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COLD-DRAWING BEHAVIOUR IN METALLOCENE-CATALYZED POLYETHYLENE

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For the purpose of structural understanding of yielding and/or necking behavior of semicrystalliene polymers, which is very important for their practical use, we investigated the crosshead speed and molecular weight (M_w) dependences of the neck formation and the natural (neck) draw ratio for metallocene-catalyzed high density polyethylenes (HDPE) with different molecular weights. Tensile tests of the comp-molded HDPE sheets were performed under a wide range of crosshead speeds. The dumbbell-shaped specimens were elongated up to λ=4.4 (before strain-hardening zone), keeping for 10 min to undergo stress relaxation. Then, they were released from the cramps and the natural draw ratio λ_n of the drawn samples was precisely estimated from the cross-section area of the necked portion.

It was found that the natural draw ratio was almost constant below 1.00 mm/sec but the λ_n values increased with increasing the crosshead speed above 1.00 mm/sec. These results indicate that strain-hardening process by the external load takes place in addition to natural drawn state above 1.00 mm/sec. The SEM images of necked portions (extended below 1.00 mm/sec) showed that the structural units with about 30-40 nm size are closely-packed in the neck transition region (shoulder region of the specimen). According to the theoretical consideration of yielding behavior by Nitta-Takayanagi, [1)] the lamellar clusters within spherlites are fragmented into the cluster units at yield point, the size of which is almost single-chain radius (38.9 nm). Therefore, it follows that the cluster units act as necking units and are rearranged to the natural draw state in such a way that the surface energy of the rearranged blocky units takes minimum. The theoretical prediction that the natural draw ratio is proportional to -3/4 power of M_w was surprisingly in accordance with the experimental data. The natural draw process was capable of being explained from structural point of view.

References

1. K.Nitta, M.Takayanagi, J.Macromol. Sci.-Phys, B42, 107(2003)