Elimination of Stress Whitening in High-Molecular-Weight Polyethylene

Y. W. LEE* and S. H. KUNG

Department of Manufacturing Engineering, Hong Kong Polytechnic, Hung Hom, Kowloon, Hong Kong

SYNOPSIS

High-molecular-weight polyethylene (HMWPE) sheets have been cold rolled biaxially to different reductions in thickness. After 40% or more reduction in thickness by cold rolling, the stress-whitening phenomenon in HMWPE was eliminated. To find out the reason of elimination of stress whitening by cold rolling, different techniques were employed. The measurement of hardness, density, and strain distribution of the specimens were carried out for the study of the differences in mechanical and physical properties of the stress whitened and nonwhitened specimens. Recovery of density, hardness, and dimensions of the specimens due to heating were also studied. Differential scanning calorimetry (DSC) and polarized-light microscopy were used to study the melting, and recrystallization behavior and scanning electron microscopy (SEM) were used to study the surface texture of the specimens. Based on the results of the different techniques employed, it is concluded that after cold rolling, especially biaxially rolled, due to the combined forces of compression and shear acting on the specimens from different directions, the macro- and micro-imperfections of the material may be eliminated to some extent. At 40% or more rolling reduction, the imperfections were largely eliminated; hence stress whitening did not occur.

INTRODUCTION

The cold rolling of polymeric materials is a useful method for modifying the mechanical and other properties of polymers. It is known that cold rolling can increase the tensile strength and improve the formability of a polymer, which is due to the orientation of molecules in the polymer.[1] Besides, cold rolling can also eliminate stress whitening in a polymer. In a previous study, it was found that stress whitening was eliminated when the high-molecular-weight polyethylene (HMWPE) sheet was reduced in thickness by 40% or more by cold rolling.[2]

Though stress whitening in polymers is a well-known phenomenon, the explanation of its origin is still a matter of some controversy. Kambour[3] found crazes extending throughout the stress-whitened region of a polypropylene specimen. Jareki and Meier[4] observed two different forms of voids in ultra-high-modulus polyethylene and believed that the whitening of the drawn polyethylene was related to an extensive formation of internal voids. Wendorff[5] described the formation of microvoids, which were generally less than 50 nm in diameter. Brever et al.[6] pointed out that the optical inhomogeneities, which give rise to opacity, may be caused by fluctuations in density (e.g., voids or crazes) or by fluctuations in structure (changes in crystal orientation). Hashimoto et al.[7] studied the crystallization of high-density PE from stressed polymer melts and found a network-type superstructure that was shown to be important in accounting for whitening of the specimens. Relatively few articles have been concerned with the elimination of stress whitening in polymers. The aim of this work is, therefore, to investigate the stress-whitening phenomenon in HMWPE and to find out the reason of elimination of stress whitening by cold rolling.

EXPERIMENTAL

Material

Commercially available 2mm-thick HMWPE sheets were used in this study. The polymer sheets were produced by extrusion.

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 46, 9–18 (1992)
 CCC 0021-8995/92/010009-10$04.00

Rolling

Initial blanks 90 mm^2 were biaxially rolled at room temperature; i.e., they were first rolled at 0° to one edge of the blank, and this was following by rolling in the mutually perpendicular direction (at 90°) to the same edge of the blank. This process was repeated until the required thickness (i.e., 1 mm) was obtained. The machine employed was a Hille Laboratory two-roll mill with 114 mm diameter and 147 mm long rolls revolving at 30 rpm. The reduction in thickness per pass was 0.05 mm.

Preparation of Stress-Whitened and Nonwhitened Specimens

An Instron 4301 tensile testing machine was used to pull the specimens at 20 mm/min straining speed and at ambient temperature ($\sim$ 25°C) to the same length (draw ratio = 2.2) and hence produced stress-whitened and nonwhitened specimens. The so-called stress-whitened specimens are those unrolled specimens drawn under tension, and hence stress whitening occurred. Those HMWPE specimens with 50% rolling reduction that did not show stress whitening when drawn under tension are termed nonwhitened specimens.

Measurements of Hardness, Density, and Strain Distribution

A Durometer (D scale) was used to determine the Shore hardness of the specimens. The density was determined dividing the mass by volume. Rectangular specimens with 120 mm length and 20 mm width were prepared; a vernier was used to measure the width and the length of the specimens to within ±0.05 mm. The thickness was measured with a micrometer to within ±0.01 mm. The weight of the specimens was measured with a Metter PC220 electronic balance.

Strain distribution studies were performed on rectangular specimens with 130 mm length and 20 mm width. Small circles of diameter 1.98 mm were marked on the specimens along the drawing axis. After tension, the circles changed into ellipses. The lengths of the major axis of the circles were measured by a Mitutoyo traveling microscope to within ±0.01 mm. The strain distributions of the specimens are shown by the relationship between the measured percentage strains and the axial locations of the specimens. The percentage major strain can be calculated by the following equation:

$$\text{Major strain } (\%) = \frac{d_f - d_0}{d_0} \times 100\% \qquad (1)$$

where d_0 and d_f are the initial and final diameters of the circles, respectively.

Recovery of Density, Hardness, and Dimensions Due to Heating

The stress-whitened and nonwhitened specimens were heated in an oven at various temperatures from 60 to 140°C, successively. In the temperature range of 60 to 110°C, the temperature increment was 10°C. However, in the range of 120 to 140°C, the increment was 5°C. The heating period for each temperature was 1 hr. The changes in density, hardness, dimensions, and stress whitening of the specimens under different heating temperatures and time were studied.

Thermal Analytical Studies

A Mettler TA 3000 differential scanning calorimeter was used to study both the melting and recrystallization behavior of the specimens. All measurements were conducted under nitrogen atmosphere; and an empty cell was used as a reference. Shavings of about 1 × 1 mm^2 were cut from the specimens for thermal analytical studies; a sample size of about 5 mg was used. A heating rate of 10°C/min and a flow rate of 5 ft^3/h for the purge nitrogen were used for the melting behavior study. And a cooling rate of 5°C/min and a flow rate of 10 ft^3/h for the nitrogen gas were used in the investigation of recrystallization.

The starting and ending temperatures for melting measurement were 60 and 200°C, respectively, and the contrary for recrystallization measurement.

Polarized-Light Microscopy and Scanning Electron Microscopy

A Nikon polarized-light microscope with hot stage was also used to study the recrystallization process of the specimens. A rotary microtome was used to cut the specimens into 10-μm-thick films. Samples were sandwiched between glass cover slips before being placed directly in the furnace of the hot stage. The samples were heated from room temperature to 200°C in about 15 min followed by cooling to room temperature in order to study the recrystallization process.

Table I Results of Hardness and Density Measurement

Specimen	Shore Hardness	Density g/cm^3
Unrolled	64	0.95
Rolled	61	0.92
Nonwhitened	58	0.90
Stress whitened	52	0.81

The surface texture of the specimens was observed using a Stereoscan Cambridge scanning electron microscope. Before scanning, the samples were gold coated under vacuum.

RESULTS AND DISCUSSION

Results of Hardness, Density, and Strain Distribution Measurement

The results of hardness and density measurement are shown in Table I. It can be seen that the stress-whitened specimen has a significantly lower hardness and density value. It is suggested that this is due to the presence of voids in the stress-whitened specimen and will be discussed in detail later.

The strain distribution studies were performed on the rolled and unrolled specimens. The results of percentage major strain versus location are shown in Figure 1. It is noted that the unrolled specimen has a large strain gradient, and the rolled specimen has uniform strain distribution along the drawing axis. These results imply that the rolled specimen has the ability to spread the strain away from the most heavily strained zones to regions of lower strain, thus the strain distribution is uniform. It was also observed that stress whitening occurred when the unrolled specimen was pulled under tension; however, for the rolled specimen, no stress whitening could be seen.

Results of Recovery Studies

Recovery of Width and Thickness of the Stress-Whitened Specimen

Stress-whitened specimens with initial width and thickness of about 10 and 1 mm, respectively, were studied. The percentage recovery is defined as follows:

$$\text{Recovery } \% = \frac{\text{final dimension} - \text{initial dimension}}{\text{initial dimension}} \times 100$$

The results of width and thickness recovery due to heating are shown in Figure 2. It can be seen that between 120 and 125°C there is a slight recovery in

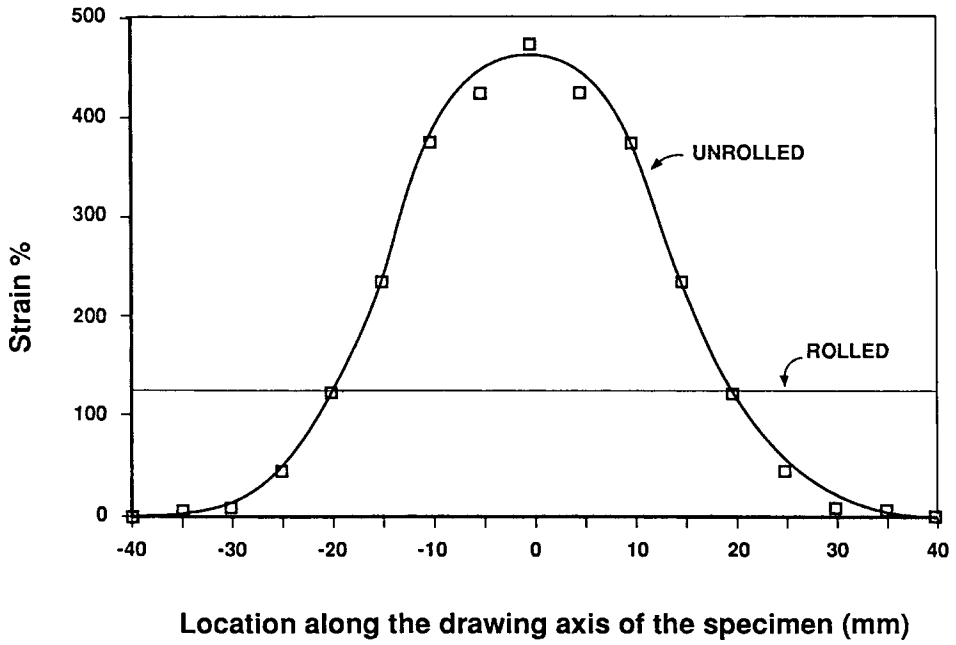

Figure 1 Strain distribution of the rolled and unrolled specimens.

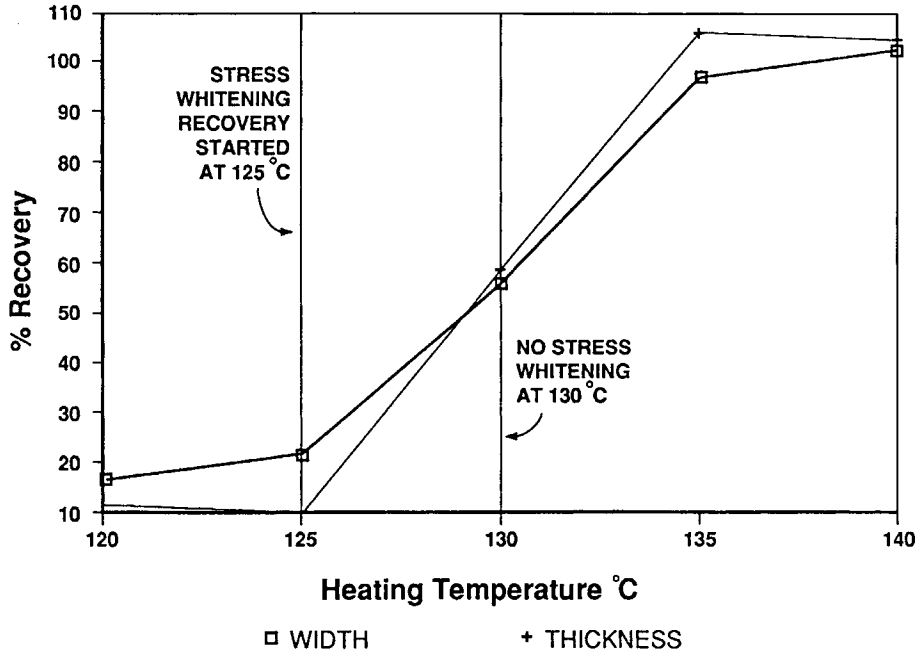

Figure 2 Width and thickness recovery of the stress-whitened specimens.

width and thickness. When the temperature is higher than 125°C, a rapid increase in percent recovery in both width and thickness can be observed; the degree of stress whitening also reduced. At 130°C no stress whitening could be seen. However, the width and thickness of the specimens still recover at temperatures higher than 130°C and has obtained 100% recovery at 140°C. It is known that the recovery of dimensions is normally due to the recoil of the oriented molecules. This implies that stress whitening does not relate to orientation.

Recovery of Hardness

Figure 3 shows the Shore hardness value of the unrolled specimen and stress-whitened specimen at different heating temperatures. The hardness of the unrolled specimens remains basically unchanged until 130°C; however, there is a slight decrease in hardness when the temperature is higher than 130°C. As for the stress-whitened specimens the hardness value also remains unchanged until 125°C; when the temperature is higher than 125°C, the hardness increases followed by the reduction of stress whitening. At 130°C no stress whitening can be seen; however, the hardness value continues to increase somewhat between 130 and 140°C. These results are in general agreement with the results given earlier, which show that rolling, tension stretching (i.e., orientation of the polymer molecules), as well as stress whitening (presence of voids) could lead to the reduction of hardness. The stress-whitening recovery was observed to start at 125°C and is completed at 130°C. It is realized that within this temperature range there may also be some extent of recoiling of the polymer molecules. Hence both the recovery of stress whitening (i.e., the absent of voids in the specimen) and the recoil of the polymer molecules contribute to the increase of hardness. It can also be observed that the hardness value further increases when the temperature is higher than 130°C where stress-whitening recovery has accomplished. It is suggested that this increase in hardness is solely due to the recoiling of the HMWPE molecules. This is further evidence indicating that stress whitening does not relate to orientation.

Recovery of Density

The density recovery due to heating shows a similar trend as in the recovery of hardness. The results are shown in Figure 4. The density of the unrolled specimens shows little changes due to heating. However, for the stress-whitened specimens, when the temperature is higher than 125°C, the density increases accompanied with decrease in stress whitening. At temperatures higher than 130°C the density value

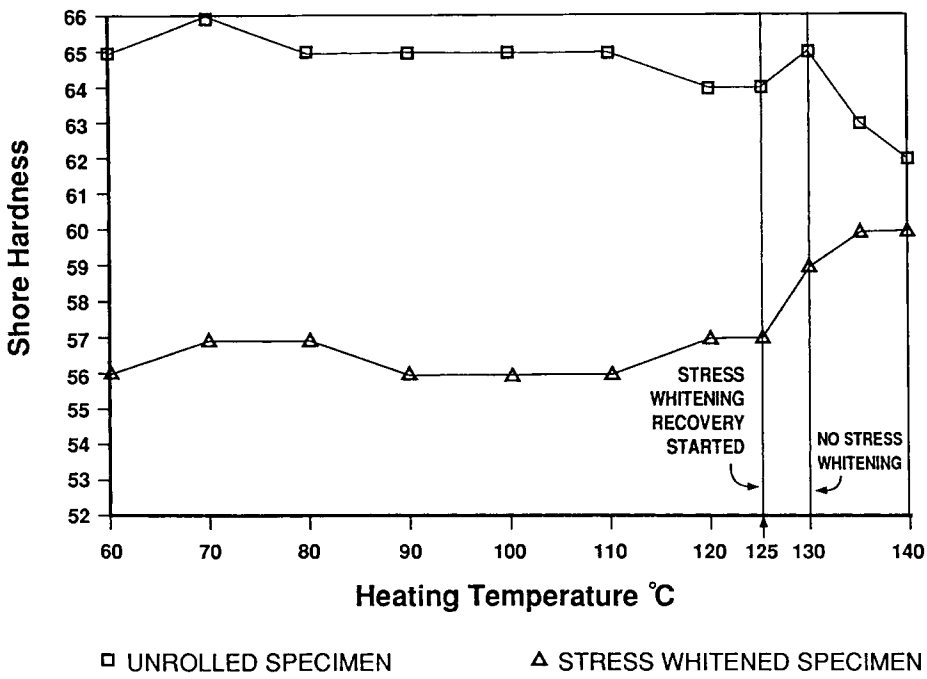

Figure 3 Hardness value of the unrolled and stress-whitened specimens at different heating temperatures.

also increases further though recovery of stress whitening had already completed. These results have the similar trends with those mentioned earlier, which indicate that rolling, tension stretching (i.e., increase in orientation and decrease in crystallinity), as well as stress whitening (presence of voids) could lead to the decrease in density. In the temperature range of 125–130°C, it is believed that the

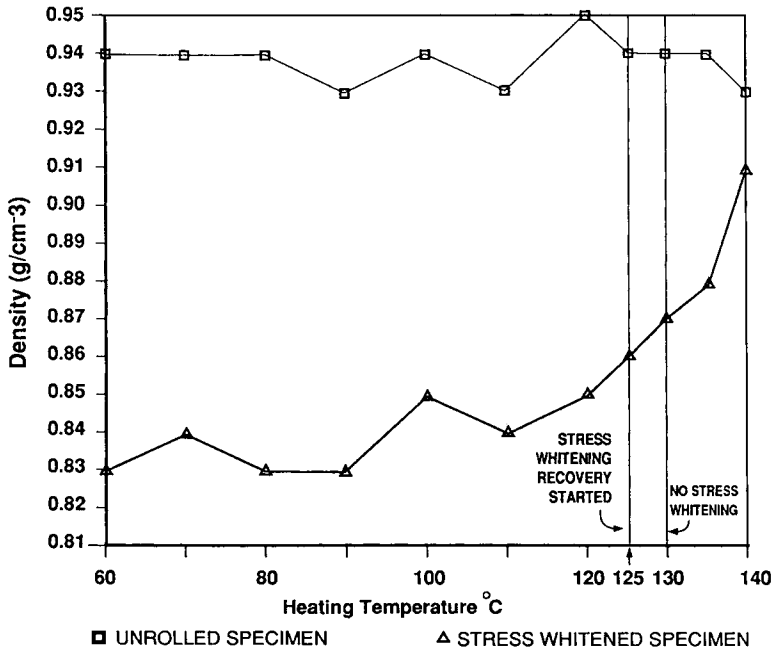

Figure 4 Density of the unrolled and stress-whitened specimens at different heating temperatures.

increase in density is due to the recovery of stress whitening (absent of voids). At higher temperatures (135–140°C), the further increase in density is probably the result of reduction in orientation and increase in crystallinity.

Results of Thermal Analytical Studies

The melting behavior of polyethylene has been studied by several authors using DSC technique and has been shown to be dependent on molecular weight and its distribution, degree of branching, crystallinity as well as heat treatment and crystallizing history.[8-10] The DSC method was used in this work to study the melting and recrystallization behavior of the unrolled and stress-whitened HMWPE specimens. A typical melting curve of HMWPE is shown in Figure 5, and information of melting point, melt range, and heat of fusion is listed in Table II.

It can be seen that there is a decrease in heat of fusion, melt range, and melting point for the stress-whitened sample. It is believed that this is the result of decrease in crystallinity. The heat of fusion obtained is directly proportioned to the crystallinity of the specimens. The crystallinity of a polymer can be calculated according to the following formula[11]:

$$\text{Crystallinity } \% = \frac{\Delta H}{\Delta H_k} \times 100\% \qquad (2)$$

where H and H_k are the heat of fusion of the polymer sample under study and the polymer with 100% crystallinity, respectively.

The heat of fusion of 100% crystalline PE is known to be 291 J/g.[11] If this is used to calculate the crystallinity of the specimens in Table II, the crystallinity of the unrolled and stress-whitened HMWPE sample is calculated to be 65 and 51%,

Table II Melting Point, Melt Range, and Heat of Fusion of HMWPE

Sample	Melting Point (°C)	Melt Range (°C)	ΔH (J/g)
Unrolled	138.1	157 − 89 = 68	189
Stress whitened	135.3	149 − 103 = 48	149

respectively. From these results the density of the unrolled and stress-whitened specimens can be calculated as follows:

Density of unrolled specimen

$$= (0.997 \times 65\% + 0.854 \times 35\%)$$
$$= 0.947 \text{ g/cm}^3$$

Density of stress whitened specimen

$$= (0.997 \times 51\% + 0.854 \times 49\%)$$
$$= 0.926 \text{ g/cm}^3$$

where 0.997 g/cm^3 is the density of PE with 100% crystallinity and 0.854 = g/cm^3 is the density of amorphous PE.[11]

Referring to Table I, it is known that the density of the unrolled sample was determined to be 0.95 g/cm^3. This coincides with the calculated value. However, the measured density value of the stress-whitened specimen was 0.81 g/cm^3, which is much lower than the calculated value (0.926 g/cm^3). These results indicate that the reduction in density due to decrease in crystallinity is small. It is believed that the large reduction in density of the stress-whitened specimen is the result of void formation.

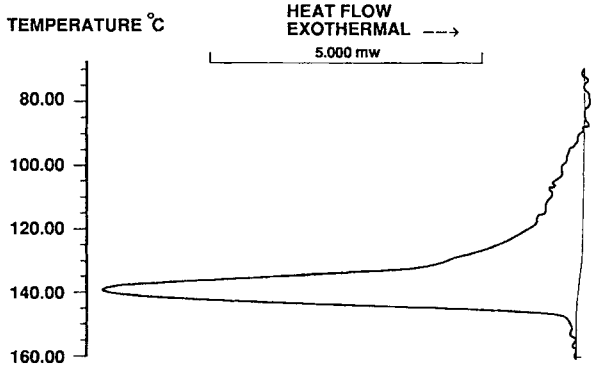

Figure 5 Typical melting behavior curve of HMWPE.

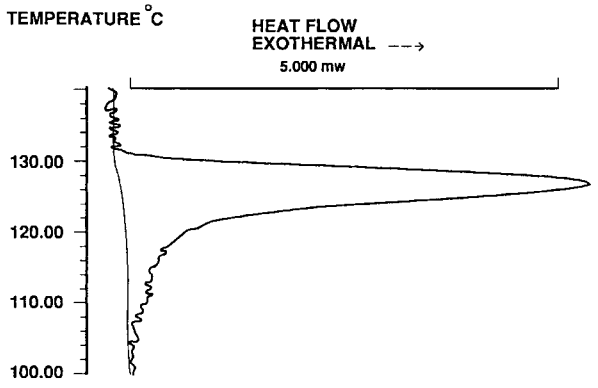

Figure 6 Typical recrystallization behavior of HMWPE.

Table III Recrystallization Data of HMWPE

Sample	Recrystallization Peak Temp. (°C)	Recrystallization Range (°C)	ΔH (J/g)
Unrolled	128.6	135 − 104 = 31	97
Stress whitened	128.9	136 − 103 = 33	101

Figure 6 is a typical recrystallization curve for HMWPE. The recrystallization DSC curves for the unrolled and stress-whitened specimens are identical. The data of recrystallization peak temperature, recrystallization range, and heat released during recrystallization are summarized in Table III.

Referring to the recrystallization DSC curves and the recrystallization data listed in Table III, it can be concluded the two specimens have similar recrystallization behavior.

Polarized-Light Microscopy and SEM

Polarized-Light Microscopy

The melting and recrystallization processes of the unrolled and stress-whitened specimens were also studied using a polarized-light microscope with a hot stage. The specimens were heated from room temperature to 200°C in about 15 min followed by cooling. It was observed that the specimens started to melt at about 140°C and shrunk at 190°C. When cooling down, recrystallization began at about 118°C, the specimens were cooled to 110°C in about 10 min, and were kept constant at that temperature to observe the growth of spherulites. The same spherulitic structure was observed in both specimens, as shown in Figure 7. No differences in the melting and recrystallization processes for the two specimens could be seen. These results are in agreement with the results of DSC measurement. As mentioned above, the changes in structure or morphology of a polymer could affect its melting behavior. Since no differences in the melting behavior of the unrolled and stress-whitened specimens could be seen through DSC and polarized-light microscopy study, it seems that there are no structural changes in the stress-whitened specimen.

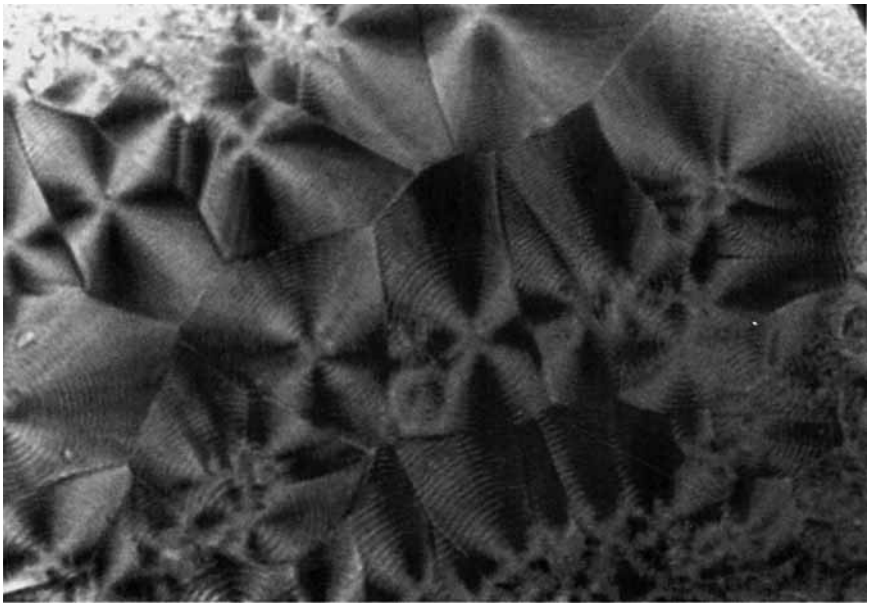

Figure 7 Spherulites observed in the recrystallization process for the unrolled and stress-whitened HMWPE specimen using polarized-light microscopy.

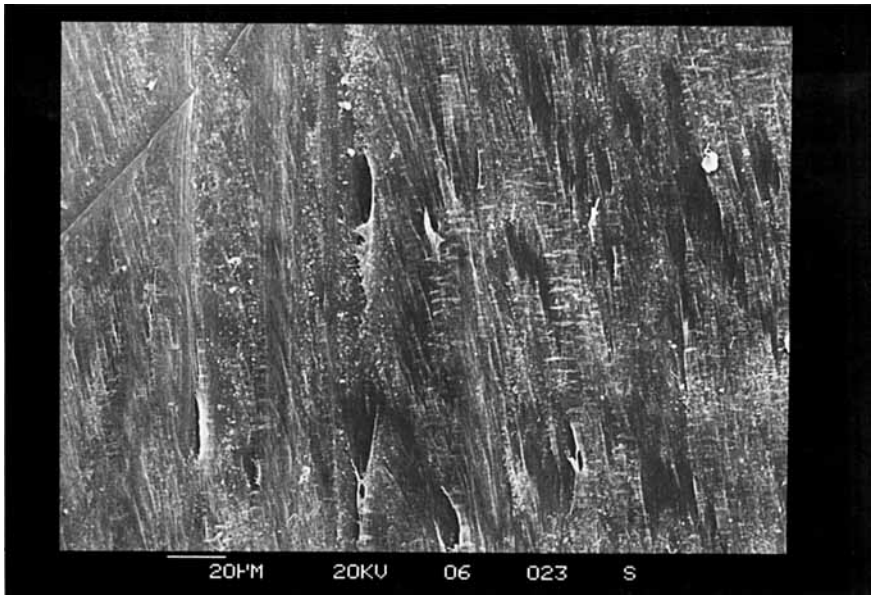

Figure 8 SEM micrograph of the stress-whitened specimen (tension pulling direction is horizontal to the photograph).

SEM

The surface texture of the stress-whitened, unrolled, rolled, and nonwhitened specimens was studied using SEM. The SEM micrographs of these specimens are shown in Figures 8–11. It is obvious that voids ranging from about 20 to 60 μm could be observed on the surface of the stress-whitened specimen; the voids are ellipse in shape and are perpendicular to the drawing direction (Fig. 8). The surface of the unrolled specimen is also not perfect, as indicated in Figure 9. However, the rolled specimen has a better surface appearance and some sort of kneading patterns could be seen (Fig. 10); this probably is

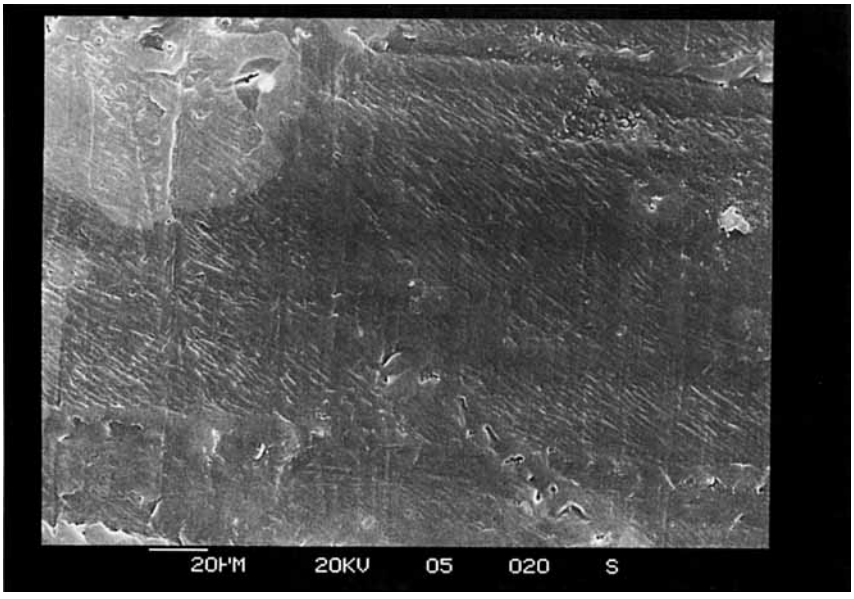

Figure 9 SEM micrograph of the unrolled specimen.

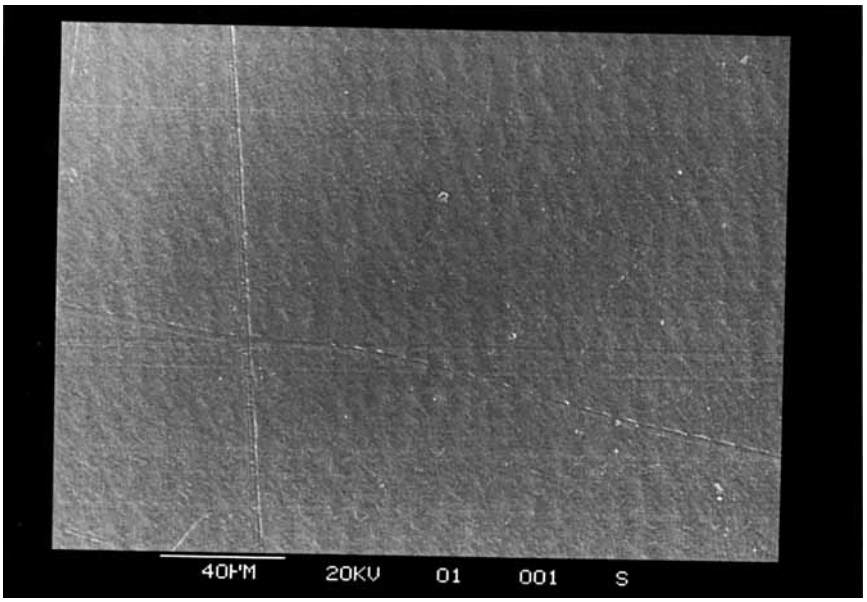

Figure 10 SEM micrograph of the rolled specimen.

the result of the combination of compression and shear forces that act on the specimen during the cold-rolling process. As shown in Figure 11, the surface of the nonwhitened specimen has "cross-fibril" texture that is believed to be the consequence of biaxial rolling.

CONCLUSION

From the results obtained, it can be concluded that the elimination of stress whitening of HMWPE by cold rolling does not relate to orientation or other structural changes. Instead, it is the consequence of

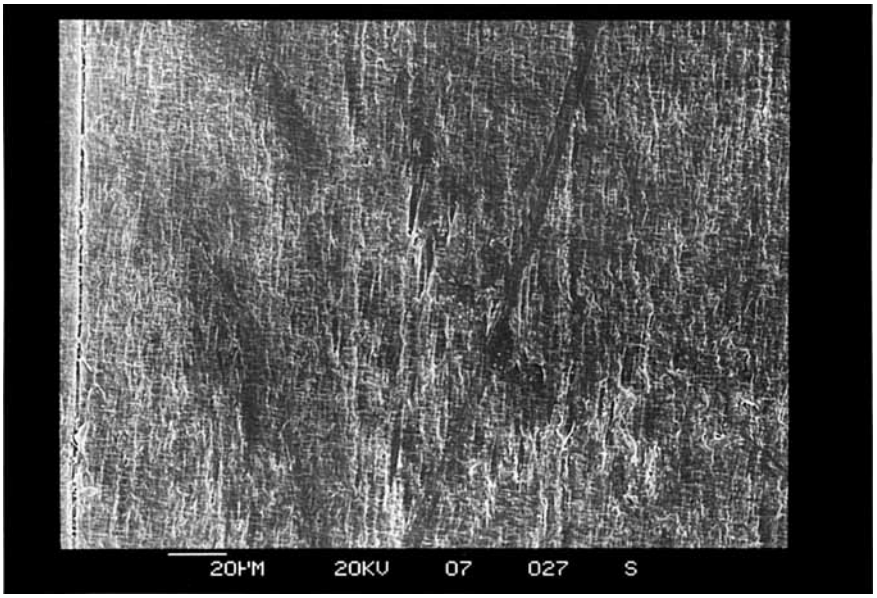

Figure 11 SEM micrograph of the nonwhitened specimen (tension pulling direction is horizontal to the photograph).

the combined forces of compression and shear acting on the specimens from different directions during the rolling process, accordingly the macro- and micro-imperfections of the material may be eliminated to some extent. At 40% or more rolling reductions, the imperfections were largely eliminated, hence stress whitening did not occur though the material was pulled under stress.

REFERENCES

1. Y. W. Lee, *Plast. Rubb. Proc. Applic.*, **13**(1), 29–35 (1990).
2. Y. W. Lee, *J. Appl. Polym. Sci.*, **43**(1), 29–37 (1991).
3. R. P. Kambour, *Macromol. Rev.*, 136–140 (1973).
4. L. Jareki and D. J. Meier, *J. Polym. Sci. Phys. Ed.*, **17**, 1611–1621 (1979).
5. J. H. Wendorff, *Polymer*, **21**, 533–538 (1980).
6. H. Brever, F. Haaf, and J. Stabenow, *J. Macromal. Sci. Phys.*, **14**(3), 387–392 (1977).
7. T. Hashimoto, K. Nagatoshi, A. Todo, and H. Kawai, *Polymer*, **17**, 1075–1085 (1976).
8. W. G. Harland, *Polymer*, **13**, 13–19 (1972).
9. D. P. Pope, and H. H. Wills, *J. Polym. Sci. Phys. Ed.*, **14**, 811–820 (1976).
10. E. S. Clark, *SPE J.*, **23**, 46–49 (1967).
11. N. J. Mills, *Plastic Microstructure, Properties and Applications*, Edward Arnold, London, 1986.

Received September 10, 1991
Accepted October 30, 1991