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THERMAL PROPERTIES OF A POLYIMIDE FIBER

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Abstract

A commercially available polyimide fiber was investigated as a possible precursor for the formation of carbon fibers. The thermal response of the fiber was thoroughly investigated using DSC, TMA and TG. These responses were dependent on the atmosphere and tension during scanning. The fiber was stabilized at high temperatures both in inert and oxidative environments and the effect of these stabilization treatments on the structure and properties of the fiber was carefully followed. During heating, the fiber showed shrinkage tendency at small tensions, but at higher tensions the fibers could be stretched. Among the two environments investigated, air was more effective than nitrogen in getting a more stable fiber.

Keywords: DSC, polyimide fiber, TMA, TG

Introduction

Polyimide films have been carbonized and graphitized [1–3] and are attractive as precursors because they carbonize with minimum change in shape. Even though the linear shrinkage during pyrolysis is about 20–40%, most of them produce carbon films with high graphitizability. The carbonized films can be converted to graphite with high crystallinity and orientation by high temperature treatment. Polyimide structure is interesting because of simple release of non-carbon atoms without any remarkable disturbance in orientation during carbonization.

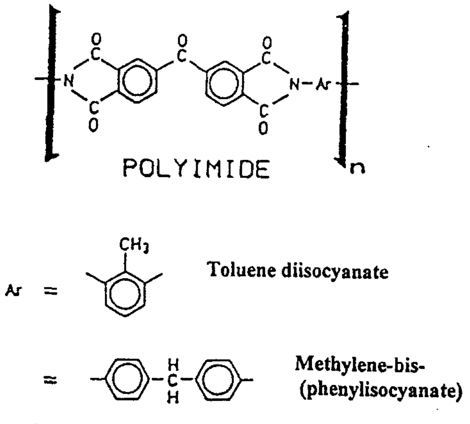

Fig. 1 Molecular structure of polyetherimide [4]

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While several different polyimides are available as polymers or films, fiber formation from them has been very limited. Only a couple of the copolyimides have been spun into fibers, and one of them is the P84 which is a semi-commercial fiber produced by the Austrian company Lenzing AG [4]. This polyimide has a structure shown in Fig. 1. Because of their excellent thermal and chemical properties, Lenzing P84 fibers are used in applications such as high temperature filtration, braided packings and protective clothing [5, 6]. This fiber does not melt and has a high glass transition temperature (T_g=315°C) [4]. The fiber has inherent flammability with limiting oxygen index (LOI) values in the range of 36–38% [7].

These properties make this fiber an interesting candidate for conversion into carbon fiber. Since this fiber is used for high temperature applications, it is of interest to know the high temperature responses of this fiber. Findings from our study conducted on this fiber are reported here.

Experimental

The fiber used in this study was supplied by Lenzing USA and their properties are reported in Table 1. Heat treatment of the fibers was carried out using a tubular furnace with a ceramic tube as shown in Fig. 2. Glass end caps cover the two sides of the ceramic tube. Gases to create the required environment in the heater were fed from both sides of the tube through the end caps. The temperature of the heater was controlled by an Omega CN2000 programmable temperature controller. Effect of different treatment time, temperature, pretension, and gaseous environment during the process were studied.

Table 1 Physical properties of the P84 fiber (Ref. [4])

Linear Density	2.2 dtex
Tenacity	35 cN/dtex
Br. Elongation	30%
Modulus	3.6 cN/dtex
Specific gravity	1.41

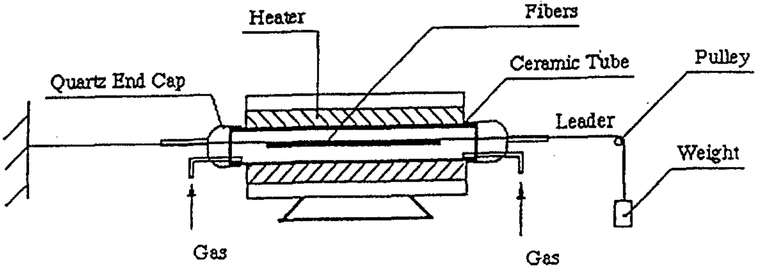

Fig. 2 Schematic of the stabilization and carbonization set-up

The polyimide fiber loops held by Kevlar leader at both ends and tensioned by hanging weights were heated for varying lengths of time at different temperatures. The temperatures were raised in steps from 300 till 560°C for stabilization and till 1175°C for carbonization. Whereas the samples were heated in air or nitrogen till 450°C, for higher treatment temperatures only inert environment was used. Samples treated under different conditions were collected and analyzed for their chemical and physical structure.

The precursor as well as the fibers treated under different conditions were characterized using thermal analyses (such as DSC, TG and TMA), elemental analysis, scanning electron microscopy, and physical properties such as fiber diameter, tensile properties of single filaments, and linear density. Thermal analyses were done using the Mettler thermal analysis system consisting of TC11 Controller, D5C25, TG50 and TMA40. The scans were done at heating rates of 20°C min^{-1} with either nitrogen or air as the purge gas. Elemental analysis was done at Atlantic Microlab, Atlanta, GA.

Results and discussion

P84 is a thermally stable fiber with no melting point and a very high glass transition temperature of around 315°C. As can be seen from the DSC scans (Fig. 3), in the vicinity of the reported glass transition temperature there seems to be an onset of reactions as well depending on the surrounding environment. The change in slope was much steeper in air with a large amount of heat evolution indicating the possible onset of reactions.

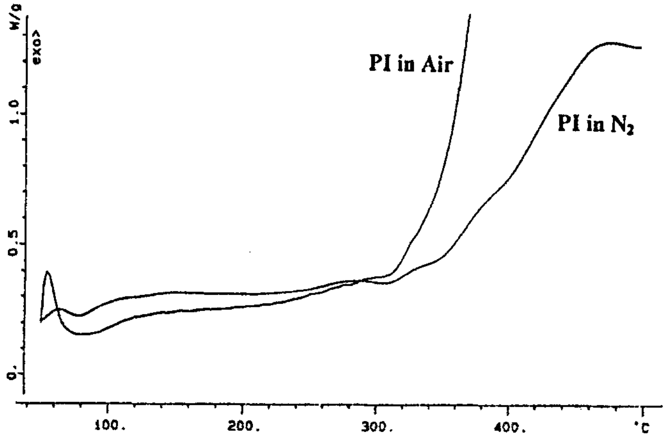

Fig. 3 DSC scans of P84 fiber in air and in nitrogen (20°C min^{-1})

The TMA scans (Fig. 4) indicate that there is dimensional change taking place around 270°C. The fiber seems to soften and flow even below the reported glass transition temperature. This dimensional change is dependent on the tension used as at low tension higher level of shrinkage was seen. For all the different tensions

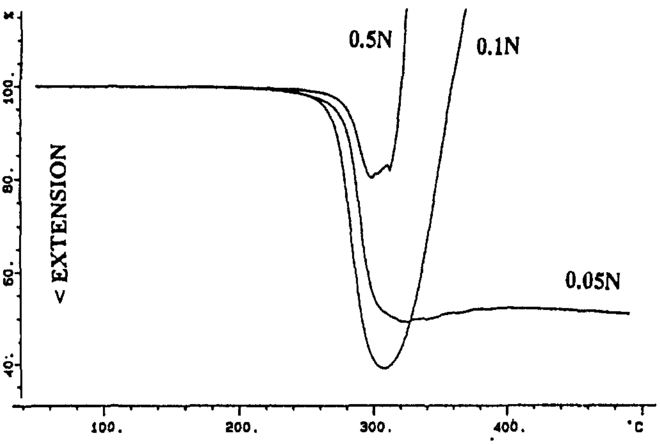

Fig. 4 TMA scans of the precursor fiber under different tensions (20°C min^{-1})

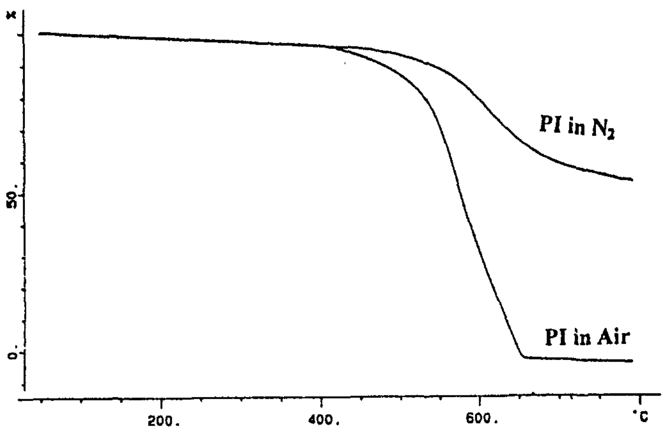

Fig. 5 TG scans of P84 fiber in air and in nitrogen (20°C min^{-1})

used the initial transition started at the same temperature, but there was considerable difference in the extent of shrinkage and subsequent deformation behavior. The fiber samples under higher tension displayed low shrinkage and then considerable extension in the proximity of the glass transition temperature. For low tension, shrinkage values were higher and no extension of the sample was observed. This behavior indicates the drawability of the fibers at higher temperatures.

The TG curves (Fig. 5) show the thermal stability and the differences in reactivity of the fibers in the inert and oxidative environments. In both air and nitrogen the fiber did not lose any significant mass, other than due to loss of moisture, until 420°C. After that, the mass loss was much faster in air and by 650°C all the fiber was lost. In nitrogen, however, about half of the original mass was retained even after heating to 800°C. This corresponds to a reasonable carbon yield for this material.

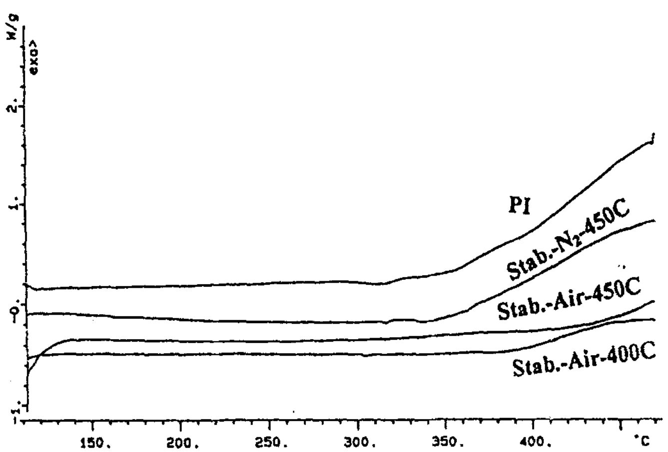

Fig. 6 DSC of P84 fiber heated under different conditions (20°C min^{-1})

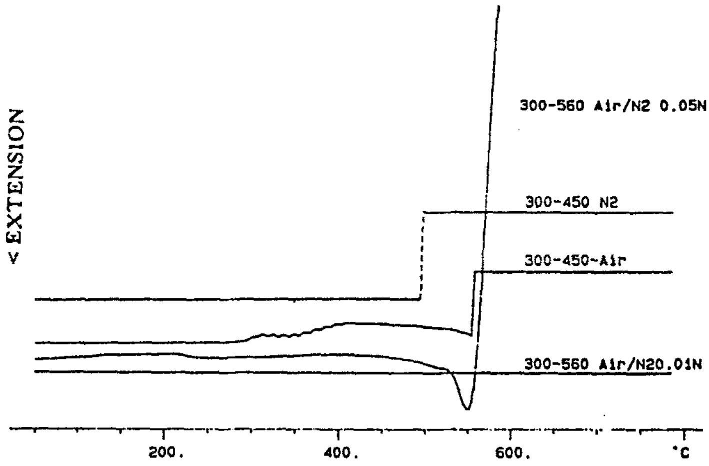

Fig. 7 TMA of P84 fiber heated under different conditions (20°C min^{-1})

The effect of heat treatment on the fibers can be seen by the DSC scans shown in Fig. 6. Fibers treated at higher temperatures show an increase in the inflection point as well as reduction in the exothermic heat evolved. This indicates higher stability of the fiber which is confirmed by the TMA results (Fig. 7). Unlike the polyimide which showed inflection around 270°C with a shrinkage tendency and extension on further heating under tension, the heat treated fibers were more stable. The fiber treated in air had higher stability as no deformation was observed till 500°C, at which point there was slight extension. On the other hand, fiber stabilized in nitrogen showed slight change in dimension between 300 and 550°C and then a small extension. For well treated fibers (heated till 560°C in combination of air and nitrogen), no dimensional change was observed under low tension even until 800°C.

This is an indication that the heat treated fiber can be carbonized by high temperature treatments. However, under higher tension, the same treated fiber broke around 550°C indicating the need to use lower tension during further heat treatments.

Another important observation is the change in color. On heat treatment, the golden colored starting material turns into black with intermediate colors in between depending on the time and temperature of the treatment. Also, on heat treatment the fibers became brittle, which is not a desirable characteristic. This aspect needs to be investigated so that by appropriately changing the treatment conditions it should be possible to retain some flexibility in the fiber to prevent it from breaking apart or becoming powder on handling.

The elemental composition of the fibers did not change significantly with initial heat treatment. Although the morphology had changed as seen from the TMA and other analytical techniques, the change in composition was minimum indicating the possible reorganization in the structure without any significant addition or loss of material. The carbon content was about 70% for the precursor and it remained the same for all treated fibers. Only difference observed on heat treatment as far as elemental composition was, depending on the environment, that of hydrogen and oxygen. For samples treated in air, the oxygen content was slightly higher (by a couple of per cent) with a simultaneous decrease in hydrogen content compared to that of the samples heated in nitrogen.

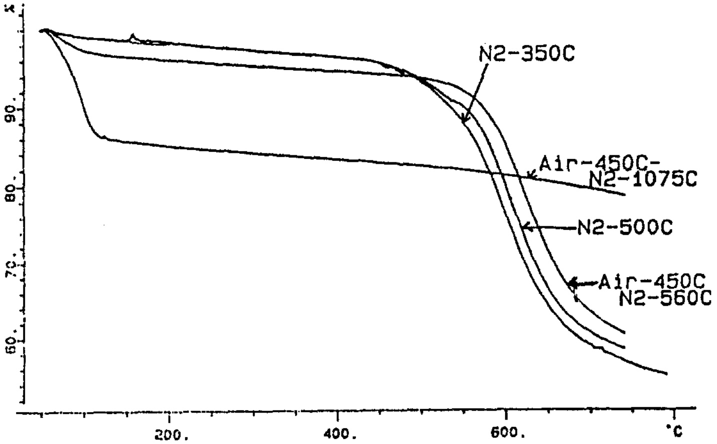

Fig. 8 TG of P84 fiber stabilized under different conditions (20°C min^{-1})

This is further confirmed by TG studies (Fig. 8) which show only a marginal change in mass retention of the heat treated samples compared to that of the precursor. The mass loss of the fiber treated to temperatures close to that of carbonization was really small. On treatment to temperatures close to or above 1000°C, the fiber had a very high carbon content with trace quantities of other elements indicating that it was essentially carbon fiber. The carbonized fiber showed heat loss around 100°C, due to the surface moisture present. Beyond that temperature, the loss in mass was less than 5% as expected for a material which has already gone through that thermal history.

Conclusion

The DSC scans of the polyimide fibers done in air and nitrogen showed the differences in reactivity with a sharper exotherm in air. Obviously the reactions were taking place faster in the presence of oxygen compared to the inert environment. Heating under carefully selected range of temperatures in the presence of air results in stabilized fibers as indicated by negligible exotherms. TG studies indicated that the polyimide lost all its mass by 650°C while heating in air, and lost about half its mass in nitrogen. However, on heating in air the samples became stable and they could be carbonized with a minimum loss in mass during that process. Among the two environments investigated, air was more effective than nitrogen in getting a more stable fiber. During heating, the fiber showed shrinkage tendency at small tensions, but at higher tensions the fibers could be stretched. The temperature of onset of deformation was lower than the glass transition temperature of the fiber. The amount of shrinkage was dependent on the environment as well as the tension. Thus by changing tension during heating, it is possible to control the morphological changes taking place during heat treatment which will affect the molecular orientation. This change in dimension with morphological transformations will have consequences on the tensile properties of the resulting fiber as well.

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