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THERMAL AND MECHANICAL PROPERTIES OF POLYETHYLENES SYNTHESIZED WITH METALLOCENE CATALYSTS

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Abstract

A series of high density polyethylenes (HDPE) were synthesized via homogeneous polymerization with metallocene catalyst in two different reactors (glass and stainless steel). The thermal and mechanical properties of the polyethylenes, synthesized with two types of reactor and different reaction parameters, are discussed.

Keywords: DMTA, DSC, mechanical properties, metallocene catalysts, polyethylene

Introduction

Metallocene compounds are becoming an important class of catalysts and opening a new field for the synthesis of polyolefins. The enhanced properties of the polymers synthesized are brought about by the improved control of molecular mass and short chain branching. Due to the fact that all catalytic sites have the same electronic and steric structure, metallocene catalysts are commonly considered as single site catalysts [1–3]. Furthermore, these systems allow tailor making of polymers due to a better control over the structure of the metallocene and the polymerization conditions [4, 5]. In order to achieve high activity these catalysts need the presence of a co-catalyst, methylaluminoxane (MAO), employed in a large excess over that of metallocene [6]. MAO interacts with metallocene to generate cationic metallocene alkyl species, the active species during the polymerization [7].

Molecular mass of polyolefins produced by homogeneous single site catalysts can range from 10^3 to 10^6 depending on the reaction conditions and catalyst systems. The polydispersities M_w/M_n are in any case close to 3 [8, 9].

The purpose of the present work is to study the mechanical and thermal properties of the polymers synthesized under different polymerization conditions, and with two types of reactor.

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Experimental

Materials

Commercial toluene was purified by refluxing over metallic sodium, with benzophenone as indicator. Polymerization grade ethylene was deoxygenated and dried by passing through columns of BASF R3-11 catalyst and 4 Å molecular sieves. Methylaluminoxane (MAO) and the catalyst $EtInd_2ZrCl_2$, all supplied by Witco, were used directly. All manipulations were carried out in an inert nitrogen atmosphere.

Polymerization

For the polymerization of ethylene, a 500 cm^3 autoclave reactor was filled with 250 cm^3 of toluene, 3 cm^3 of MAO (1.66 M) and 2 cm^3 of metallocene solution ($5.9\cdot10^{-6}$ M). The polymerizations were normally carried out at 60–65°C for 0.5 h at 1.2–1.6 bar monomer pressure. In the glass reactor the monomer pressure was smaller, 0.6 bar, while the rest of conditions were maintained.

Characterization

Molecular masses and molecular mass distributions were determined by means of size exclusion chromatography with a Waters 150°C equipment connected in line to a viscometer Viscotek 150 R, at 145°C in 1,2,4-trichlorobenzene and with three columns of Polymer Labs. (two mixed B of 10 μm and one of 10^{-2} μm). Polyestyrene standards were used for calibration.

Differential scanning calorimetric (DSC) measurements were made with a Perkin Elmer DSC 7, at a heating rate of 10°C min^{-1}. The mass of the samples ranged from 6 to 10 mg. The enthalpies of fusion were converted to degrees of crystallinity $(1-\lambda)_{\Delta H}$ by taking 290 J g^{-1} as the enthalpy of fusion of the perfect polyethylene crystal [10].

Specimen densities were measured at 25°C using a density gradient column filled with an ethanol-water mixture.

Polymer films were prepared in a Collins press, fitted with smooth-polished plates, by hot pressing at 5 MPa for 3 min, at a temperature 20°C above the melting temperature of the sample. The cooling process was carried out by quenching with water cooled plates.

Dumb-bell specimens 2 mm width and 15 mm gauge length were uniaxially drawn in an Instron dynamometer model 4301 with a crosshead speed of 10 mm min^{-1} . The values are expressed as the mean value from three specimens.

Dynamic mechanical measurements were carried out with a Polymer Laboratories MK II Dynamic Mechanical Thermal Analyser working in the tensile mode. The complex modulus and loss tangent of the samples were determined at 1, 3, 10 and 30 Hz over the temperature range –140 to 120°C. The heating rate was 1.5°C min^{-1}. The apparent activation energies were calculated according to an Arrhenius type equation, from the maximun values of the loss modulus at the four mentioned frequencies.

Microhardness measurements were obtained by using a Vickers indentor attached to a Leitz microhardness tester. A load of 4.809 N was used, with a loading cycle of 10 s. *MH* values (in MPa) were calculated according to the relationship:

$$MH=2\sin 68P/d^2$$

where P (in N) is the contact load and d (in mm) is the diagonal length of the projected indentation area.

Results and discussion

Differences in the activity of the catalyst according to the employed reactor have been found (Table 1). It can be observed that the polymerizations in the glass reactor present higher activity than those of the stainless steel autoclave. This behavior had been already discussed and attributed in a previous paper as a result of the different experimental variables in both reactors [11].

Characterization and thermal properties

All GPC curves obtained for the PE samples show a unimodal molecular mass distribution and the values of polydispersity are below 4, typical of metallocene catalysed olefin polymerizations (Table 1). However the samples synthesized in the glass reactor display polydispersity factors somewhat higher than those corresponding to samples obtained in the autoclave.

The values of the density determined after the first moulding of the specimens are typical of high density polyethylenes (HDPE) and the samples obtained in autoclave show values slightly superior than glass ones (Table 2). Moreover, DSC curves present in all the cases a unique maximum of fusion, typical of HDPE (Fig. l). The synthesized samples show a melting temperature of 131±2°C and an apparent melting heat of 180 J g^{-1}, with a crystallinity higher than 62% (Table 2). These values are similar in all the samples, except the H_B one that gives values slightly higher for

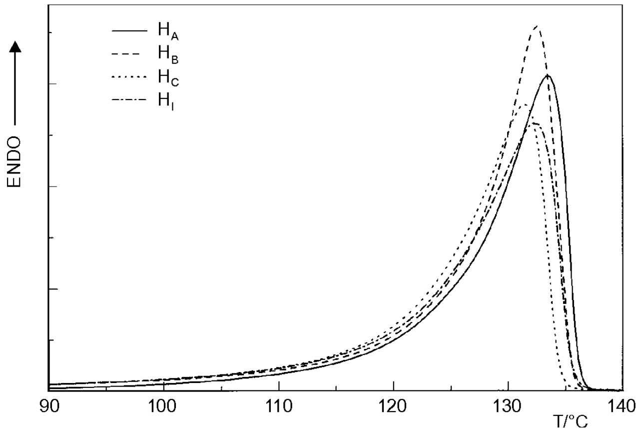

Fig. 1 DSC traces for the PE samples

Table 1 Polymerization details of the different samples (catalyst: $EtInd_2ZrCl_2$)

Sample	Reactor	Activity* Kg/mol Zr h p	M_n	M_w	M_w/M_n
H_A	autoclave	15300	75300	203700	2.7
H_B	autoclave	14200	–	–	–
H_C	glass	25000	78100	405400	5.2
H_I	glass	24600	138100	635100	4.6

**p*(autoclave)=1.6 bar, *p*(glass)=0.6 bar, *t*=30 min

Table 2 Melting heat, melting temperature and crystallinity of the samples synthesized

Sample	ΔH /J g^{-1}	T_m /^{o}C	$(1-\lambda)_{\Delta H}$/%	Density/g cm^{-3}	$(1-\lambda)_{\Delta d}$/%
H_A	179	133	62	0.946	67
H_B	197	133	68	0.942	64
H_C	181	131	62	0.935	60
H_I	182	132	63	0.937	61

Table 3 Young modulus (*E*), Yield stress (σ_y), deformation at the yield point (ε_Y) and at break (σ_B), Tensile strength at break (ε_B) and microhardness (*MH*)

Sample	*E* /	σ_y /	ε_Y /	ε_B /	σ_B /	*MH* /
	MPa		%		MPa	
H_A	510	21	96	915	26	48
H_B	580	14	223	1055	34	42
H_C	540	21	122	675	24	40
H_I	600	19	105	935	35	39

melting enthalpy and crystallinity. It is likely due to a crystal size larger than that of the other samples.

Mechanical properties

The results of the stress-strain curves are listed in Table 3. These curves display a sharp force maximun at low strain, corresponding to the yield point. Beyond this point there is a decrease in the force with a further increase in elongation. In all cases the behaviour of the samples is typical of HDPE [11] but the deformation progress through multiple necks along the specimen. Upon formation of the neck the deformed region whitens, due to void formation. In all cases the deformation is, therefore, not homogeneous. Finally it is observed a strain hardening until reaching the breaking point [12, 13].

The correlation between mechanical properties (modulus and yield stress) and microhardness is well established for various series of polyethylenes previously reported [14] and it is also fulfilled by the polyethylenes synthesized with metallocenes. These correlations exist because the yield stress and the modulus as well as the microhardness are mainly governed by the degree of crystallinity. The results of nineteen different polyethylenes, including HDPE, synthesized either with classic Ziegler-Natta catalysts or with metallocenes, and LLDPE have been compared. Their densities range from 0.917 to 0.960 g cm^{-3}. Figure 2 (up) is a plot of the Young modulus as a function of microhardness. It is observed a correlation between *E* and *MH* [14, 15]. The classic HDPE's are included in the range where *MH* is between 45

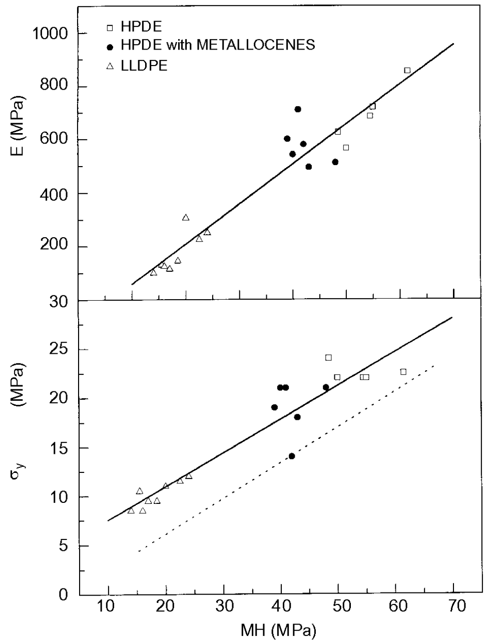

Fig. 2 Young modulus *vs*. microhardness *MH* (upper) and Yield stress *vs*. *MH* (lower). (Points line Tabor relation [16])

Table 4 Temperatures (E'' basis, 3 Hz) and apparent activation energies corresponding to the α and γ relaxations, and sortage moduli at room temperatures, for the samples synthetized

Sample	T_α /	T_γ /	ΔH_α /	ΔH_γ /	E'25°Cü›5ç[Eçc% ÇéçÇÂ25ç§2ççH	E'–130°C
	°C		kJ mol^{-1}		MPa	
H_A	47	–116	135	100	1340	5360
H_B	43	–114	140	128	1420	5900
H_C	43	–113	140	136	1330	5130
H_I	44	–114	145	92	1210	5700

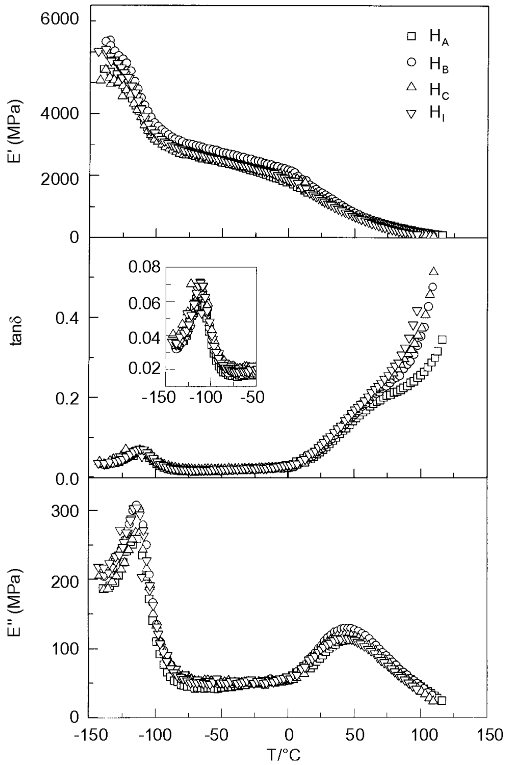

Fig. 3 Values of E', E'' and tanδ, at different frequencies, for sample H_c

and 60 MPa, and E is between 500 and 900 MPa, while metallocene HDPE's show *MH* lower than 50 MPa and E values around 600 MPa. The LLDPE samples present *MH* and E values around 20 MPa and 200 MPa, respectively. Finally, it is interesting to consider the correlation between microhardness and yield stress (Fig. 2, down). As these two properties increase linearly with the degree of crystallinity, a linear relation is expected. Tabor [16] proposed, for metals, a microhardness-yield stress ratio equal to 3, but semicrystalline polymers approach to this value only for high crystallinity contents [14].

Dynamic mechanical thermal properties

The temperatures of the α and γ relaxations, their apparent activation energies and the storage moduli at low and room temperature, for all the polyethylenes studied, are listed in Table 4. As can be seen in this table, the reaction parameters have little effect on the dynamic mechanical results. The temperature location of the relaxations has been obtained from the loss moduli *vs*. temperature plots. As an example, the results corresponding to H_C sample are plotted in Fig. 3. It shows that the β relaxation does not appear in the polyethylenes studied. Therefore, the dynamic mechanical behavior of the polyethylenes synthesized with metallocene catalyst is more akin to that of linear (high density) polyethylenes.

All samples display well-defined and slightly asymmetric α and γ relaxations as found in other HDPE's [17, 18]. The former was associated with the crystalline phase at temperatures around 40°C and with an activation energy of 140 kJ mol^{-1} [19], and the latter one, produced by formation, inversion and migration of chain kinks in the amorphous phase [20], occurs at temperatures around –115°C. The γ relaxation is practically constant in temperature location and activation energy (~100 kJ mol^{-1}), even when the last value is somewhat higher than the previously reported ones [13].

Conclusions

There is no marked influence of the reaction parameters on the mechanical behavior of the polymers synthesized. Moreover, high density polyethylenes synthesized with metallocene catalysts have mechanical and dynamic-mechanical properties close to those of classic Ziegler-Natta polyethylenes.

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