) to obtain a constant extrusion rate. The conditions of extrudate were observed at various extrusion rates.

Thermal Analysis

DTA and TGA measurements were carried out with DT-30 and TG-30 (Shimazu, Japan), respectively, at a heating rate of 10°C/min in the presence of oxygen. These conditions were same as those used for the pyrolysis and sintering of the fibers.

Wide Angle X-ray Scattering (WAXS)

Wide angle X-ray scattering (WAXS) was recorded on an X-ray diffractometer (Rigaku Denki, Japan) with Ni-filtered CuK_α radiation (operated at 40 kV and 27.5 mA).

Tensile Measurements of Fiber

Because of the very brittle character of the specimen, test pieces were made as follows[6]: A single filament was placed in the center of a paper frame of 20 × 30 mm, having a square window of 10 × 10 mm and then fixed with an ethyl α-cyanoacrylate adhesive. After both upper and lower portions of the frame were grasped in the jaws of the tensile tester (TOM-200D, Shinko Tsushin, Tokyo, Japan), both of the side edges of the paper frame were carefully cut by

scissors. Then the tensile measurements were made as usual at a crosshead speed of 0.5 mm/min.

Dry Spinning

A concd solution of 3-EPA (dope) was loaded in a syringe equipped with a capillary (3 mm length, 0.7 mm inner diameter) and degassed as complete as possible. The syringe was fixed on a laboratory feeding instrument (JP-100G, Furue Science, Tokyo, Japan) and the solution emerged at a constant rate. The extrudate was passed through a drying column kept at 70°C and taken up on a roll at 32 m/min. The filament thus obtained was then dried completely in an air oven at 100°C.

Pyrolysis of the Precursor Filament

The precursor filament was cut into 100 mm long pieces and inserted into an alumina tube of 1 mm in inner diameter. Several of these were placed on a alumina boat and pyrolyzed in a tubular electric furnace under an air atmosphere. The temperature of the furnace was raised at a constant rate of 10°C/min.

RESULTS AND DISCUSSION

Linear Viscoelasticity

Elastic modulus G' and loss modulus G'' of 20–50 wt % solution were plotted on Figures 1 and 2, respectively, as a function of frequency ω. log G' vs. log ω and log G' vs. log ω curves seem to be linear at low ω region with slopes of 2 and 1, respectively. These are very similar to those of the concd solutions and
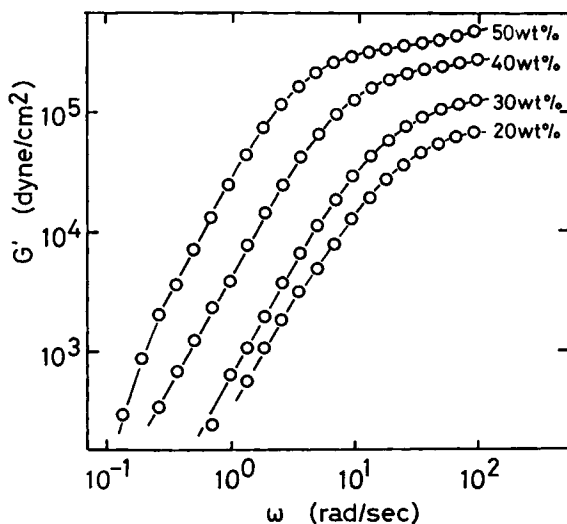

Fig. 1.   Elastic modulus G' of the P-3EPA concd solutions as functions of frequency ω and concentration.
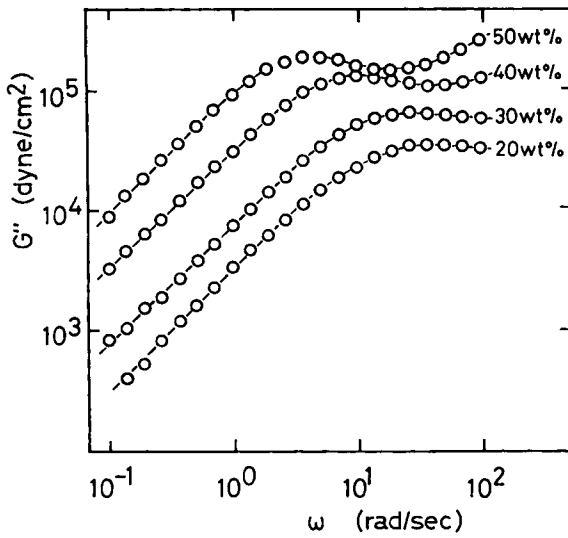
Fig. 2. Loss modulus G'' of the P-3EPA concd solutions as functions of frequency ω and concentration.

melts of the conventional organic polymers.[7] At high regions both log G' and log G'', especially those of 40 and 50 wt % solutions, level off, showing a rubbery plateau. log G' and log G'' curves cross at a ω region of 10^0–10^2 (s^{-1}). These results indicate that the molecular weight of P-3EPA employed is higher than the critical one for entanglement even for 20 wt % solution, which is one of the most important factors for spinnability.

The complex viscosity η^* was calculated from G' and G'' and plotted in Figure 3 as a function of log ω. At a low ω region, η^*'s are constant, showing a Newtonian
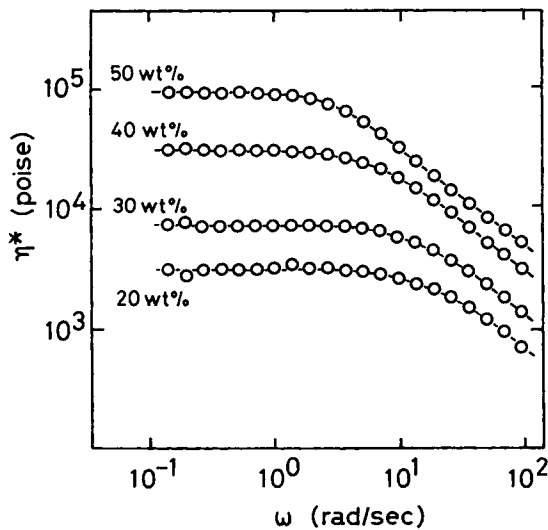
Fig. 3. Complex viscosity η^* of the P-3EPA concd solutions as functions of frequency ω and concentration.

behavior and tend to decrease with increasing ω at high ω, a strain rate softening behavior. The zero shear viscosities η_0 are proportional to the 4.9th power of the concentration for 30–50 wt % solutions and the 2.2nd power of the concentration for 20 and 30 wt % solutions.

It may be considered that 20 wt % solution of 3-EPA is close to the critical concentration for entanglement so that the concentration dependency of η_0 decreases in this concentration range. Unfortunately, it was almost impossible to determine the exact rheological properties of more dilute solutions because of the vaporization of solvent.

Extrusion

There are two types of the extrudate instabilities observed, depending upon the extrusion rate and the concentration of the polymer. These are mapped on Figure 4. When the liquids emerges from a die, the extrudate is subject to the gravity and the diameter decreases. Liquid rods of small diameter possess large external surface relative to their volume, and surface tension tends to play a major role in the behavior of such rods especially if the liquid has a low viscosity.[8] Indeed the extrudates of low concentrated P-3EPA solution tended to break into droplets (Capillarity) especially at low extrusion rate. At high extrusion rate, the diameter decreased rather slowly and fine extrudate resulted.

When the concentration of the polymer is increased, both the viscosity and the entanglement density which give rise to higher elastic character in the solution increases; the extrudate tends to have irregular surface and cross section (solution fracture) especially at high extrusion rate.[9] Such a phenomenon was observed at any extrusion rate examined ($\dot{\gamma}_a$ = 150–900 s^{-1}) for 40 and 50 wt % solutions. The solutions which contain ES showed the solution fracture at a slightly lower concentration and an extrusion rate.
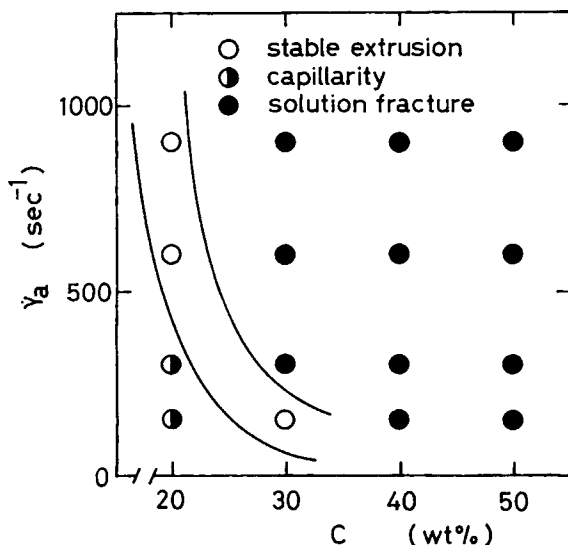

Fig. 4. The map representing the stable extrusion condition: (O) stable extrusion; (◑) capillarity; (●) solution fracture.

Both of these phenomena, capillarity and solution fracture, limit the spinnability. Although the onset of the solution fracture is known to depend on the shape and the dimension of the die through which the solution emerges,[10] the map obtained for the die used can be used to determine the extrusion rate for fiber spinning by using other extrusion devices. For the dry spinning, a die with smaller inner diameter (0.7 mm) was used and the extrusion rate was 0.27 cm^3/min, which corresponds to the apparent shear rate of 130 s^{-1}. The concentrations determined for the dry spinning were 35 wt % for the solution without ES and 30 wt % for that with ES. Under these extrusion conditions, the extrudates were smooth and fine filaments of 20–30 μm were easily obtained.

Thermal Analysis of Precursor Fibers

Typical DTA and TGA curves for precursor fibers without ES are shown in Figure 5. A drastic weight loss between 200 and 320°C and a mild one between 320 and 600°C recorded in TGA trace correspond to the exothermic peaks in DTA curves, indicating a strong peak between 200 and 320°C and a broad one between 320 and 600°C. These data probably imply that the thermal decomposition of the polymer starts at about 200°C, and then the secondary decomposition of organic residue between 320 and 600°C.

In the same conditions as used for the thermal analysis, the precursor fibers were pyrolyzed in the electric furnace up to 1400°C. Fibers pyrolyzed up to 900°C were still black in color, indicating the contamination by the residual carbon, and these pyrolyzed up to over 1000°C turned to be white. On the other hand, the fibers with ES pyrolyzed even up to 1200°C were still black probably because of the formation of the silicon carbide, although it was not detected by WAXS.
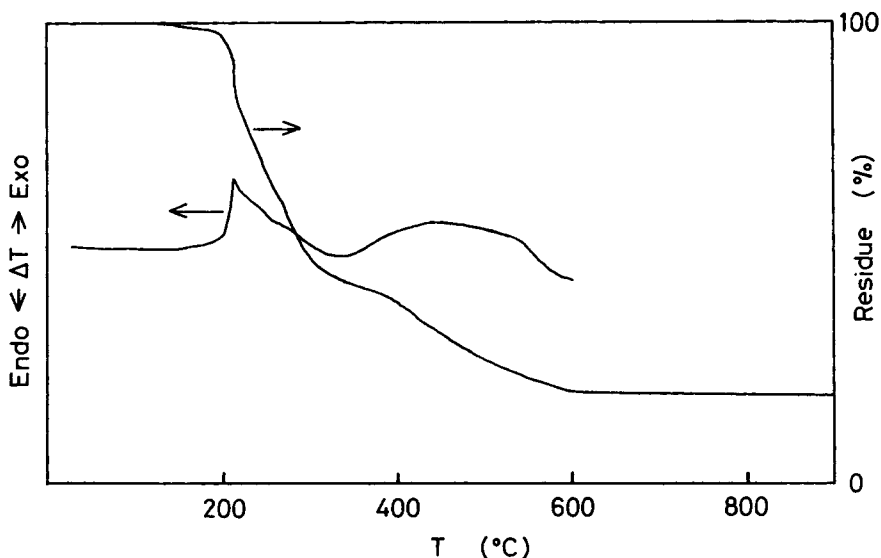

Fig. 5.   DTA and TGA curves for P-3EPA fibers without ES.

Sintering of the Fibers

It is known that the sintering process of the precursor polymers to ceramics passes through various phase transitions.[11] Among them, the crystalline transitions which occur during the sintering of P-3EPA were studied using WAXS. Figure 6 shows the X-ray diffraction patterns of P-3EPA fiber without ES pyrolyzed and sintered up to various temperatures. There is only a broad peak at $2\theta = 10$–$30°$ for the precursor fiber, indicating the amorphous state. Crystallization seems to occur when the fiber was heated below 200°C, where we found a small decrease in weight in TGA section, as evidenced by a sharp peak at $2\theta = 17$–$25°$. WAXS patterns from the fibers pyrolyzed up to 400, 600, and 800°C do not show any crystalline peaks. At 1000°C, a weak peak at $2\theta = 67°$ which is assigned to be γ-alumina[12] began to be observed, and then, at 1100°C, there were observed only peaks of γ-alumina. At 1200°C, both of the peaks of γ-alumina and α-alumina were recorded in the WAXS diagram. Further heating resulted in the disappearance of γ-phase and the growth of α-alumina. These phase transitions, especially γ–α transition, have a great influence on the mechanical properties of the fiber.

Figures 7 and 8 show the changes in the mechanical properties of the fiber with pyrolysis and sintering temperature. The mechanical properties of the fiber pyrolyzed up to 200°C were slightly higher than those of precursor fibers, probably due to the crystallization of the organic side groups as was detected by WAXS. Then once the mechanical properties decreased to the minimum at 400°C, reflecting the decomposition of the organic side groups, these tended to
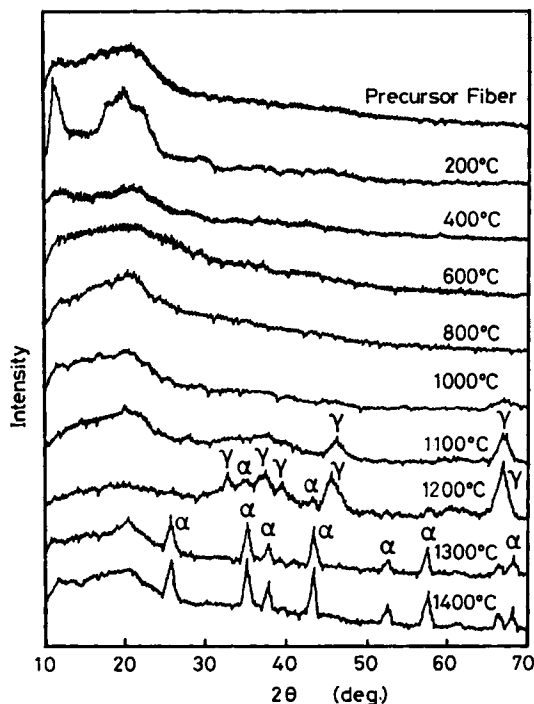

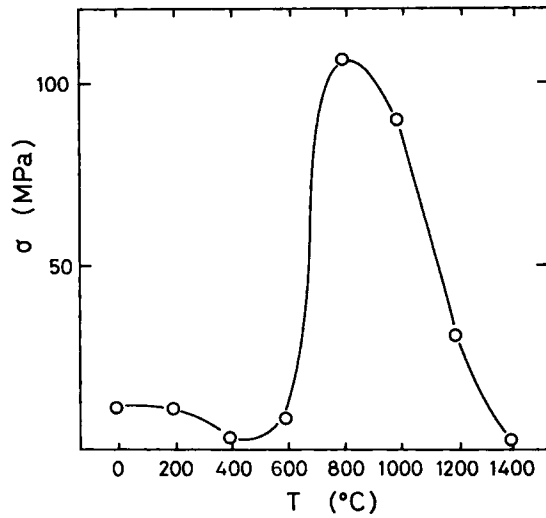Fig. 6.   WAXS patterns of P-3EPA fibers without ES sintered up to various temperatures.

Fig. 7.   Change in tensile strength σ of P-3EPA fiber with sintering temperature T.

increase with temperature. After the maximum values of the tensile strength and the modulus were recorded at 800–1000°C, these were decreased again with sintering temperature.

The electron micrographs of the fibers unsintered and sintered up to various temperatures are shown in Figures 9–12. The precursor fibers have irregular wavy surface, which seems to be due to the rapid evaporation of the solvent in the spinning process. Some voids can be seen in the cross section of the unsintered fiber attributable to the incomplete degassing of the spinning solution. In the cross section of the fiber sintered up to 1000°C, very fine particles were
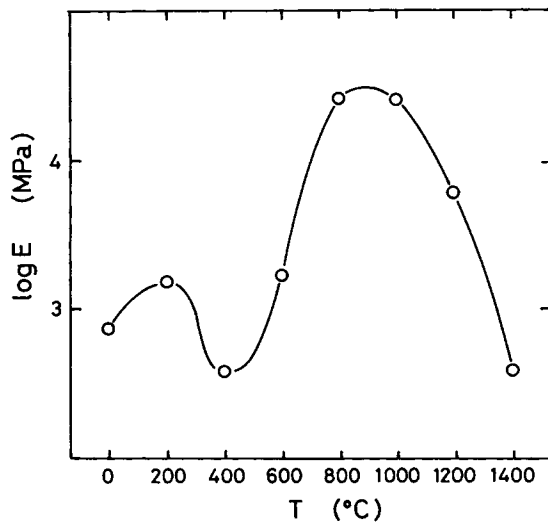
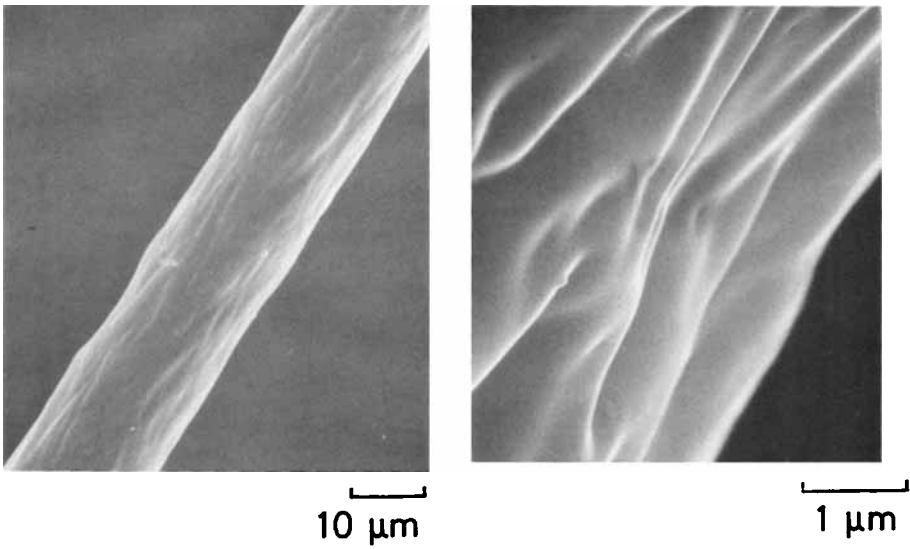Fig. 8.   Change in tensile modulus E of P-3EPA fiber with sintering temperature T.

Fig. 9. Scanning electron micrographs of P-3EPA fiber unsintered.

observed and the size of these tend to increase with increasing sintering tem-
perature. The size of particles observed in the fibers sintered up to 1200°C was
as large as 0.3 μm. Besides, there are some large cracks. Comparing the me-
chanical properties of the sintered fibers with WAXS patterns obtained, it is
considered that the deterioration of the mechanical properties should be as-
sociated with the phase transition of amorphous alumina to γ-alumina and
then to α-alumina.
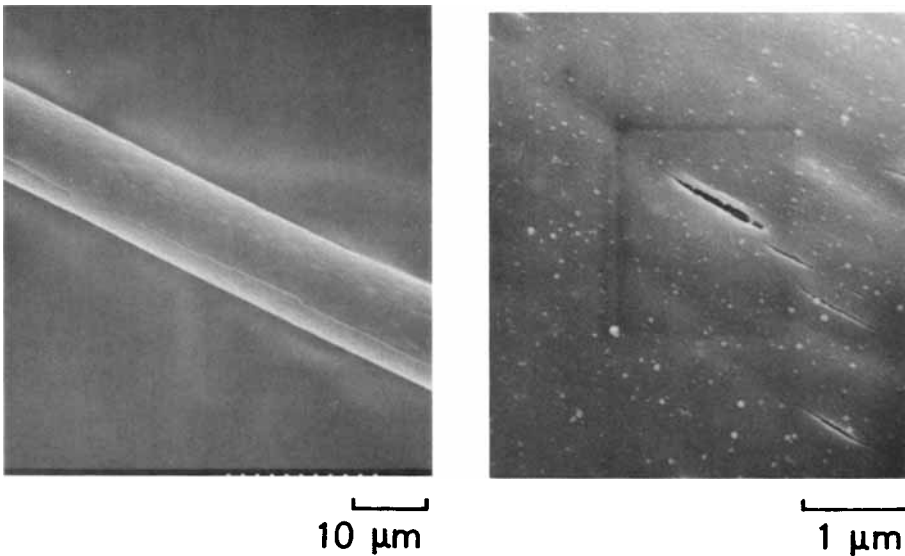
Fig. 10. Scanning electron micrographs of P-3EPA fiber sintered up to 800°C.
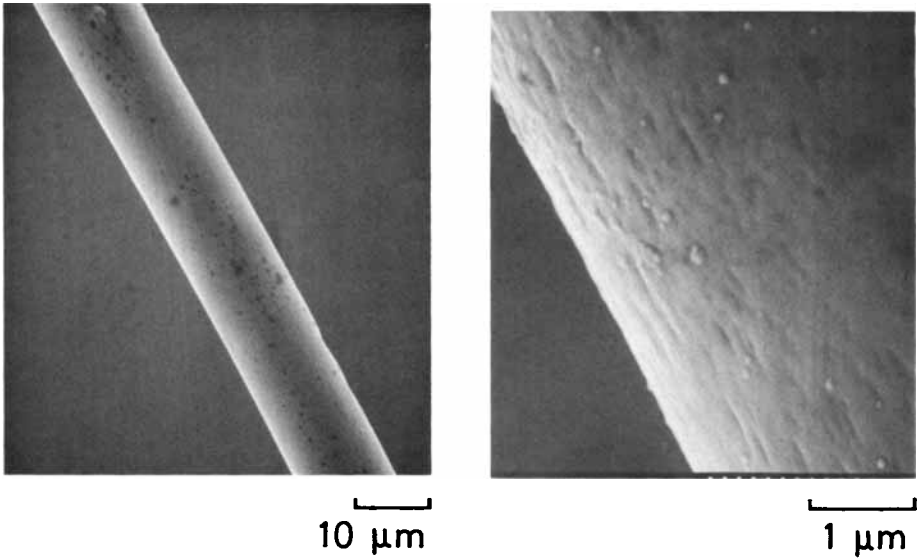
10 µm   **1 µm**

Fig. 11.   Scanning electron micrographs of P-3EPA fiber sintered up to 1000°C.

Since the crystallization of ceramics is a rather rapid process above the transition temperatures, it is generally followed by an abrupt shrinkage and a grain growth in the fiber, and sometimes microcracks prevail in the boundaries of the grains, causing the strength deterioration. Therefore, there seem to be at least two factors to be improved to obtain a high performance fiber in terms of the pyrolysis and sintering conditions. (1) The atmosphere in which the thermal decomposition of the precursor polymers occur rather slowly. When the precursor polymer is pyrolyzed in the air, the exothermic process detected
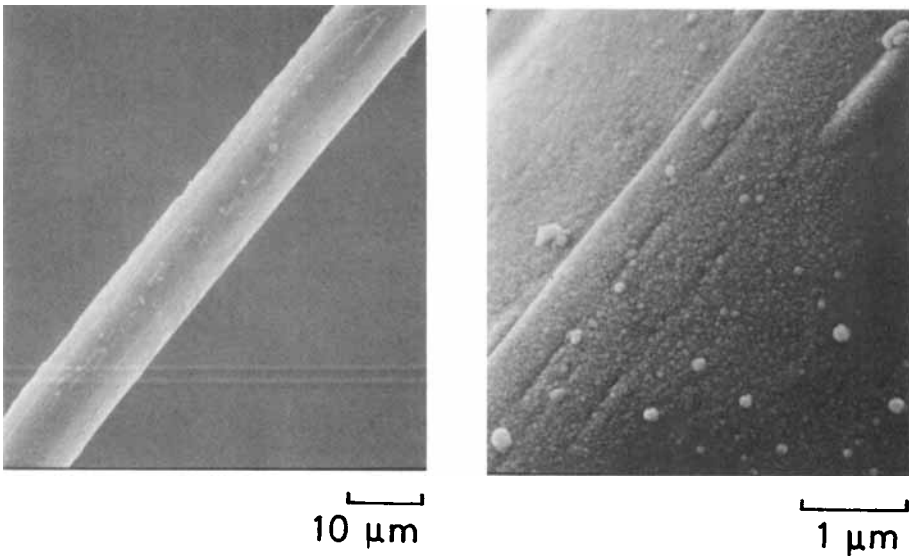

10 µm   **1 µm**

Fig. 12.   Scanning electron micrographs of P-3EPA fiber sintered up to 1200°C.

by DTA seems to cause the inner defects in the fiber. The alumina fiber with much better mechanical properties was obtained in our laboratory from a similar but melt processable precursor polymer, when it was sintered in a nitrogen.[5] (2) Addition of some sintering agents to suppress the abrupt phase transition of the ceramics at an elevated temperature. In a following section, the effect of the sintering agent will be discussed.

Effect of the Sintering Agent

Figures 13 and 14 show the comparisons of X-ray diffraction patterns obtained from the fibers with and without ES sintered up to 1200°C and held at that temperature for various periods of time. WAXS from the fibers without ES have peaks of both γ- and α-alumina, the intensity of the former tends to decreases while those of the latter increases with sintering time. On the other hand, those from the fibers with ES (1/18 ES/P-3EPA) show weak peaks of γ-alumina and some strong peaks of mullite ($3Al_2O_3$–$2SiO_2$),[11] which also increase with increasing sintering time. From the fibers with higher content of ES (1/8 ES/P-3EPA), only the diffraction patterns of mullite were recorded and no alumina peak was detected.

The SEM photographs of the surface of the fibers with and without ES sintered up to 1200°C are shown in Figures 12 and 15. The fiber with ES have no large particle and have smoother surface than that without ES. This morphological difference must be attributed to the fact that the fibers without ES sintered up to 1200°C have a mixture of γ- and α-alumina which grow into
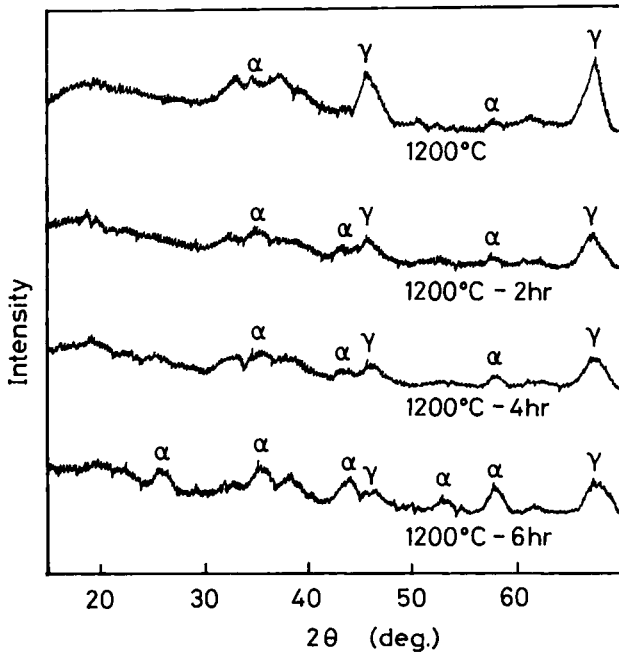

Fig. 13.   WAXS patterns of P-3EPA fiber sintered up to 1200°C and held at that temperature for various periods of time.
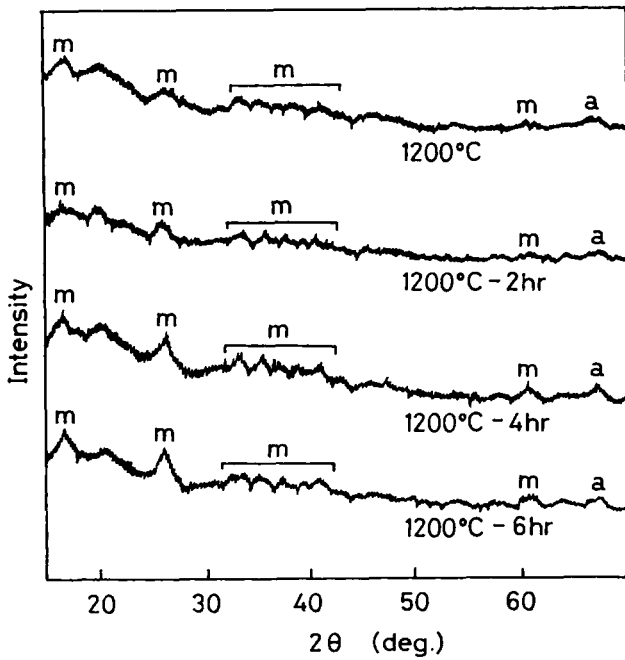
Fig. 14. Waxs patterns of ES/P-3EPA fiber sintered up to 1200°C and held at that temperature for various periods of time.

large particles while those with ES seem to mainly consist of mullite which may keep the alumina crystal from growing and make a denser structure.

Such morphology difference reflects on the mechanical properties as shown on Figures 16 and 17, where the tensile strength and the tensile modulus are
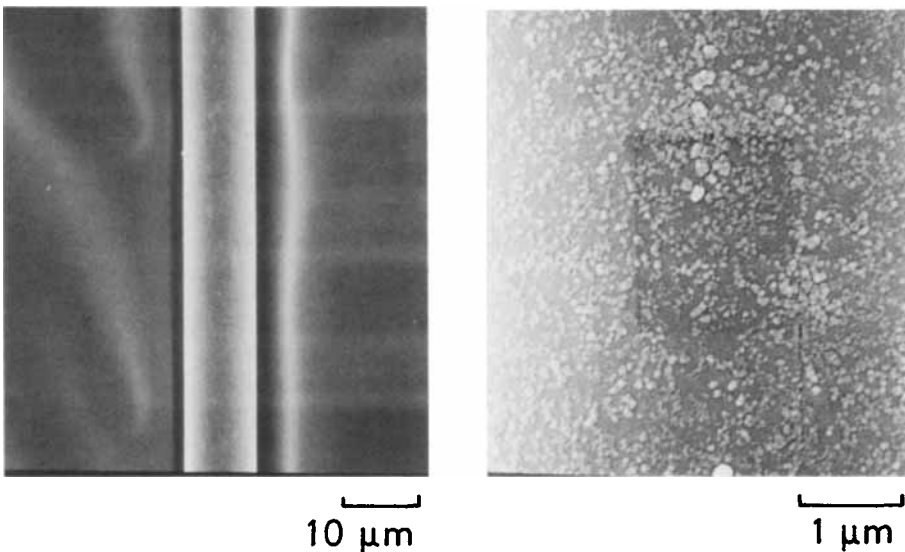

Fig. 15. Scanning electron micrographs of P-3EPA/ES fiber sintered up to 1200°C.
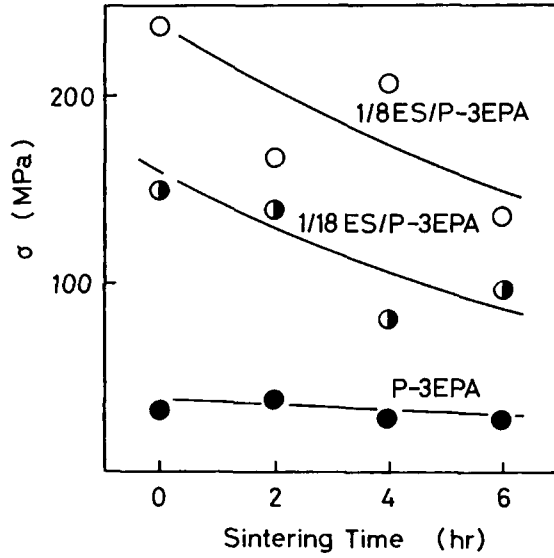
Fig. 16. Change in tensile strength σ of ES/P-3EPA fiber with sintering time at 1200°C.

plotted as functions of the sintering time at 1200°C. As was mentioned previously, the fiber without ES sintered up to 1200°C already have some cracks and particles grown so that the mechanical properties are low and do not decrease significantly with sintering time. The fibers with ES have better mechanical properties because the sudden phase transition and the grain growth which cause the defects in the fiber are suppressed. However, the mechanical properties decreased with increasing sintering time. Though the fiber with ES sintered up to 1200°C was still black in color, indicating the residual carbon,
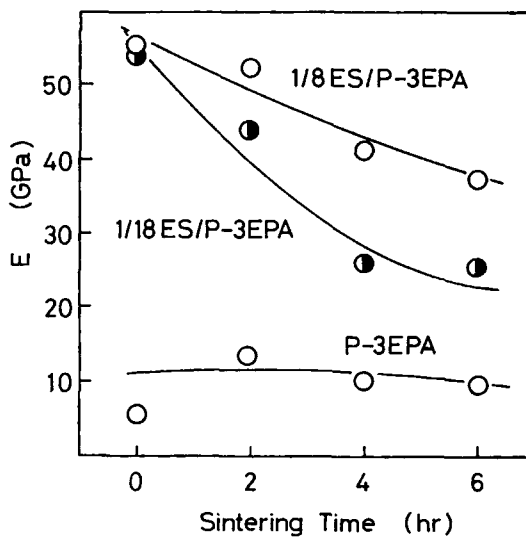

Fig. 17. Change in tensile modulus E of ES/P-3EPA fiber with sintering time at 1200°C.

the fiber has a very dense structure. The fiber held at 1200°C for 2 h turned out to be white and the residual carbon seemed to be removed. There were, however, some cracks observed in the cross section of the fiber. Probably these cracks were produced due to the sudden removal of the carbon at high temperature.

As a conclusion, the poly[((3-ethoxypropanoyl)oxy)aloxane] synthesized has a potential possibility to be converted into alumina. γ-Alumina $\rightarrow$ α-alumina transition was suppressed by the addition of silicon component and so were the sudden volume change and the grain growth, which cause the deterioration of mechanical properties. However, even with ES, the mechanical properties of the fiber deteriorate when sintered for a longer period of time to eliminate all carbon residue completely. Further improvements of the choice of the sintering condition may be required.

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