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The Preparation of a New Type of Synthetic Fiber from Linear Polyethylene by Irradiation Cross-Linking*

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A lightly cross-linked polyethylene filament was obtained by a conventional melt-spinning and an irradiation with an electron beam from Van de Graaff. This cross-linked filament was stretched to a high extent in the perfectly molten state at high temperatures above its melting temperature and quenched. Through these procedures a new type of synthetic fiber having high melting temperatures as well as excellent mechanical and fiber properties was prepared. The fiber obtained did not shrink appreciably if boiled in water for more than two hours and holded its fiber properties.

INTRODUCTION

Synthetic fibers with excellent mechanical properties such as high tenacity and low elongation at the break can be produced from linear polyethylene with a proper average molecular weight through a conventional melt spinning and following drawings. In comparison with other synthetic fibers those are excellent in various properties such as electro resistance and chemical stability. Hence, those are widely used at present when such properties are required. However, since the melting temperature or softening point of those fibers are not high enough and usually shrink to high extents if boiled in water or heated in air at relatively low temperatures such as 110°C, their uses as usual clothing fibers are rather limited.

The polyethylene fibers, as those are first spun from the melt through a screw extruder, are very dull such that those tenacity is as low as 1 gram per denier and elongation at the break exceeds several hundred percents even if those are spun with a very high rate of stretch. To improve these fiber properties those are usually drawn to high extents at high temperatures below the melting point of the polymer after melt spinning. This heat-drawing process sufficiently increases the tenacity and decreases the elongation at the break. However, it never elevates the melting point and no improvement in those poor heat-resistant property is obtained but the temperature at which the fibers begin to shrink by heating becomes lower owing to the improved molecular orientation parallel to the drawing direction of the process. In the circumstances fibers that simultaneously have excellent mechanical and heat-resisting properties have not been made from polyethylene to date. However, in a recent paper[1] it is found that if a lightly cross-linked polyethylene

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of adequate cross-link density is crystallized from the melt under conditions involving high degree of molecular orientation, a transparent product with very high melting temperature is obtained. Furthermore, the origin of the transparency and the high melting temperature for the sample is investigated in relation to the crystalline structure.[3] These works may suggest a possibility to prepare fibers with excellent mechanical properties as well as high melting temperature from linear polyethylene by irradiation cross-linking. This paper deals with a novel method to prepare such fibers.

EXPERIMENTAL

Samples

A commercial whole polymer Marlex 50 from Philips Petroleum Co. was used as starting material. It had a viscosity average molecular weight of 136×10^3.

Spinning

The polymer was extruded out through an orifice of 2.0 mm diameter at a temperature of 220°C by a spinning apparatus equipped with a screw of 15 mm diameter and wound up on a cylindrical bobbin at room temperature with stretch rates of 1.0 or 5.0. Here, the stretch rate is defined to be a ratio of the winding speed to the speed by which the molten polymer is extruded out from the orifice. Hence a stretch rate of 1.0 means that the melt-spinning was done without stretch. The smaller and larger stretch rates gave us filaments with diameters of 1.5 mm and 0.67 mm, respectively.

Irradiation

The filaments wound on a cylindrical bobbin were next irradiated with an electron beam from 2 MEV Van de Graaffin air to dosages of 10, 20, and 30 mega-rads, respectively. The dose rate was 0.24 mega-rad per second and the sample bobbin was rotated during the irradiation. The gel fraction W_g of the irradiated samples (mass fraction of the non-soluble part in the total mass) was evaluated by extracting with boiling xylene and drying. The results are listed in Table I.

As well-known, the presence of air greatly reduces the cross-linking effect of irradiation but relatively large values of W_g are imparted to the samples depending on the stretch rates, though the W_g are of course much smaller than that when the irradiation was conducted *in vacuo*.[1] It is supposed that because very high rate of irradiation was employed the diffusion of air in the solid samples during the irradiation was much limited and the effect thereof on the cross-linking was minimized.

Table I. The Gel Fraction of the Filaments and the Dosage Irradiated.

Sample	Dosages irradiated in mega-rads		
Filament spun with a stretch rate of	10	20	30
1 (non-stretch)	0.127	0.430	—
5	0.314	0.533	0.612

Table II. The Properties of the Filaments Spun without Stretch and Drawn after Irradiation.

Sample		Drawing		Density	Tensile Properties			
No.	Description	Temp. °C	Ratio*	g/cm³	Strength at Break, g/denier	Elongation at Break, %	Young's Modulus kg/mm²	Shrinkage in Boiling water, %
1	non-	—	(non-drawn)	0.9463	0.23	590	—	—
2	irradiated	25	8.5	0.8800	—	—	—	13.3
3	W_g=0	100	8.5	—	3.21	30	314	8.3
4	Irradiated	—	(non-drawn)	0.9463	0.22	560	34	—
5	10 MR	25	7.0	0.8800	—	—	—	16.5
6	W_g=0.127	100	9.5	0.9495	3.4	15.8	333	8.5
7		180	14.3	0.9466	2.8	15.8	431	2.1
8	Irradiated	—	(non-drawn)	—	0.22	340	—	—
9	20 MR	25	5.0	—	—	—	—	14.5
10	W_g=0.436	100	7.8	—	2.8	23.4	258	8.9
11		180	10.0	—	3.2	21.1	323	2.3

* Ratio of the length of drawn filaments to the original length before the draw.

Table III. The Properties of the Filaments Spun with a Stretch Rate of 5 and Drawn after Irradiation.

Sample		Drawing		Density	Tensile Properties			
No.	Description	Temp. °C	Ratio*	g/cm³	Strength at Break, g/denier	Elongation at Break, %	Young's Modulus kg/mm²	Shrinkage in Boiling water, %
12	non-	—	(non-drawn)	0.9326	0.54	813	52.6	2.2
13	irradiated	25	6	0.9352	—	—	—	14.0
14	W_g=0	100	5.5	0.9428	—	—	—	4.8
15		100	12	0.9483	4.68	18.4	361.9	8.3
16	Irradiated	—	(non-drawn)	0.9332	0.52	713.4	57.7	—
17	10 MR	100	5.5	0.9405	—	—	—	4.8
18	W_g=0.314	185	5.5	0.9420	1.99	56.4	256.7	2.1
19		180	9.0	0.9495	2.67	12.4	344.7	4.2
20	Irradiated	—	(non-drawn)	0.9336	0.45	620	56.2	—
21	20 MR	100	5.5	—	2.03	94	178.4	3.7
22	W_g=0.533	180	7.5	0.9463	3.11	10.5	359.0	6.7
23	Irradiated	—	(non-drawn)	0.9340	0.44	560	55.7	—
24	30 MR	100	5.5	—	2.00	66.4	184.4	8.3
25	W_g=0.612	180	5.0	0.9420	2.52	41.2	203.4	5.3

* Ratio of the length of drawn filaments to the original length before the draw.

Drawing

The irradiated and non-irradiated filaments were next drawn in air or water at various temperatures. Here, the irradiated samples were used without extracting those soluble

fractions. The non-irradiated samples could be drawn only at temperatures below the melting point of the polymer but the irradiated samples could be drawn to high extents even at much higher temperatures, since those had rubbery elasticity in the molten state because of the presence of inter-molecular cross-linkages introduced by the irradiation. Under the circumstances the non-irradiated samples were drawn at temperatures of 25 and 100°C, and the cross-linked samples were drawn to different extents at temperatures of 25, 100, and 180°C. The drawing at 25 and 180°C was conduced in air but that at 100°C was done in boiling water. The various fiber properties of the drawn samples were measured and the results are summarized in Tables II and III.

Measurements of Fiber Properties

The density was measured by a conventional density gradient column of toluene and carbon tetrachloride at 30°C.

The strength and elongation at the break and Young's modulus were measured by a tensile tester, Tensilon MT-III from Toyo Baldwin Co. With a stretching rate of 200%/min at 25°C.

The heat resistance was estimated with the length shrinkage of samples when boiled in water or heated in air. The fibers tested were boiled in water for one hour under a load of 10 mg/denier and the shrinkage was measured. The results are shown in the last columns in Tables II and III. The length change of the samples under a load of 10 mg/denier was observed during heating in air with a rate of 1°C/min. The shrinkage based on the original length before the heating was plotted against temperature in Fig. 1.

RESULTS

Some fiber properties of the drawn filaments that were made from the melt-spinning without stretch and irradiation according to the aforementioned procedures are shown in Table II. The filament spun without stretch is very dull as shown by its very low strength and extremely large elongation at the break (see data for Sample 1 in the table). The effects of the irradiation to 10 or 20 mega-rads on the tensile properties are rather negligible if minor decrease in the elongation was recognized (Samples 4 and 8). However, enhanced improvement in the fiber properties is obtained by the drawing for both non-irradiated and irradiated samples irrespective of the irradiation and the temperature at which the drawing was conducted. Thus fibers that have a high strength as large as more than 3 g/denier and a small elongation as low as 30% were obtained. However, the filaments made from non-irradiated sample shrink more than 8 percents even if drawn at a high temperature of 100°C in boiling water. Contrary, the filaments from the irradiated samples drawn at a temperature of 180°C not only have excellent fiber properties but also they shrink only to 2 or little larger percents in boiling water. Note the data for Samples 7 and 11. These exhibit enough high strength and low elongation at the break together with high moduli.

In Table III, the fiber properties made by the melt-spinning with a stretch rate of 5 and following irradiation and drawing are listed. In this case also, it is shown that if the irradiated samples are drawn in the molten state to high extents, the tensile mechanical properties not only are improved but also the resistance to boiling water is improved. Although the shrinkage percents in boiling water for those filaments made from the spin-

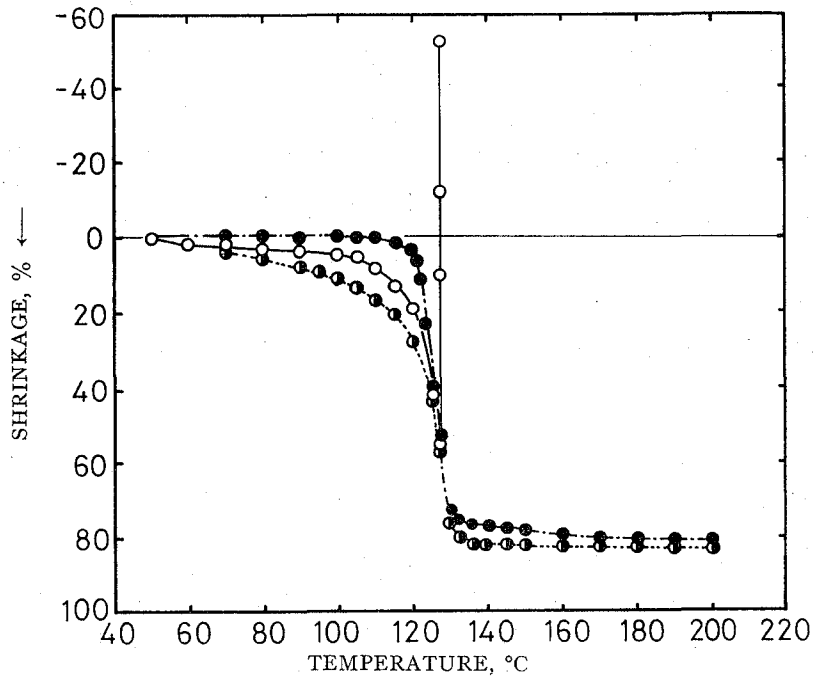

Fig. 1. Shrinkage percents *vs.* temperature for 5.5-fold drawn filaments at different temperatures. Open, half closed, and closed circles show data for uncross-linked filament drawn at 100°C, 10 MR-irradiated filaments drawn at 100° and at 185°C, respectively (Samples 14, 17, and 18 in Table III, respectively).

ning with the higher stretch rate are little larger than those for samples made from the spinning without stretch (shown in Table II), the heat-resistance of those is still excellent. For example, the shrinkage percent of Samples No. 14, 17, and 18 in air are plotted against in Fig. 1. Sample 18 that was obtained from the cross-linked sample by drawing in the molten state does not shrink appreciably until 110 or 120°C, while the fibers drawn at the lower temperatures below the melting point begin to shrink at much lower temperatures.

Thus a novel method to prepare a new type of fiber that has excellent mechanical and thermal properties from linear polyethylene is principally established. As mentioned already the practical use for polyethylene fibers is much limited by those poor heat-resistant properties despite those excellent mechanical, chemical, and electric properties. Moreover, olefinic synthetic fibers including isotactic polypropylene fibers are sometimes disliked by those waxy feel in the use for clothing fibers. It was noted that the waxy feel of the polyethylene filaments was almost removed by the irradiation cross-linking and following drawing in the molten state. Therefore, the procedure reported here to improve the heat-resistant properties and remove waxy feel of polyethylene fibers will become to be of very interest according to the progress in petroleum and radiation industries.

However, to realize this procedure in the industrial scale many problems still remain to be resolved. For example, as discussed elsewhere[1] cross-linked units must be introduced into polyethylene fibers by irradiation at least more than one unit per one polymer molecule to guarantee the rubbery elasticity of the polymer in the molten state, that enable us to draw in that state. Hence, if the small molecular weight of sample is used, the larger amount of cross-linked units (the larger cross-link density) is needed. However,

since cross-linked units act as non-crystallizable units during the crystallization, those should be as fewer as possible in so far as the rubbery elasticity in the melt is guaranted. Thus it is clear that the molecular weight and molecular linearity of the sample used should be as large as possible. As a matter of fact, when a lower molecular weight of sample was used, any improvement in the heat-resistant properties of the resultant products was not recognized. However, if the molecular weight becomes to be large the melt-spinning will become to be very difficult. Even the polymer with a molecular weight of 136×10^3 that was used in this work was very difficult to spin so that enough thin filament could not be obtained by the present spinning technique. If higher stretch rate is employed for the spin, of course thinner filaments could be obtained, but it will result in an increase of molecular orientation before the irradiation cross-linking. As the result, the character of the process during which the crystallization is achieved under high degree of molecular orientation will be lost. Thus the spinning technique for a polymer with very high molecular weight and hence with very high viscosity in the melt without occurrence of appreciable molecular orientation will be one of problems to be resolved to realize the process reported in this paper for the practical application.

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