Differences between Low Density Polyethylenes Synthesised at Homogeneous and Heterogeneous Reacting Conditions

It is a well known fact that low density polyethylene (LDPE) could be obtained at great variety of synthesis conditions, which include pressure range 100–300 MPa and temperatures 423–573 K. Under these process conditions the reacting mixture between ethylene and polyethylene can exist as a homogeneous one, where the complete miscibility between the monomer and polymer is achieved, or at certain combinations of process parameters the phase separation can occur, whereby two separate phases are formed. The boundary curves between the homogeneous and heterogeneous phase state of the ethylene–polyethylene system, at the investigated pressure and temperature ranges, have been studied by many authors.[1-9] It was also found that the boundary curve depends on many factors such as pressure, temperature, concentration of polymer formed, and its structural characteristics (molar mass, degree of branching etc.), type and concentration of chain transfer agent, design characteristics of the reactor for the polymerization, etc. The detailed discussion of the parameters which influence the phase boundary of the ethylene–polyethylene mixture will not be discussed in this work, but could be found elsewhere.[1,3,5,6,8-12] As pressure and temperature are the main parameters which infuence phase boundary, it could be generally regarded that the heterogeneous phase state exists at lower temperatures and pressures.

Although the patent literature[13,14] and other published data[15,16] undoubtedly indicate that the manufacture of LDPE at heterogeneous reacting conditions could be prformed commercially, nevertheless, many authors still recommend the polymerization of ethylene exclusively at homogeneous conditions.[17-19] Hence, it is the purpose of this work to give the comparative data of ethylene polymers, synthesized on both above-mentioned manners, which are intended for the same application.

RESULTS AND DISCUSSION

Table I shows the main structural characteristics as well as the physical properties of two polyethylenes A and B, manufactured at different process conditions. Polyethylene resin A is obtained heterogeneous, and B at homogeneous synthesis conditions, taking into account the pressures and temperatures applied for their production. As criterion for the existence of homogeneous or heterogeneous phase state of the reacting mixture the existing data of Ehrlich,[1] Swelheim,[2] Steiner,[5] and Loos et al.[11] were used. Both resins A and B are obtained in the industrial stirred reactor with capacity of 45,000 tons per year of LDPE, and are intended for heavy duty film packaging application. As could be expected, higher pressures applied during the polymerization process favor the increase of average molar masses (especially M_w) and broadening of molar mass distribution. The most interesting feature is the decrease of long chain branching, which occurs during demixing of the reacting mixture. Although it could be expected that phase separation will result in an increase in long branch formation, due to increase of intermolecular chain transfer in the viscous phase, this general assumption was not experimentally confirmed. On the countrary, Constantine and Machon[20] recently proved that long chain branching decreases and density increases, when phase separation occurs. These facts were undoubtedly confirmed by our experiments as well. The direct consequences of these structural changes in polyethylene molecule are different physical properties which determine their suitability for the end use.

As could be seen from Table I, polymer A, synthesized at heterogeneous reacting conditions, shows improved properties compared to resin B, except the impact resistance. In spite of the worse impact resistance of resin A, compared to resin B, this property still retains a value satisfactory for film application (e.g., more than 0.6 kg for 200 μm film thickness). Besides the investigated physical properties given in Table I, it should be emphasized that melt ex-

TABLE I

Structural and Physical Properties of Two Polyethylenes Obtained at Heterogeneous and Homogeneous Phase State of the Ethylene–Polyethylene System at High Pressures

	Resin A	Resin B
Structural characteristics:		
$M_w \times 10^{-a}$	11.01	44.32
$M_n \times 10^{-4a}$	2.39	2.54
$M_w/M_n{}^a$	4.6	17.3
$g'{}^b$	0.49	0.28
$CH_3/1000C^c$	22.3	24.6
Δn^d	8.4	4.5
Physical properties:		
Melt index[e] (g/10 min)	0.33	0.24
Density[f] (kg/m³)	922.0	919.6
Tensile strength at break[a] (MPa)	16.7	12.9
Yield[g] (MPa)	9.99	6.88
Elongation[g] (%)	704	540
Vicat softening point[i] (K)	371	370
Film properties(measured on blown extruded films of 35 m thickness:		
Hase[j] (%)	6.0	30.9
Gloss[k] (%)	10.9	3.2f
Tensile strength at break[l] (MPa), MD/TD	26.5/25.8	18/16.8
Yield[l] (MPa) MD/TD	-/11.3	-/9.5
Elongation[l] MD/TD	517/722	326/473
Impact resistance[m] (kg)	0.18	0.23
Tear resistance[n] (kg), MD/TD	0.15/0.25	0.074/0.10

[a] From GPC Waters Model 200; 1,2,4-TCB at 408 K, Universal calibration.

[b] As ratio of (v)branch/(v)linear, $(v)_{br}$ measured in 1,2,4-TBC at 408 K; $(v)_{lin}$ determined from the computed M_w.

[c] As total degree of branching, determined on pressed films according to ASTM D 2238-68 (method A).

[d] As a measure of width of SCBD determined from integral SCBD curve of the sample fractionated by preparative TREF technique.

[e] ASTM Method D-1238-65 procedure A; test condition E, 463, K, load 2.16 kg.

[f] ASTM Method D-1505-67 at 296 K, sample prepared by procedure A; ASTM Method D-1928-68.

[g] ASTM Method D-638-68 on compression molded specimen.

[h] ASTM Method D-2240-68 on compression molded specimen.

[i] ASTM Method D-1525-65 on compression molded specimen.

[j] ASTM Method D-1003-61 (procedure A).

[k] ASTM Method D-523-67 with 60 deg geometry.

[l] ASTM Method D-882-67.

[m] ASTM Method D-1709-67.

[n] ASTM Method D-1922-67.

tensibility* of resin A is found to be superior, probably associated with lower degree of long chain branching in conjunction with broad short chain branching distribution of this resin. Generally speaking, the ethylene polymers obtained during existence of the heterogeneous phase state in the reacting mixture have better balance of mechanical and optical properties, and hence offer several benefits for the resin processors. The comparative results about the structure and basic properties of identical LDPE types, obtained at various phase state of the

*Sometimes called draw-down rate. This property is a measure of the resistance to tearing of the viscous film, and is defined as maximum takeoff rate of a film without breaking, extruded through a given die opening at established constant flow and temperature.

reacting ethylene–polyethylene mixture and intended for the same end use, have not been published before, if known. The obtained results represent typical values for commercial types of LDPE, obtained in our industrial process, involving the use of continuous autoclave reactor with stirrer, and could be regarded highly informative and suitable for industrial use.

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V. BOGDANOVIĆ
J. SRDANOVIĆ

Hemijska Industrija Pančevo
Petrochemical Complex
26000 Pančevo, Yugoslavia