

# Mechanical Properties of Polyethylene Mixtures Crystallized Under High Pressure

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**ABSTRACT:** The mechanical properties of a medium molecular weight polyethylene (MMW-PE) and an ultrahigh molecular weight PE (UHMW-PE) binary mixture with different weight fractions crystallized from the melt at 0.1 and 450 MPa were studied. The tensile modulus, yield stress, and strain were obtained as a function of the weight fractions in the PE mixtures at 25 and 85°C. The tensile modulus in the sample crystallized at 0.1 MPa decreased from 1.5 GPa of pure MMW-PE to about 0.4 GPa of pure UHMW-PE with the UHMW-PE content but it did not decrease with the UHMW-PE in the sample crystallized at 450 MPa in testing

at 25°C. A decreasing rate of the storage modulus  $E'$  of UHMW-PE in a dynamic measurement for the sample crystallized at 0.1 MPa with the temperature is larger than that of the sample crystallized at 450 MPa. These experimental facts are interpreted in relation to the molecular motion and crystallinity of the sample. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1962–1968, 2003

**Key words:** polyethylene (PE); modulus; mechanical properties; differential scanning calorimetry (DSC)

## INTRODUCTION

It is known that medium molecular weight polyethylene (MMW-PE) (molecular weight from about 10,000 to about 100,000) crystallized from the melt under high pressure above 350 MPa yields so-called extended chain crystals (ECCs).<sup>1,2</sup> Electron micrographs of the fracture surfaces of high-pressure crystallized PE show a band structure with striations normal to the band. The melting temperature ( $T_m$ ) of this sample increases from about 133°C of the folded chain crystal (FCC) to about 142°C of the ECCs. The crystallinity of the high-pressure crystallized sample increases to above 90%, although the sample crystallized from the melt at 0.1 MPa is about 60 or 70%, depending on the crystallization condition. The high-pressure crystallized sample is very hard and brittle so that tensile testing was impossible to perform.

In recent years, ultrahigh molecular weight PE (UHMW-PE) has been used for many objects. Many authors have reported on the mechanical properties of fibers of UHMW-PE obtained by gel-spinning and drawing<sup>3–9</sup> and solid-state extrusion.<sup>10,11</sup> Extremely large values of the Young's modulus and tensile strength were reported.

ECCs were also observed in the fracture surface of a UHMW-PE sample crystallized from the melt under high pressure above 350 MPa.<sup>12,13</sup> In this sample, iso-

lated fibrils, a textile structure, and a band structure were observed in the scanning electron micrograph. The  $T_m$  of this sample was 147.6°C, which is about 15°C higher than the  $T_m$  of the sample crystallized from the melt at 0.1 MPa.<sup>13</sup>

High-pressure crystallized UHMW-PE is not as brittle as is high-pressure crystallized MMW-PE. The existence of entanglement in the long molecule results in the formation of a low crystallinity sample compared with the high-pressure crystallized MMW-PE and the sample becomes ductile. Therefore, it should be possible to measure the mechanical properties of high-pressure crystallized PE with ECC by mixing UHMW-PE and MMW-PE. The mechanical properties of the MMW-PE and UHMW-PE mixture should change with the fraction of UHMW-PE in the mixture.

In this article, the mechanical properties of UHMW-PE and MMW-PE mixtures crystallized at 0.1 and 450 MPa were studied. Tensile tests were performed at 25 and 85°C because the  $\alpha$ -relaxation of PE occurs about 80°C in PE and the crystal becomes soft in this temperature region. Dynamic mechanical measurements and differential scanning calorimetry (DSC) were performed for the mixture with different weight fractions of UHMW-PE crystallized at 0.1 and 450 MPa. The temperature change of the dynamic modulus and the relation to the crystallinity of the sample was studied.

## EXPERIMENTAL

An unfractionated UHMW-PE powder sample (Hizex Million 145M) and an MMW-PE sample (Hizex 2200JP) supplied by the Mitsui Chemical Ltd. (Tokyo,

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**TABLE I**  
 $T_m$ ,  $\Delta H_m$ , and  $\chi$  for Different Weight Fractions of UHMW PE of the Sample Crystallized at 0.1 MPa

W(UHMW-PE)	$T_m$ (°C)	$\Delta H_m$ (cal/g)	$\chi$ (%)
0.0	134.8	45.2	65
0.1	135.4	48.2	69
0.15	134.5	45.8	66
0.2	135.0	39.9	57
0.4	135.2	43.6	62
0.6	134.6	35.8	51
0.8	134.4	36.3	52
1.0	132.7	29.5	42

Japan) were used. The  $M_w$  and  $M_n$  of the UHMW-PE sample determined by high-temperature GPC were 980,000 and 130,000, respectively. The  $M_w$  and  $M_n$  of the MMW-PE sample according to the supplier's data are 64,000 and 11,000, respectively.

PE-PE mixtures were obtained as follows: The mixed powder with a desired weight fraction was dissolved in xylene at 115°C and then cooled to room temperature. The solvent was evaporated at room temperature and a sheet of the mixture was obtained. The sheet was dried in a vacuum oven. The film sample was formed by compression molding from the melt.

The crystallization of the PE samples was performed as follows: A film sample of 6 × 25 mm with a thickness of about 0.1 mm was put between glass slides and covered by epoxy resin to avoid contact with the pressure medium (silicon oil of 10 cs). The sample was set in the pressure vessel and pressure was applied to 450 MPa. The vessel was heated at a heating rate of about 10 K min<sup>-1</sup> and afterward reached 260°C, which is 10°C higher than the  $T_m$  of UHMW-PE at 450 MPa; then the sample was cooled. In the cooling process, the sample was slowly cooled to just above the  $T_c$  of PE at 450 MPa and held at this temperature for 10 min. The sample temperature was then cooled to 50°C below the  $T_c$  and then the pressure was released. The sample was cut into 5 × 25-mm pieces before the experiment.

Tensile tests were performed using a tensile testing machine with a temperature-control system constructed in our laboratory. The load on the sample was detected by a load cell of the Shinko Electric Co. (type LBP1) and sample elongation was detected by a linear transformer of the Shinko Electric Co. (type 1516). A load-extension curve was drawn in the X-Y recorder. This load-extension curve was transferred to a nominal stress-strain curve using an initial sample size and the distance of the upper and lower grips measured before testing. The strain rate in the extension was 0.3 min<sup>-1</sup>.

Dynamic mechanical measurements were performed by using a Rigaku TMA8140C with a TAS 200

control system. The period of extensional strain was 0.1 s and the heating rate during measurement was 4 K min<sup>-1</sup>.

DSC was performed using a Rigaku DSC8530D. The heating rate was 6 K min<sup>-1</sup>. The degree of crystallinity  $\chi$  was determined after the method of Liangbin et al.,<sup>14</sup> using the equation  $\chi = \Delta H_m / \Delta H_m^0$ , where  $\Delta H_m^0$  is the heat of fusion in an infinitely thick crystal of PE (70.1 cal/g). The calorimeter was calibrated by means of indium melting. Tables I and II list the  $T_m$ ,  $\Delta H_m$ , and  $\chi$  of the samples crystallized at 0.1 and 450 MPa, respectively. The  $T_m$  around 142–144°C of the high-pressure crystallized sample indicates the melting of the ECC and that around 129–135°C indicates the melting of the FCC. The DSC melting peak of the sample crystallized at 450 MPa indicates that ECC is formed in this sample, because the low-temperature peak or shoulder indicates that the melting of the FCC is very little. Figure 1 shows the change of crystallinity with the W(UHMW-PE) for both samples. The crystallinity of the high-pressure crystallized sample is larger than that of the sample crystallized at 0.1 MPa. It changes only slightly with the W(UHMW-PE) below 0.4 and then decreases to 1.0.

## RESULTS AND DISCUSSION

Figure 2(a) shows nominal stress-strain curves at 25°C of the PE-PE mixture crystallized at 0.1 MPa. The curve is the same as is the typical stress-strain curve of PE.<sup>15,16</sup> The samples in this experiment were made by compression molding, so that the samples of W(UHMW-PE) below 0.4 break without showing necking after yielding. In the sample of W(UHMW-PE) above 0.6, necking is observed after yielding. The yield stress was almost the same with the change of the W(UHMW-PE) between 0.0 and 0.6 except for 0.4 and it decreased in 0.8 and pure UHMW-PE.

**TABLE II**  
 $T_{mi}$ ,  $T_{mh}$ ,  $\Delta H_m^t$ , and  $\chi$  for Different Weight Fraction of UHMW PE for the Sample Crystallized at 450 MPa

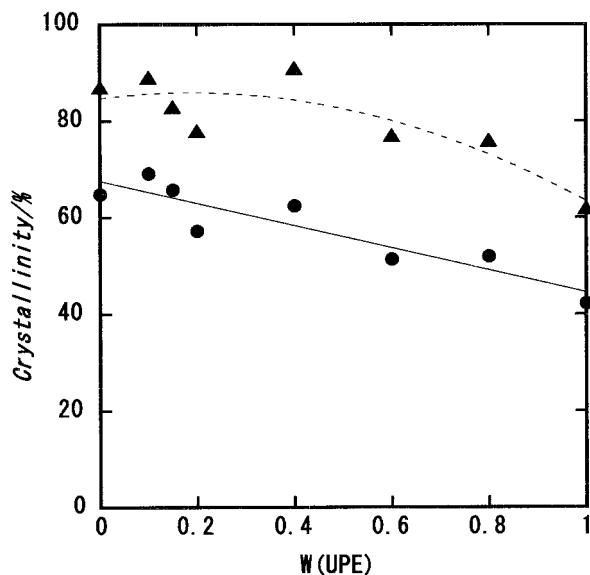
W(UHMW-PE)	$T_{mi}$ (°C)	$T_{mh}$ (°C)	$\Delta H_m^t$ (cal/g)	$\chi$ (%)
0.0	129.2	141.8	60.8	87
0.1	129.3	142.7	62.3	89
0.15	129.9	142.7	57.5	83
0.2	129.5	143.0	54.6	78
0.4	129.2	144.4	63.6	91
0.6	129.0	144.2	53.4	77
0.8	—	144.2	53.1	76
1.0	127.1	147.8	43.4	62

$T_{mi}$ : peak temperature in low-temperature melting peak in DSC.

$T_{mh}$ : peak temperature in high-temperature melting peak in DSC.

$\Delta H_m^t$ : total heat of fusion in DSC melting peak.

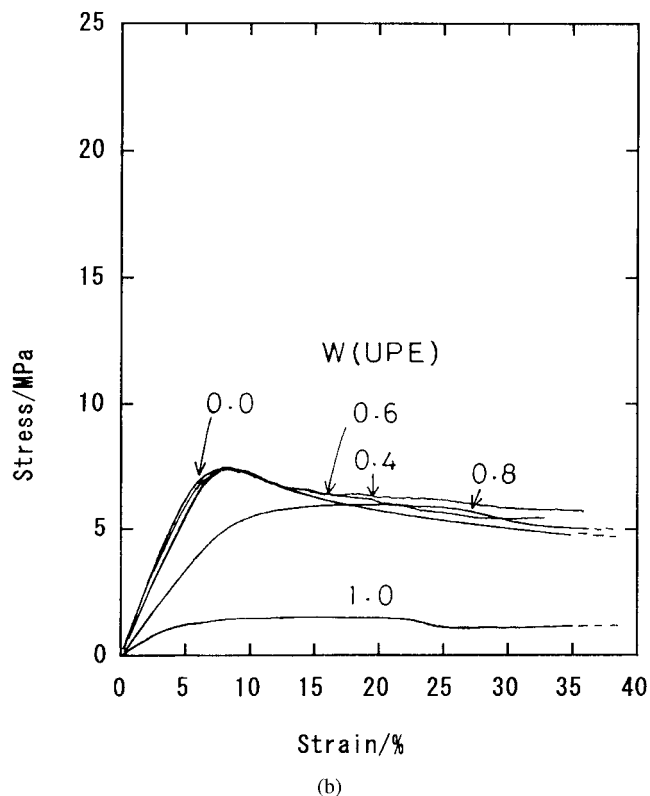
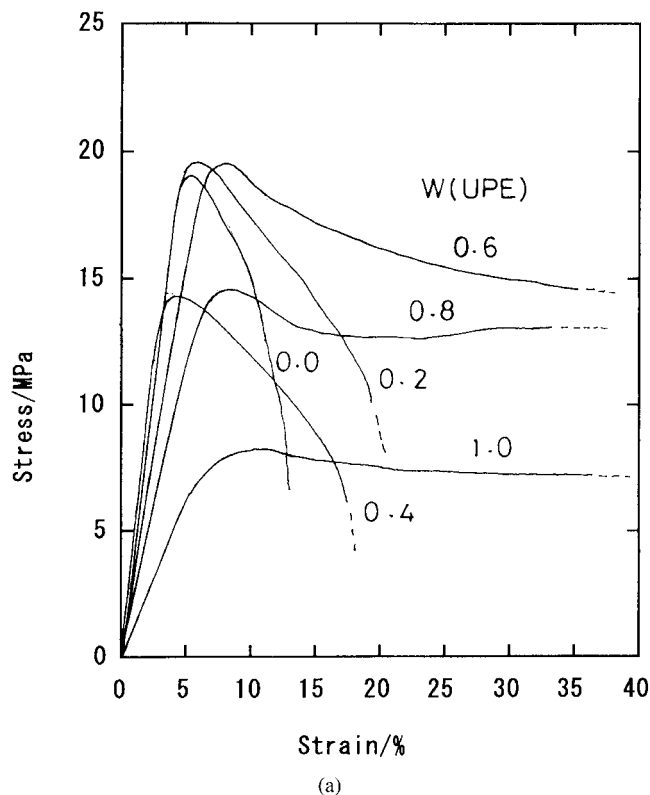
$\chi$ : crystallinity.



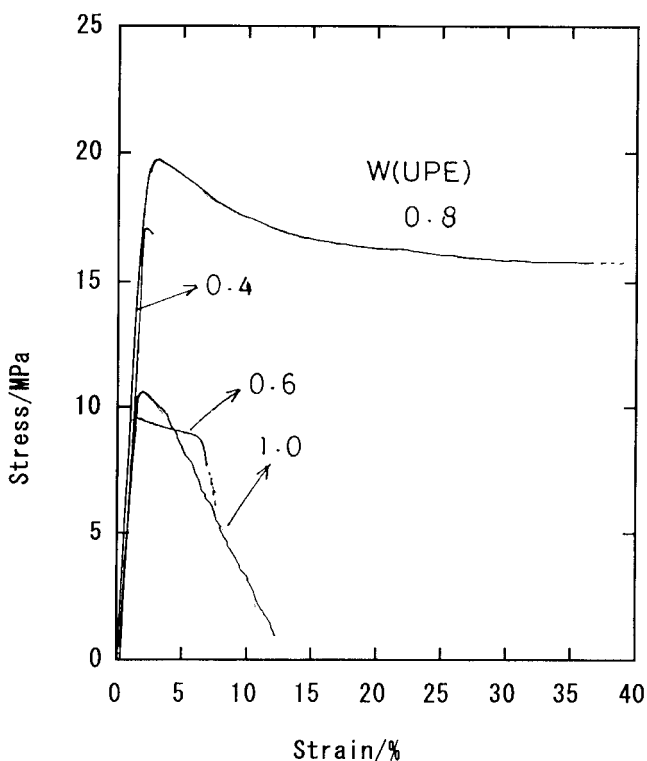
**Figure 1** Weight fraction dependence of crystallinity of the sample crystallized at 0.1 MPa and 450 MPa.  $\blacktriangle$ ;  $P_c = 450$  MPa and  $\bullet$ ;  $P_c = 0.1$  MPa.

Figure 2(b) shows the nominal stress-strain curve at 85°C of the PE-PE mixture crystallized from the melt at 0.1 MPa. The initial increase of the curve at this temperature is smaller than is the increase of the curve at 25°C, suggesting a smaller tensile modulus at this temperature. The yield stresses are also smaller than those at 25°C. In PE, crystalline relaxation occurs at about 80°C (refs. 17-21) and the crystalline region in PE becomes soft. Necking occurs after yielding for the sample of  $W(\text{UHMW-PE})$  below 0.6. Above 0.8, drawing of the sample occurs without appearance of a clear yield point.

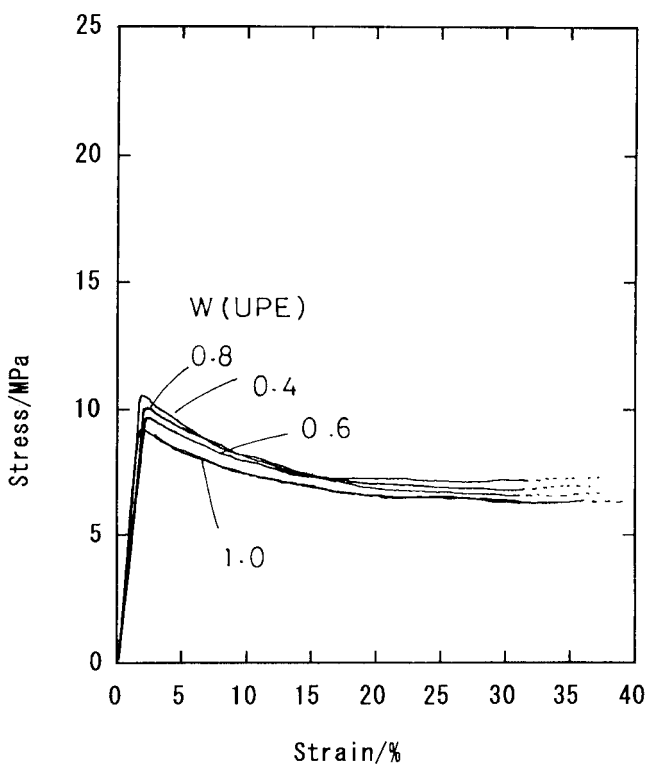
Figure 3(a) shows a nominal stress-strain curve at 25°C of the PE-PE mixture crystallized from the melt at 450 MPa. Stress increased steeply in all samples in comparison with the stress-strain curve that appeared in Figure 2. In these samples, ECC is formed and the crystallinity of the sample increased drastically. Therefore, the brittleness of the sample increased and it was impossible to perform tensile testing below  $W(\text{UHMW-PE}) = 0.2$ . In the sample of  $W(\text{UHMW-PE}) = 0.8$ , necking occurs after yielding. This is observed in the other sample of the same  $W(\text{UHMW-PE})$ . Crystallinity of this sample is larger than that of pure UHMW-PE; therefore, increase of the crystallinity is not the only reason for the increased brittleness. If cocrystallization of the MMW-PE molecule and the UHMW-PE molecule occurs, 20 weight % of the MMW-PE molecule disperses in the UHMW-PE. This dispersed MMW-PE molecule should act as a lubricant, and the UHMW-PE molecule may be drawn into this sample. In pure UHMW-PE, the crystallinity is 62%. The remainder of the UHMW-PE molecules should exist as amorphous. It is considered that the



**Figure 2** (a) Nominal stress-strain curve of PE-PE mixture for different weight fractions crystallized at 0.1 MPa at 25°C. (b) Nominal stress-strain curve of PE-PE mixture for different weight fractions crystallized at 0.1 MPa at 85°C.



(a)



(b)

**Figure 3** (a) Nominal stress-strain curve of PE-PE mixture for different weight fractions crystallized at 450 MPa at 25°C. (b) Nominal stress-strain curve of PE-PE mixture for different weight fractions crystallized at 450 MPa at 85°C.

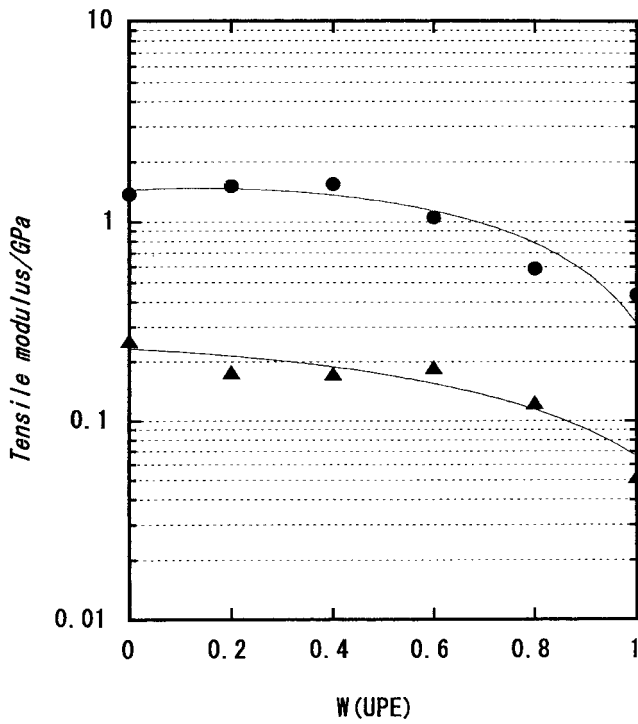
physical state of the amorphous molecular chain in the sample crystallized at 450 MPa should differ from the sample crystallized at 0.1 MPa.

In this sample, crystallinity is high and the crystallite is large, so that the remaining small amount of the amorphous chain should be in a stressed state by extension. This stress in the amorphous chain increases the modulus  $E$ . This idea is also applied to the small value of yield strain in high-pressure crystallized UHMW-PE sample. Flores et al.<sup>22</sup> reported that the tensile modulus of the high-pressure crystallized UHMW-PE depends on the crystallization conditions such as the pressure and temperature and the values of  $E$  are between 1 and 2.5 GPa. The stress existing in the amorphous chain which links the ECCs should appear as a steep increase of stress with an increasing strain.

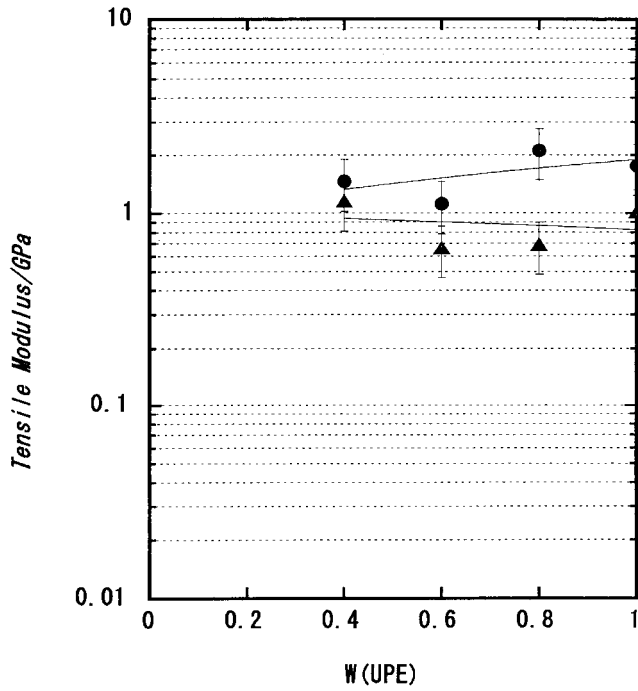
Figure 3(b) shows a nominal stress-strain curve at 85°C of the PE-PE mixture and pure UHMW-PE crystallized from the melt at 450 MPa. The stress-strain behaviors are almost the same for all the samples. The stress increased steeply and the yield stress is almost the same for different weight fractions. At this temperature, necking occurs even in the  $W(\text{UHMW-PE}) = 0.4$  sample which is crystallized at 450 MPa, due to the increased molecular motion around the crystalline relaxation region in the PE.

Figure 4(a) shows the weight-fraction dependence of the tensile modulus  $E$  at two testing temperatures of the PE-PE mixture crystallized at 0.1 MPa.  $E$  decreased with an increasing UHMW-PE above  $W(\text{UHMW-PE}) = 0.6$  at the testing temperature of 25°C and 0.8 at 85°C. The change of  $E$  with  $W(\text{UHMW-PE})$  almost corresponds to the change of the crystallinity with UHMW-PE. At a lower UHMW-PE content below 0.6,  $E$  does not change with the UHMW-PE content. Crystallinity is almost the same below  $W(\text{UHMW-PE}) = 0.4$  for both samples. In this region, lamellar crystals of MMW-PE are dominant and most of the UHMW-PE is considered to exist as an amorphous state. At a higher UHMW-PE content,  $E$  decreases with the UHMW-PE content due to the increased fiberlike material as observed in fracture surface of the UHMW-PE sample.<sup>13</sup> The crystallizability of the UHMW-PE molecule decreased with the existence of entanglement in the long molecular chains. The absolute value of  $E$  at 85°C decreased due to the increased molecular motion in the crystalline relaxation region of PE.

Figure 4(b) shows the weight-fraction dependence of the tensile modulus  $E$  of the PE-PE mixture crystallized at 450 MPa. Contrary to the sample crystallized at 0.1 MPa,  $E$  at  $W(\text{UHMW-PE}) = 0.8$  and 1.0 did not decrease from the value at 0.6. The crystallinity of the blend sample decreased above the  $W(\text{UHMW-PE}) = 0.8$  for the sample crystallized at 450 MPa as shown in Figure 1; therefore, the decrease of  $E$  did not depend only on the crystallinity. It is clear that ECC was formed



(a)

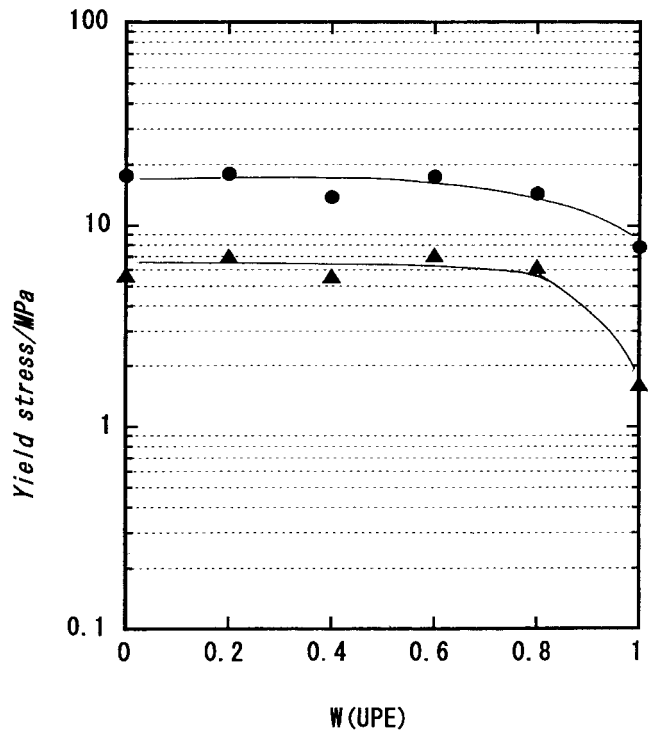


(b)

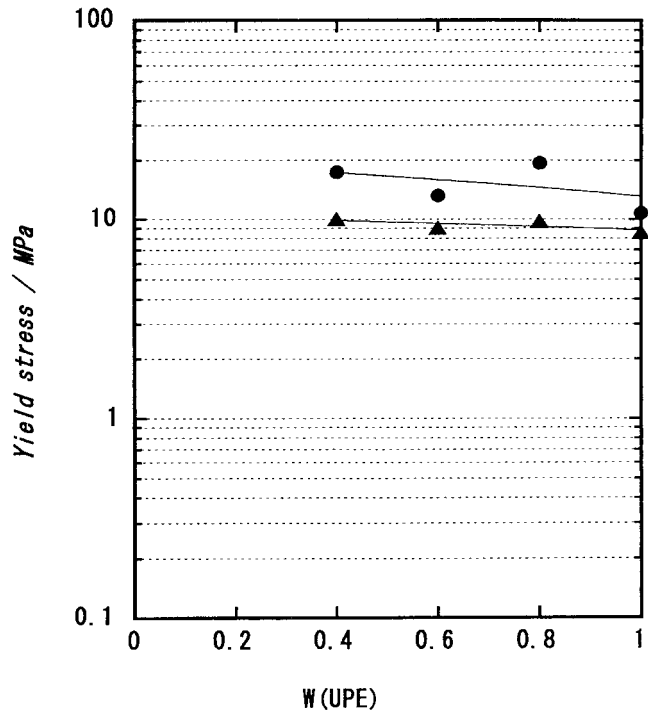
Figure 4 (a) Weight fraction dependence of tensile modulus in the sample crystallized at 0.1 MPa. ●; 25°C, ▲; 85°C. (b) Weight fraction dependence of tensile modulus in the sample crystallized at 450 MPa. ●; 25°C, ▲; 85°C.

in the high-pressure crystallized sample at melting temperatures above 140°C (Table II), so that the existence of ECC and amorphous chains under tension keeps the modulus at a high level in this sample.

Figure 5(a) shows the weight-fraction dependence of yield stress  $Y$  for the sample crystallized at 0.1 MPa.  $Y$  decreased at  $W(\text{UHMW-PE}) = 1.0$  for both measur-



(a)



(b)

Figure 5 (a) Weight fraction dependence of yield stress in the sample crystallized at 0.1 MPa. ●; 25°C, ▲; 85°C. (b) Weight fraction dependence of yield stress in the sample crystallized at 450 MPa. ●; 25°C, ▲; 85°C.

ing temperatures. Yield stress did not change with the  $W(\text{UHMW-PE})$  between 0.0 and 0.8, so that only a slight existence of the crystalline phase of MMW-PE should hold  $Y$  at a constant level. The crystallinity of the sample of  $W(\text{UHMW-PE}) = 1.0$  is about 40% and it includes an amorphous region of about 60%, so that yield stress should decrease at  $W(\text{UHMW-PE}) = 1.0$ .

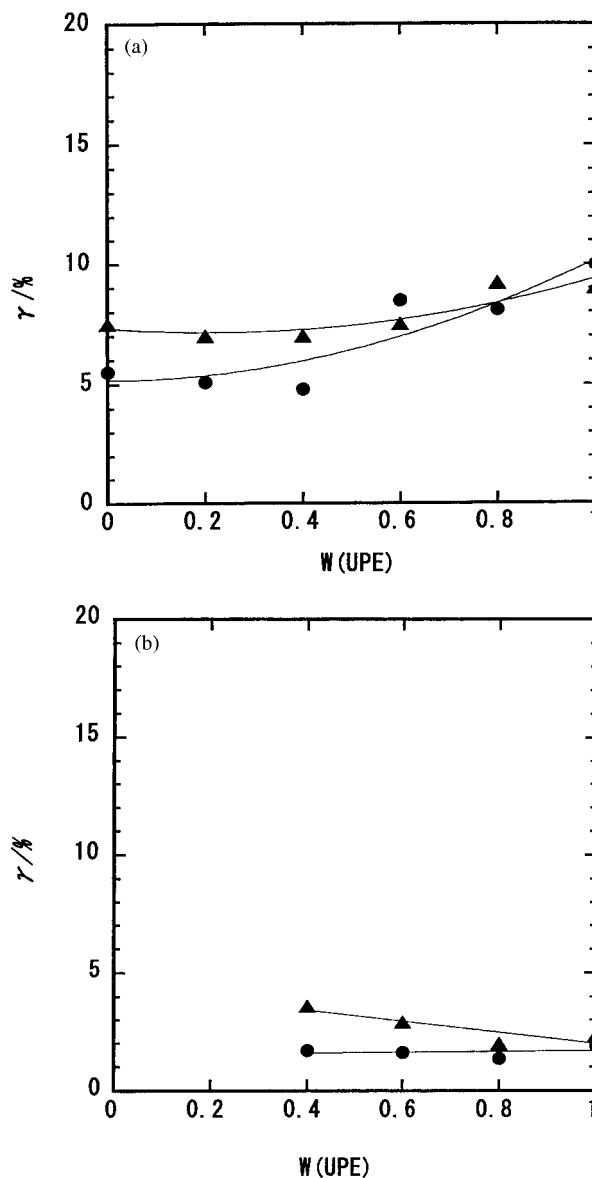
Figure 5(b) shows the weight-fraction dependence of the yield stress  $Y$  for the sample crystallized at 450 MPa.  $Y$  did not decrease even at  $W(\text{UHMW-PE}) = 1.0$  within experimental error for both temperatures. The crystallinity of the sample decreased from about 80% of  $W(\text{UHMW-PE}) = 0.6$  to 62% of pure UHMW-PE, but  $Y$  did not decrease. Therefore, the existence of ECC and a small part of the amorphous region play an important role on the yield stress in the high-pressure crystallized PE mixture. In general, yield stress in the highly stretched fiber sample increased. If the molecules of the amorphous region are stretched for all the mixture,  $Y$  for the high-pressure crystallized sample should not change with the change of  $W(\text{UHMW-PE})$ .

The values of  $Y$  at 85°C are slightly smaller than these of  $Y$  at 25°C. In the crystalline-relaxation region, the tensile modulus and yield stress in the FCC sample crystallized at 0.1 MPa decreased but those in the ECC sample crystallized at 450 MPa only decreased slightly.

Figure 6(a) shows the weight-fraction dependence of yield strain  $\gamma$  of the sample crystallized at 0.1 MPa. It increased with an increasing  $W(\text{UHMW-PE})$  both at 25 and 85°C. The crystallinity of the mixture decreased with an increasing UHMW-PE and the sample became soft. Therefore,  $\gamma$  increases slightly due to the increased drawability with the UHMW-PE content.

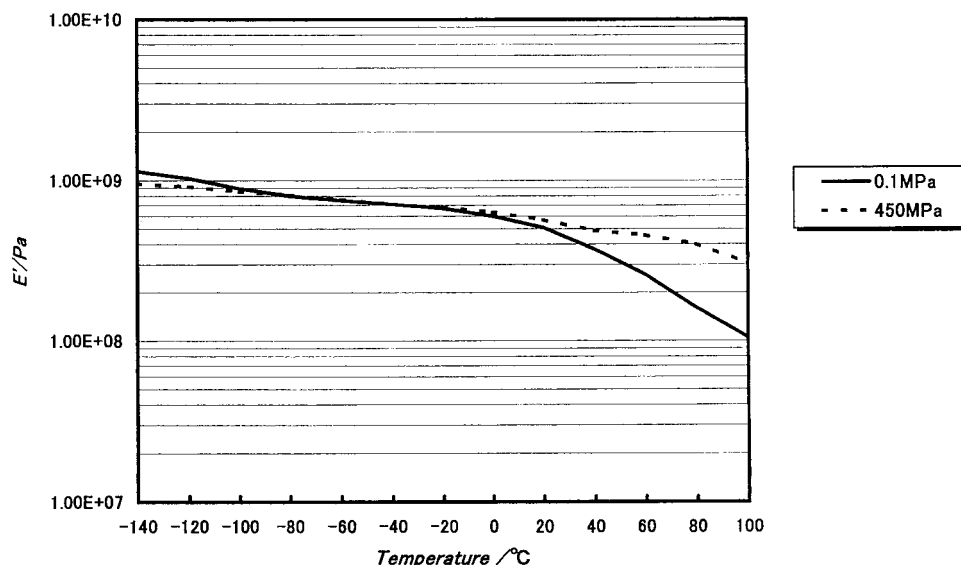
Figure 6(b) shows the weight-fraction dependence of the yield strain  $\gamma$  for the sample crystallized at 450 MPa.  $\gamma$  is almost the same with the change of the  $W(\text{UHMW-PE})$  at 25 and 85°C. The absolute value of  $\gamma$  is very small compared with that of the sample crystallized at 0.1 MPa. An increased strain of the amorphous chain and increased crystallinity results in the increased brittleness of the sample, so that the value of  $\gamma$  decreased.

The above results of the temperature change of the tensile modulus were supported by measuring the temperature dependence of the dynamic storage modulus  $E'$ . Figure 7 shows the temperature dependence of  $E'$  for the pure UHMW-PE sample crystallized at 0.1 and 450 MPa. The absolute value in the sample crystallized at 0.1 MPa is smaller than that of the sample crystallized at 450 MPa. The same feature was observed in the sample with different weight fractions. This is due to the lower crystallinity of the sample crystallized at 0.1 MPa of UHMW-PE.  $E'$  for both samples decreased with the temperature, but above 20°C, it especially decreased for the sample crystallized at 0.1 MPa due to the crystalline relaxation of PE. On the contrary, the decreasing rate is small for



**Figure 6** (a) Weight fraction dependence of yield strain in the sample crystallized at 0.1 MPa. ●; 25°C, ▲; 85°C. (b) Weight fraction dependence of yield strain in the sample crystallized at 450 MPa. ●; 25°C, ▲; 85°C.

the sample crystallized at 450 MPa. It is known that two different mechanisms exist in the crystalline relaxation of PE. One is an incoherent rotational motion of the molecular chain normal to the chain axis direction in the crystal.<sup>21</sup> The other process is considered to occur at the grain boundary of the crystals,<sup>17-20</sup> because the activation energy is smaller than that of the crystalline relaxation due to the molecular motion. Energy loss due to sliding of blocks in the crystalline lamellae or that at the surface of the crystalline lamellae was considered. Incoherent rotational motion should occur for both FCC and ECC, because the only difference of the texture in the crystallite is the thickness and the existence of the fold at the crystallite



**Figure 7** Temperature dependence of storage modulus  $E'$  in  $W(\text{UPE}) = 0.4$  crystallized at 0.1 MPa and 450 MPa. ———; 01. MPa, - - - - -; 450MPa.

surface of the FCC. On the other hand, a sliding process of the crystal blocks may be impossible in ECC because ECC is a very thick crystal, so that such a large motion is not considered to occur.

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