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An estimation of the chain branching effects in butene/ethylene copolymers from microhardness measurements

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SUMMARY

In this work a simple microhardness test to evaluate the degree of chain braching in butene-ethylene copolymers is proposed. The random introduction into the chain of co-units, reduces the level of crystallinity in the copolymer, a characteristic easily measurable through indentation experiments. A comparative study between density and microhardness values in samples with different concentration of chain braching is presented.

INTRODUCTION

In recent years great interest has grown in linear low-density polyethylene (LLDPE) copolymers. In this sense butene-1/ethylene polymers are materials with flexible properties (mainly mechanical and optical), conditioned by their structural configuration and conformation, aspects regulated by the concentration of the olefin and catalytic conditions of the copolymerization reaction (1).

In general a random incorporation of the α-olefin co-units leads to the introduction of side groups in the polyethylene backbone, with a consequent difficulty in achieving a regular chain folded arrangement and therefore a reduction of their degree of crystallinity (2). That is why the incorporation of short units derived from butene implies a decrease of the melting temperature and stiffness and increases in the elongation at break and impact strength of LLDPE copolymers.

The determination of the crystallinity by means of X-ray diffraction, spectroscopic or calorimetric measurements is a normal task in fundamental laboratories. Therefore the industrial use of these techniques, in order to estimate the influence of the olefin proportion incorporated in the polymerization, is rather problematic. For this reason a density measure is the

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*To whom offprint requests should be sent test normally employed in this valuation; it is well known that an aproximate degree of crystallization can be obtained in polyethylene from density values, by means of the relation of Chiang and Flory (3) .

However, we have verified that a density evaluation is not an optimal test because wide variations in crystallinity of the LLDPE results in only weak relative variations of density ; for example a variation of 10 % in the degree of crystallinity of the copolymers causa a change in density of approximately 1 % .

For this reason we have sought a more sensitive tool for testing this chain branching effects in LLDPE by the use of an indentation technique (Vickers microhardness measurements) in which our laboratory has a wide experience (4 - 6) . In our experiments of the last few years, we have demostrated that a measure of the material resistence against local deformation is a simple and sensitive method capable of detecting small structural changes in semicrystalline polymers .

EXPERIMENTAL

Samples

LLDPE samples were obtained conventionaly by copolymerization of ethylene with different amounds of butene, at 200 - 210ºC and 800 atm.of pressure, in a heterogeneous Ziegler-Natta catalys system composed of $MgCl_2$ supported $TiCl_4$ and triethyl aluminium . Molecular characteristics of these samples are given in table I .

Table I . Molecular characteristics of the butene-ethylene copolymers studied .

sample	M_w	M_w/M_n	% comonomer in copolymer
GS 29441	76,300	6.8	10.92
GT 03443	45,000	6.5	8.76
GT 17443	72,300	5.9	8.20
GS 22442	83,800	4.5	6.80
GT 10442	51,900	5.1	6.08
GT 11442	39,600	5.6	4.96

Molecular weights and molecular weight distributions were determined by gel permeation chromatography in the conventional manner(7) . The percentage of short chain branching derived from butene-1 units, was obtained by IR spectroscopy using methyl symmetric deformation band at 1378 cm^{-1}(8).

Specimens of each sample were compression-molded between smooth-heated plates (170°C / 500 $MN.m^{-2}$) to obtain sheets having a thickness of about 2 mm, and allowed to cool freely to room temperature (about 1 hour) .

Microhardness

In the Vickers method used, a square based diamond pyramide of face $\alpha = 136$ is pressed into the surface of the specimen . The hardness number MHV is obtained as the ration of the applied load to the projected area of the resulting indentation. With the given pyramid geometry the MHV is expressed by

$$MHV = \frac{2\ L\ \mathrm{sen}(\alpha/2)}{9.807\ d^{2}} = 0.1891\ (L\ /\ d^{2})$$

where L is the applied load in N and d is the mean diagonal length of indentation in mm .

Measurements were performed at room temperature in a Zeiss equipment . Specimen indentations were made under optimal conditions previously calculated resulting an indentation load of 10 ponds and a loading time of 30 sec ; 6 impressions were made at each load . Values were obtained inmediatly after the load was removed .

Density

The density of the six samples were determined at 23ºC in an isopropanol-water gradient column which has been calibrated with glass floats.

RESULTS

Figure 1 shows both microhardness and density experimental values obtained for the different samples whose comonomer porcentage is refered in Table I . A linear correlation between these measurements can be observed in this figure .

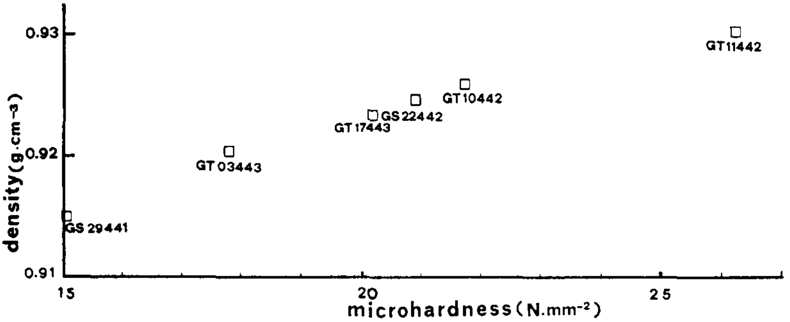

Figure 6 . Plots of density against microhardness values.

On the other hand these results demostrate that the incorporation at the backbone of short chain branches, derived from butene comonomer units , is correlated with a decreasing in density and microhardness . Nevertheless,in the incorporation range that we have studied , while the relative variations in density are of a 1.7% approximately, the variations in microhardness correspond to a 55% , a 32 times higher sensitivity .

In conclusion the results of the present work have clearly shown that a simple microindentation technique, which is directly vinculated to a measure of crystallinity in semicrystalline polymers, can give important information on the level of incorporation of groups linked laterally to the LLDPE backbone .

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