

Mechanical and Transport Properties of Drawn Low-Pressure Low-Density Polyethylene

The new low density polyethylene (LDPE) obtained under low pressure in the reactor, the so-called low pressure low density polyethylene (LLDPE), with a great many short branches seems to replace the conventional LDPE with long branches obtained in the reactor under high pressure (high pressure LDPE = HLDPE). It has a higher tensile strength, impact strength, elastic modulus, elongation at break, and resistance to heat and stress cracking. The replacement goes on in film extrusion, blow molding, and wire and cable coating. The material seems also to be a good mixing component in polymer blends.¹

The most obvious physical differences between the short and long branch LDPE are the higher crystallinity and the narrower molecular weight distribution, higher melting temperature (122° instead of 108°), and a narrower melting range in the former than in the latter case.

The thicker and more perfect crystals are the main cause of these changes. The higher melting point, however, means a higher processing temperature that may be more harmful to the material and require a higher energy input.

The increased technical interest in this type of material prompted us to investigate the mechanical and transport properties of Dowlex 2045, a Dow Chemical made LLDPE with a density 0.9139 g/cm³ that corresponds to $\alpha_v = 0.414$. This is less than the density 0.9152 g/cm³ of the formerly investigated conventional HLDPE with $\alpha_v = 0.423$. The ratio 10–35 of side chain ends CH₃ per 1000 CH₂ on the backbone and side chains of the molecule indicates a large number of side chains. According to the producer the side chains are much shorter than in the conventional HLDPE. (Certain commercial material is identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material identified is necessarily the best available for the purpose.)

The enormous elastic modulus of the crystals as compared with that of the amorphous component makes the mechanical properties of the semicrystalline polymer depend primarily on the fraction of taut tie molecules crossing the amorphous layers and on the mechanical properties of these layers. Although they are in the rubbery state, the amorphous molecules are so intimately bound to the crystals that the properties of the amorphous component substantially deviate from those of a completely amorphous rubber. In particular the specific volume of the amorphous component changes upon straining. Instead of the shear modulus G one must introduce the about 1000 times higher expansion modulus K of the rubber.

The best method for the investigation of the amorphous component is the measurement of the transport properties. In first approximation they depend on the fractional free volume. It increases with the deformation if the specific volume does the same. The plastic deformation of drawing, however, reduces quite substantially the specific volume and hence the transport properties. This means that the amorphous layers between the crystal blocks of the microfibril in highly drawn material have a higher density, i.e., a smaller fractional free volume than in the undrawn sample.

The experimental details of the investigation of the mechanical and transport properties of the drawn material we used in this note are described in the former paper by Araimo et al.² The transport and mechanical properties of drawn HLDPE were investigated by Araimo et al.² and de Candia et al.^{3,4} The transport data on high density polyethylene (HDPE) were derived by Williams and Peterlin,⁵ and the mechanical data by Meinel and Peterlin.⁶ The density of the drawn samples of HDPE was studied among others by Fisher et al.^{7,8} and Glenz et al.⁹

The results obtained do not differ substantially from those obtained in conventional HLDPE. The elongation strain before the neck formation is 100% corresponding to $\lambda = 2$. This is marginally smaller than in HLDPE with $\lambda = 2.2$ but larger than in HDPE with $\lambda < 1.5$. Such a behavior may be explained by the smaller creep in thicker and more ideal crystals of LLDPE as compared with HLDPE while HDPE has thicker crystals with less defects than LLDPE. The smaller the creep the earlier the transformation from the lamellar to the fibrillar structure sets in.

The draw ratio in the neck increases by about 3 (in HLDPE by about 2 and in HDPE by between 7 and 10 depending on the temperature and draw rate, but primarily on the shape of the neck). At room temperature the samples may be drawn to $\lambda = 7.5$ (HLDPE to 6) while at 60°C the maximum

λ goes to 8 (HLDPE has $\lambda_{\max} = 6$ and HDPE has 30 and more depending on the temperature, draw rate, and molecular weight composition). The rapid increase of the draw ratio in the neck does not allow the investigation of the mechanical and transport properties below the true draw ratio $\lambda_{\text{loc}} = 6$.

The density of LLDPE starts with 0.9139 g/cm^3 and reaches 0.922 g/cm^3 at the highest obtainable draw ratio. In HLDPE one started with $\rho = 0.9153 \text{ g/cm}^3$ and arrived to 0.918 g/cm^3 . In HDPE one started with $\rho = 0.954 \text{ g/cm}^3$ and reached 0.967 g/cm^3 at $\lambda = 20$. Although the data of drawn samples do not correspond to the same draw ratio, one may conclude from $\rho_{\max} - \rho_0 = 0.0013$ for HLDPE, 0.0081 for LLDPE, and 0.013 for HDPE that as far as the density changes with the drawing are concerned LLDPE is closer to HDPE than to HLDPE.

The axial elastic modulus reaches 1.1 GPa while with HLDPE we never succeeded in obtaining E above 0.75 GPa. The differences seem to be primarily connected with the higher draw ratio obtainable in LLDPE. The HDPE starts already with a higher value, $E = 1 \text{ GPa}$, than can be obtained by drawing of HLDPE or LLDPE. Upon drawing it reaches values about 100 GPa.¹⁰ As far as the axial elastic modulus is concerned, no branched PE can compete with the linear PE.

If one does not pay any attention to the finite crystallinity of the sample one may deduce at the pressure p of the penetrant the sorption S from the measured sorbed concentration $c = S \cdot P$. One may write quite generally for the sorption coefficient of the amorphous component $S_a = S/(1 - \alpha_m)$ and the sorbed concentration $c_a = S_a p = c/(1 - \alpha_m)$ of the penetrant at activity $a = p/p_T$. The diffusion coefficient is usually expressed in the form $D = D_0 \exp(\gamma c)$. It is connected with the diffusion coefficient of the amorphous material by the tortuosity factor $\Psi < 1$ that takes into account the fact that the diffusing molecule has to travel a longer path from the surface to the interior as a consequence of the completely impermeable crystals. One has $D = \Psi D_a$. The zero concentration diffusion coefficient $D_{a0} = D_0/\Psi$ is inversely proportional to the tortuosity factor Ψ while γ is completely independent of it.

The starting values of LLDPE at a vapor activity $a = p/p_T = 0.8$ (p_T is the equilibrium pressure of methylene chloride vapor in contact with the liquid phase at $T = 25^\circ\text{C}$), $c_a = 11.2 \times 10^{-2} \text{ g/g}$, $D_0 = 7.0 \times 10^{-8} \text{ cm}^2/\text{s}$, and $\gamma = 12.5$, do not substantially differ from those of HLDPE with $c_a = 11.8 \times 10^{-2} \text{ g/g}$, $D_0 = 7.0 \times 10^{-8} \text{ cm}^2/\text{s}$, and $\gamma = 11.5$. They also do not differ too much from those observed on HDPE, i.e., $c_a = 12.4 \times 10^{-2} \text{ g/g}$, $D_0 = 2.7 \times 10^{-8} \text{ cm}^2/\text{s}$, and $\gamma = 10$. The higher penetrant concentration in LLDPE and HLDPE as compared with that in HDPE may be primarily caused by the quenching process of the film that seems to have been more drastic in the case of the HDPE than in LDPE. This view is corroborated by γ . The difference in D_0 may be caused by the substantially higher tortuosity, i.e., lower tortuosity factor Ψ of the HDPE with the higher crystallinity. By the more numerous and more densely packed crystals the HDPE poses more restraints on the path of the diffusing molecules than the LDPE.

As a consequence of the higher draw ratio, the sorption S and the zero concentration diffusion coefficient D_0 drop further and the exponential concentration coefficient γ increases to a higher

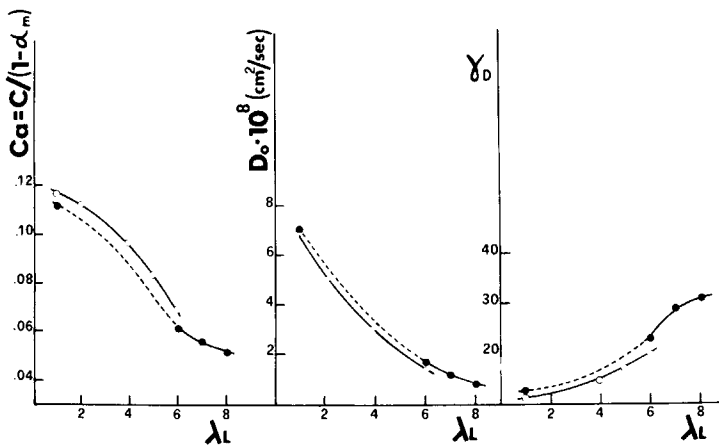


Fig. 1. The equilibrium concentration of methylene chloride in the amorphous component, $c_a = S_a p$, at $p = 0.8 p_T$ and 25°C , D_0 and γ vs. the true draw ratio λ_{loc} for LLDPE (●) and HLDPE (○).

value than in conventional LDPE (Fig. 1). The specific sorption of the amorphous component drops by a factor 2.2 while in HLDPE the drop is only by a factor 1.8. HDPE, however, shows a much larger drop by a factor of 6. The smaller reduction in HLDPE than in LLDPE is mainly caused by a smaller draw ratio we were able to obtain. But while in the former material the sorption still drops almost linearly with the draw ratio it seems to level off in the latter case.

The tendency of D_0 and γ to level off at the highest draw ratio suggests that at the draw ratio 8 the system is very near to a complete transformation of the original lamellar material into the new microfibrillar structure. The critical draw ratio λ_c for the completion of this transformation agrees quite well with that obtained for HDPE, λ_c between 8 and 9 for drawing at 60°C. The increase of γ from 12.5 of the lamellar to 31.5 of the microfibrillar material by a factor 2.5 is higher than in conventional LDPE, 1.7, and smaller than in HDPE, 20. The decrease of D_0 , however, from 7.0 to 0.85×10^{-8} cm²/s seems to be higher than in HLDPE, where it drops from 7.0 to 1.4×10^{-8} cm²/s. But it is enormously smaller than in HDPE where D_0 drops from 2.7×10^{-8} cm²/s to 1.0×10^{-10} cm²/s at $\lambda = 9$ and continues to drop to 5.3×10^{-10} cm²/s at $\lambda = 25$.

The smaller decrease of D_0 in HLDPE as compared with LLDPE is mainly the consequence of the smaller draw ratio as it was in the case of S_a or c_a . Hence the difference between HLDPE and LLDPE are mainly caused by the drawing behavior. Even the leveling off of S_a , D_0 , and γ at the highest λ of LLDPE seems to be a general property of polyethylene that is almost independent of branching. If the same draw ratio would be obtainable with HLDPE the effect would occur also in this system at λ close to 8.

Hence it is questionable whether the transport properties of LLDPE differ at all from those of HLDPE. The observed differences are mainly caused by the difference in the draw ratio that is higher in the former than in the latter material. The situation is very much the same with the elastic modulus.

The higher drawability of LLDPE as compared with HLDPE must be a consequence of the shortness of the branches because the crystallinity is practically the same in both cases. From this fact one may conclude that at equal crystallinity the maximum draw ratio increases if the branches are shorter. The mechanical and transport properties of the drawn material are mainly determined by the draw ratio.

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