The two- and three-dimensional dendrites grown in the first stage, had their main stems extending horizontally along [100] directions from which the primary and the secondary branches grew at 90°, both horizontally and vertically to the original direction. In the second stage of growth, the secondary branches became indistinct because of the filling up of the space between these branchings by growth sheets giving rise to lathlike or plate-like crystals.

The growth kinetics of  $PbCl_2$  needle crystals in gels follow a parabolic law which is characteristic of one-dimensional diffusion-controlled processes.

Needle-shaped crystals grow at low concentrations of the feed solution whilst at high concentrations dendritic growth occurs.

The growth at higher concentrations seems to occur in two stages: first the formation of twoor three-dimensional dendrites and second the filling up of the space between secondary branchings by growth sheets.

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Microhardness for evaluation of the environmental stress cracking resistance (ESCR) of low-density polyethylene (LDPE)

The object of the work reported in this letter was the determination of the most important physicochemical parameters which occur in the environment stress cracking (ESC) phenomenon for telephonic cable sheath materials.

It was found necessary to characterize physically the texture of the polymers and a technique was used between the two crystalline-amorphous phases approximation and an accurate size distribution of spherulites. Methods of test for environmental stress rupture under constant tensile load [1] or under constant bending [2] often arbitrarily determine the environmental stress cracking resistance (ESCR), where Antarox Co 630 is the environmental agent. Its behaviour with regard to the polymer is not completely understood. Some workers [3] believe that it plastisizes the polymer and changes the stress concentration at the craze tip; others [4] suggest the ability of the liquid to penetrate into the craze to decrease the strain energy release rate.

However, in this work, we are particularly interested in the structural parameters which modify the ESCR of low-density polyethylene (LDPE). Attention has been given to the influence of the average molecular weight, the molecular weight distribution and density on the resistance, also investigated previously by many authors [5], but consideration of only these indirect parameters (for example, molecular weight and longchain branching) was insufficient for an understanding of the behaviour of LDPE since account must also be taken of the thermal and the shearing history of the sample. For this reason two LDPE samples having the same crystalline ratio may



Figure 1 ESCR value,  $F_{50}$ , plotted against the Knoop microhardness value, where  $F_{50}$  is the probable time for 50% of the specimens to fail in a brittle manner.

show a different resistance into an Antarox solution because their average spherulite size is quite different.

Therefore, it is important to know more about the physical organization of crystallites than the sample density. For this purpose, we have found that Knoop microhardness  $(MH_K)$  measurements supply a convenient method giving an idea of the texture of the material correlated to the ESCR.

Experimentally many samples of LDPE were tested in a constant uniaxial stress device immersed in an Antarox Co 630 solution (1 vol % in water) at a temperature of 323 K. The specimens were moulded by compression and annealed or quenched. All the samples observed which had a  $MH_K$  value between 20 and 40 MPa were not resistant to crack propagation. Below 20 MPa and above 40 MPa the sample resisted crack propag-

ation quite well. A LDPE sample which was annealed and recrystallized at a rate of  $6 \text{ K h}^{-1}$ showed a MH<sub>K</sub> value around 25 MPa and quickly showed cracking; however, when it was quenched from the melt it exhibited a MH<sub>K</sub> value below 20 MPa and showed no indications of failure after three weeks. A LDPE sample that was slowly recrystallized having a MH<sub>K</sub> value higher than 40 MPa resisted cracking; however, when it was quenched from the melt, its MH<sub>K</sub> value was found to be in the failure zone (30 MPa) and it failed after a week. Measured ESCR values are plotted against Knoop microhardness values in Fig. 1.

It is assumed that the 20 to 40 MPa zone corresponds to the region where spherulites of the critical size for interlamellar failure are formed [6].

Accordingly it seems that  $MH_K$  measurement can be a convenient method for estimating the ESCR for LDPE moulded samples. This result will be supported using other methods of investigation, such as small-angle X-ray scattering (SAXS), wideangle X-ray scattering (WAXS) and light scattering to seek the morphology and size of crystallites which produce this range of  $MH_K$  values.

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