Evaluation of the Tensile Properties and Thermal Stability of Ultrahigh-Molecular-Weight Polyethylene Fibers

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ABSTRACT: The thermal stability of ultrahigh-molecular-weight polyethylene (UHMWPE) should be paid attention in its applications, although the fiber has excellent flexible tensile properties. The measurements for two kinds of UHMWPE fibers, Dyneema SK65 (The Netherlands) and ZHF (Beijing, China), were carried out at different annealing temperatures and for different aging times. Experimental and regression analysis results showed that the aging behavior of the fibers followed an exponential attenuation with the annealing temperature and aging time. The critical temperature for the safe use of the fibers was equal to or lower than 70°C and depended on the glass-transition temperature; this was validated by tensile tests. The difference between the two fibers in the thermal properties resulted from the intrinsic supermolecular structures of the two fibers. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 310–315, 2005

Key words: annealing; fibers; modulus; polyethylene; thermal properties

INTRODUCTION

Eldib[1] reported that ultrahigh-molecular-weight polyethylene (UHMWPE) is gaining market share from *p*-aramid Kevlar fiber for rope, cable, and ballistic applications. The demand for UHMWPE fiber made in the United States has exceeded production since 1993, despite the tremendous imports of Dyneema fiber. According to the American Society for Testing and Materials, UHMWPE has a molecular weight of 3 million or more.[2] The advantages of UHMWPE include good abrasion and impact resistance, self-lubrication, a low coefficient of friction, minimal moisture absorption, light weight, and easy processing.

DSM Corp. (The Netherlands)[3] invented the gel-spun and ultradrawn technology used to manufacture UHMWPE and broke through the traditional concept to obtain a high-tenacity and high-modulus material only with a rigid macromolecule. The orientation degree of Dyneema fibers is greater than 95%, and the crystallinity is greater than 85%, whereas for conventional polyethylene fiber, the orientation degree is low, and the crystallinity is less than 60%.[4] The ultradrawing of the fiber not only increases the orientation degree and crystallinity but also transforms the folded-chain lamellar crystal into an extended-chain crystal of fiber molecules; therefore, the structure and properties of the fiber molecules are improved greatly.[5] Because of their high performance, UHMWPE fibers can be used for protective bullet armets, protective clothing, canvas, water-proof cloth, and filter materials. Furthermore, UHMWPE can be used for protective covers from radar and armor hulls if some coating or finishing is added.[6,7] However, polyethylene is a typically flexible material with a low glass-transition temperature and low melting temperature, even for UHMWPE.[8] Therefore, the study of the thermal behavior of UHMWPE is very important for manufacturing and using this kind of thermoplastic fiber.

There has been some research on the thermal behaviors and mechanical properties of UHMWPE fibers at different temperatures,[9,10] the supermolecular and fine structure (i.e., shish-kebab structure) of the fibers,[11] and the effect of the temperature on the fiber structure.[12,13] However, the most important factor for end uses is the mechanical stability under different thermal conditions. The effect of different thermal aging conditions on the mechanical properties of UHMWPE fibers is, therefore, discussed in this article.

EXPERIMENTAL

Materials and tester

Two kinds of UHMWPE fibers were used: ZHF, a 432dt/120f multifilament made by Beijing Zhong Fang Science and Technology Industry Company, Beijing, China, and Dyneema SK65, a 1320dt/1170f multifilament made by DSM Corp., the Netherlands.

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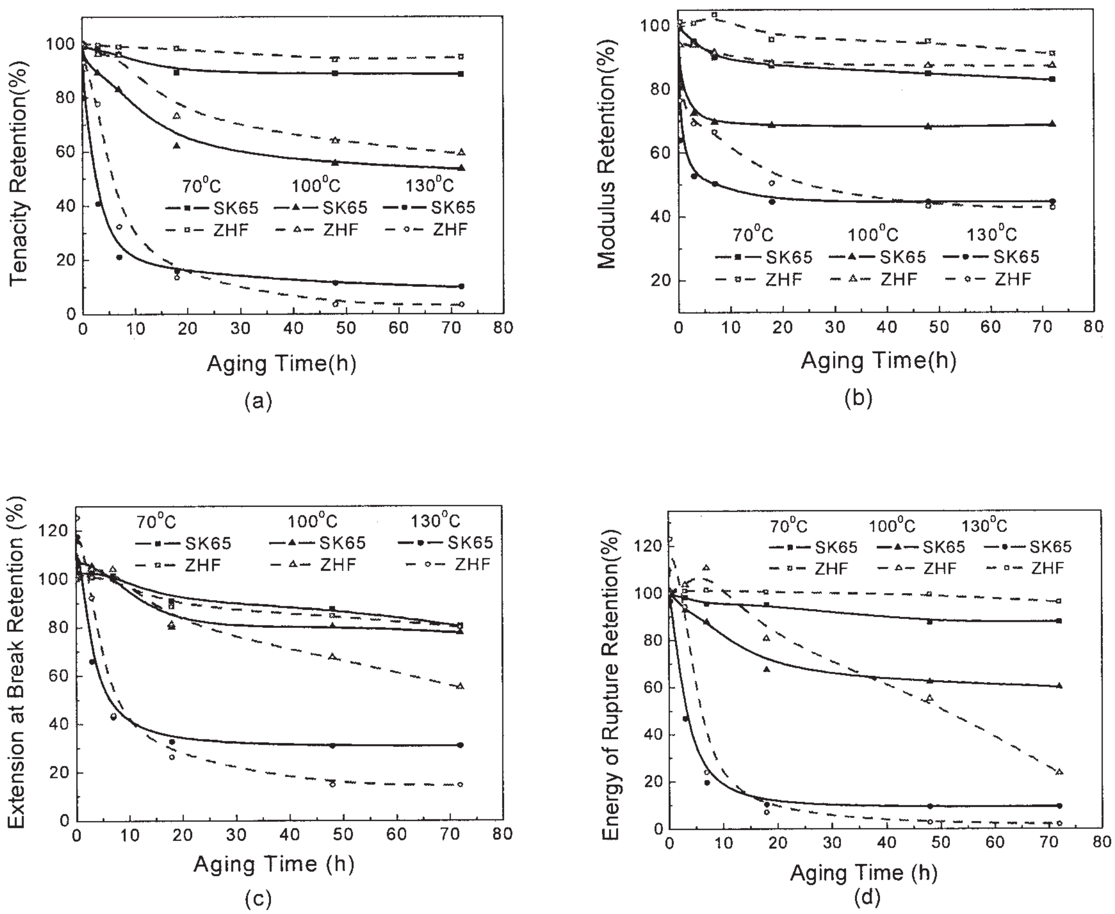

Figure 1 Relationship between the mechanical properties and aging time: (a) tenacity, (b) modulus, (c) extension at break, and (d) energy of rupture.

During the experiments, the temperature was controlled with a heat-aging tester, and the tensile tests were carried out with an Instron 1122 electronic tensile tester (Instron Ltd., Buckinghamshire, England).

Method and conditions

The UHMWPE filaments were cut and clamped between two jaws in a parallel–straight state under the pretension of 0.005cN/dtex during the heat treatment. The tenacity, modulus, extension at break, and energy of rupture were measured with an Instron 1122 instrument. Moreover, the retention of each parameter was calculated. The conditions of the tensile tests were a 50-mm gauge length and a 50 mm/min stretching speed. Each sample was tested five times under the same conditions.

According to the applications of the fibers, temperatures of 70, 100, and 130°C were set as the measuring points for comparison. The aging times were 20 min, 3 h, 7 h, 18 h, 48 h, and 72 h. Therefore, the effect of the heat treatment on the mechanical properties could be discussed.

All the measurements were conducted at 20°C and 65% relative humidity.

RESULTS AND DISCUSSION

Effect of the aging time on the tensile properties

The tenacity of the fibers decreases with the aging time, as shown in Figure 1(a). When the annealing temperature is raised, the tenacity loss increases. At an annealing temperature of 100°C and an aging time of 20 min, the tenacity does not obviously change, whereas with the 130°C and 20-min treatment, the tenacity decreases markedly. The loss of tenacity for the ZHF fiber is a little less than that for SK65 at a low aging temperature, but the tenacity of ZHF decreases more quickly than that of SK65 at a high annealing temperature, especially with longer aging times.

Comparing Figure 1(b) and Figure 1(a), we find that the modulus has an attenuation trend similar to that of the tenacity, whereas the extent of change of the modulus is less than that of the tenacity; the difference

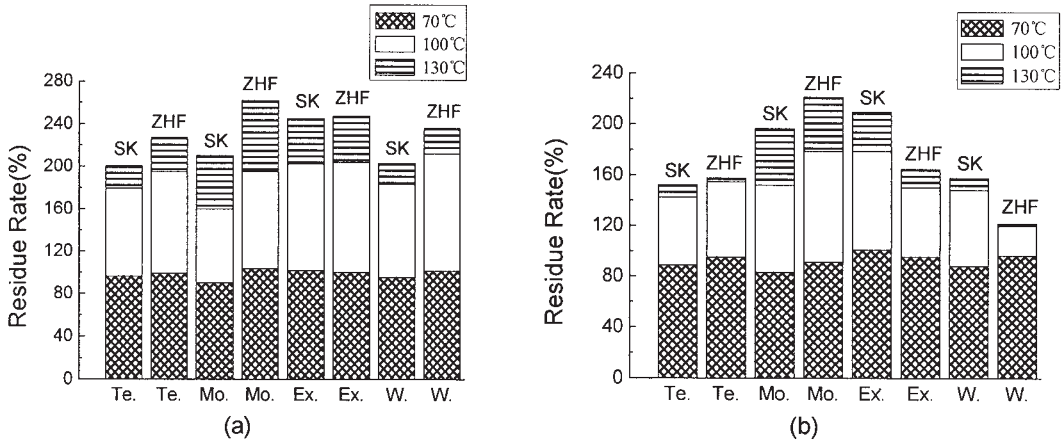

Figure 2 Mechanical comparison of the residue rate of the tensile properties of Dyneema SK65 and ZHF fibers (Te. = tenacity, Ex. = extension, Mo. = modulus, W. = work) at aging times of (a) 7 and (b) 72 h..

between the modulus curves of the two kinds of polyethylene becomes larger. At different annealing temperatures and aging times, the modulus drops first and then tends to be stabile.

The extension at break does not change much at the low temperature of 70°C and almost maintains its original level. However, at annealing temperatures of 100 and 130°C, the extension at break first increases in short times (7 h at 100°C and 20 min at 130°C) and then decreases as the aging time increases [Fig. 1(c)]. Moreover, the ZHF fibers decline more rapidly than the Dyneema SK65 fibers, and this implies that the Dyneema SK65 fibers are superior to the ZHF fibers, especially at high temperatures.

The increasing retention of the extension at break during the short aging time at 100 and 130°C is mainly due to the heat shrinkage of the filaments. However, the shrinkage happens only when the temperature is near the melting point because of the high crystallinity and high crystallinity zone of UHMWPE. The reduction of the extension retention with a long aging time may be due to the change in the crystallinity and the crystalloid dimension. In addition, the thermal oxidative degradation probably causes the breakage of the molecular chains or the rearrangement of the molecular chains.

The integration of the tenacity and extension at break determines the energy of rupture; that is, the product of the tenacity times the extension is in direct proportion to the specific work. Figure 1(d) shows that the energy of rupture for SK65 fibers decreases with the aging time, whereas that of ZHF fibers first increases a little in a short time and then decreases. Through a comparison with Figure 1(a,c), we find that the extension at break has a large effect on the work of rupture because the retention curves of the energy of rupture agree with those of the extension at break in Figure 1(c). For the energy of rupture, with a high annealing temperature and long aging time, the residue rate of the energy of rupture for ZHF is lower than that for SK65, but the retention of ZHF is higher than that of SK65 at low temperatures and at high temperatures but for a short aging time.

The mechanical property retention of the two kinds of fibers, including the tenacity, modulus, extension at break, and energy of rupture, for 7 and 72 h of aging is illustrated in Figure 2. There is less difference between the two types for the extension at break with 7 h of aging, whereas a certain difference exists in the other mechanical evaluation indices. However, the resistance to aging of the ZHF fibers is worse than that of Dyneema SK65 fibers with the 72-h aging treatment, especially for the extension and work properties, although it is better than that of Dyneema SK65 fibers with 7 h of annealing.

Regression analysis of the retention of the tensile properties

From Figure 1(a–d), we can derive the exponential relationship between the y-axis values of the retention of the tensile properties and the x-axis values of the aging time at the experimental annealing temperature. The fundamental regression function can be expressed as follows:

$$y = y_0 + A_1 e^{-t/t_x} \quad (1)$$

where y is the retention of the mechanical properties, A_1 is the coefficient, t is the aging time, and t_x is the value depending on the temperature.

On the basis of the data for SK65 in Figure 1(a), the corresponding regression equations of the tenacity retention can be obtained as follows (where R is a correlation coefficient):

$$70°C: \quad y = 88.34 + 11.66 \exp\left(-\frac{t}{11.732}\right) \quad (R^2 = 0.96774) \quad (2)$$

$$100°C: \quad y = 53.35 + 44.91 \exp\left(-\frac{t}{13.29}\right) \quad (R^2 = 0.98574) \quad (3)$$

$$130°C: \quad y = 12.78 + 82.39 \exp\left(-\frac{t}{2.729}\right) \quad (R^2 = 0.98974) \quad (4)$$

According to the relationship between y_0 of these equations and the annealing temperature (T), the following regression formula can be found:

$$y_0 = 177.4 - 1.26T \quad (R = 0.99) \quad (5)$$

Because $A_1 + y_0 = 100$, $A_1 = 100 - y_0 = 1.26T - 77.4$. Therefore, eq. (1) can be modified as follows:

$$y = (177.4 - 1.26T) + (1.26T - 77.4) \times \exp\left(-\frac{t}{t_{Te}}\right) \quad (6)$$

TABLE I
Constants of Equations (8) and (9)

x	A	B	C_1	C_2	R^2
Tenacity	77.4	1.26	12.5	165.3	0.98
Modulus	28.4	0.61	4.4	100.9	0.97
Extension	54.7	0.9	36	715.9	0.98
Work	79.6	1.28	22.2	396	0.97

According to the relationship between T and t_x of eqs. (2)–(4), t_{Te} is regarded as the parameter of mechanical property, including tenacity, modulus, extension and work, and the value of t_{Te} can be expressed [eq. (7)] in terms of a Gaussian equation, and regression analysis shows that the R value of the equation is relatively high ($R^2 = 0.98$).

$$t_{Te} = 12.51 - \frac{165.34}{25.5\sqrt{\pi/2}} \exp\left[-2\left(\frac{T-130}{25.5}\right)^2\right] \times (R^2 = 0.98) \quad (7)$$

Therefore, eq. (7) can be substituted into eq. (6) to reveal clearly the variation of the tenacity retention

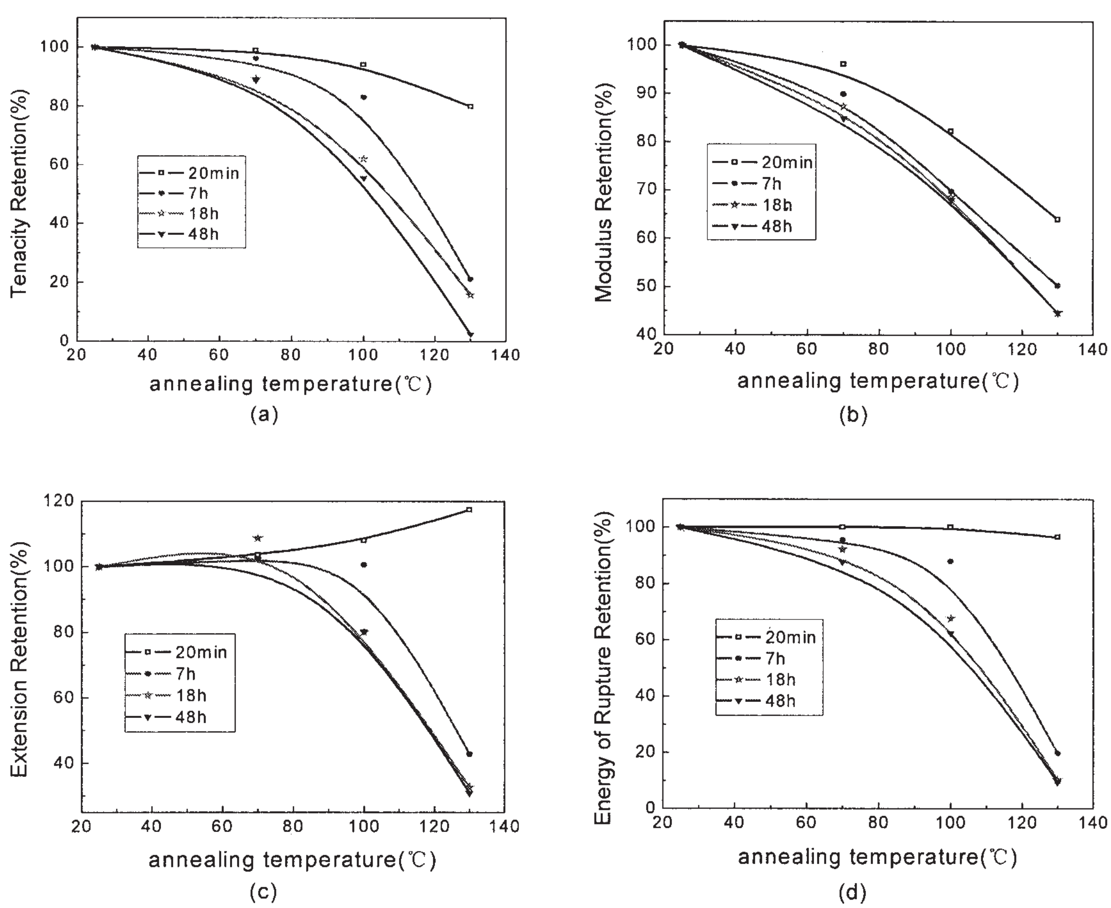

Figure 3 Relationship between the tensile properties and annealing temperature: (a) tenacity, (b) modulus, (c) extension at break, and (d) energy of rupture.

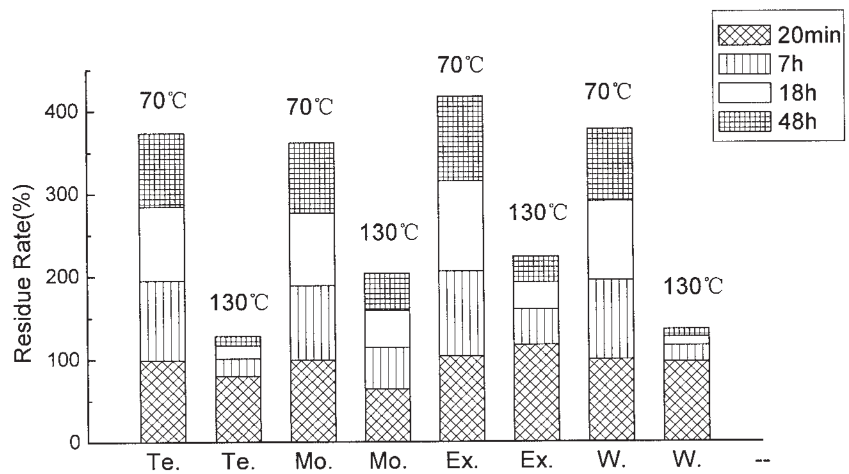

Figure 4 Mechanical comparison of the residue rate of the tensile properties of Dyneema SK65 fibers at 70 and 130°C (Te. = tenacity, Ex. = extension, Mo. = modulus, W. = work).

with the annealing temperature and the aging time, and it involves the effect of two simultaneous variables. The experimental results show that the final equation is correct and agrees with the actual data.

By analogy, the residue rate of the modulus, extension at break, and energy of rupture for SK65 in Figure 1 can also be formulated. The four tensile parameters (y), including the tenacity, can be expressed with the following general equations:

$$y = [(100 + A) - BT] + (BT - A)\exp\left(-\frac{t}{t_x}\right) \quad (8)$$

$$t_x = C_1 - \frac{C_2}{25.5\sqrt{\pi/2}}\exp\left[-2\left(\frac{T-130}{25.5}\right)^2\right] \quad (9)$$

where A, B, C_1, and C_2 are constants derived from regression analysis. C_1, C_2, A, and B of each tensile parameter x are summarized as Table I.

According to the regression equations and the constants of the equations, there exists a first-order exponential relation between the mechanical properties and the aging time and annealing temperature; all of the R^2 values are greater than 0.95, so eq. (8) is proved to be effective for all four parameters.

Effect of the annealing temperature on the tensile properties

The tensile tenacity, modulus, extension at break, and energy of rupture of ZHF fibers have change tendencies similar to those of Dyneema SK65 and are a little superior to those of SK65 fibers in general. Thus, only the regression curves of the tensile properties of the SK65 fibers versus annealing temperatures of 25, 70, 100, and 130°C are illustrated in Figure 3.

The reduction of the tensile parameters becomes significant and sharp as the annealing temperature increases, especially at long aging times, as shown in Figure 3, except for the extension retention with annealing for 20 min [see Fig. 3(c)]. The tenacity and modulus do not change markedly below 70°C, but above 100°C, both decrease quickly with an increase in the annealing temperature.

Figure 3(c) shows that the extension at break increases with the annealing temperature at a short aging time (20 min), whereas the extension at break increases first and then decreases with the temperature for a longer aging time (7 and 18 h). However, with more than 48 h of annealing, the extension at break decreases with the temperature. The fiber undergoes thermal oxidation degradation when further annealing takes place at a temperature higher than 100°C, and the molecular chain structure changes; therefore, the extension at break decreases. The extension at break has a tendency to increase with a 70°C heat treatment, and this mainly results from the change in the molecular configuration and supermolecular structure.

The energy of rupture decreases more than the other parameters with the temperature [Fig. 3(d)], although the change in the energy of rupture is not obvious with a short aging time. In addition, the residue rate of the energy of rupture always decreases as the annealing temperature increases.

The results for Dyneema SK65 with different aging times (20 min, 7 h, 18 h, and 48 h) and temperatures (70 and 130°C) are illustrated in Figure 4. Obviously, for various aging times at 70°C, Dyneema SK65 fiber has favorable stability, but at the high annealing temperature of 130°C, Dyneema SK65 fiber is obviously unstable. On the basis of the diagram, the Dyneema

SK65 fiber can be safely used at 70°C, and its mechanical properties can be kept consistent.

CONCLUSIONS

When the temperature is constant, with the aging time increasing, the residue rates of the tensile properties (the tenacity, extension at break, modulus, and energy of rupture) follow an exponential attenuation law. On the other hand, when the time is constant, the tensile parameters decrease as the annealing temperature increases. Theoretical models based on regression analysis have been obtained.

At a low annealing temperature, the extension at break changes very little. However, at a high annealing temperature, the extension at break increases remarkably in a short aging time and then declines with an increase in the aging time.

When UHMWPE is annealed above 70°C in the relaxation state, the tensile tenacity, the modulus, the extension at break, and the energy of rupture show a decreasing tendency. At the same time, a time–temperature equivalent exists.

At a high annealing temperature of 130°C, each tensile parameter of ZHF is a little inferior to that of SK65, whereas at low temperatures of 70 and 100°C, every tensile property of ZHF fibers is superior to that of SK65. UHMWPE fibers can be safely used below 70°C for a long time but between 70 and 100°C for less than 7 h.

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