STUDIES ON RHEOLOGICAL METALLOCENE POLYOLEFINS CHARACTERIZATION USED TO MANUFACTURE MULTILAYER FILMS

Daniela TEODORESCU[1], Gheorghe HUBCĂ[2]

Determinările experimentale efectuate asupra poliolefinelor metalocene au scos în evidență comportări reologice superioare ale poliolefinelor de tip Affinity 1170 şi Affinity 1880 față de Luflexen 0322 0322. Toate compoundurile cu Affinity 1880 prezintă o dependență a momentului de turația şnecului în procesele de extrudere. Compoundurile cu Affinity 1170 au comportări similare, cu valori uşor mai scăzute în comparație cu Affinity 1880, lucru explicabil datorită valorii mai mari a indicelui său de curgere.

Experimental measurements performed revealed higher rheological behavior for metallocene polyolefins Affinity 1170 and Affinity 1880 types, related to Luflexen 0322 0322. All compounds with Affinity 1880 have a dependence of the moment related with screw revolution in extrusion processe . Compounds with Affinity 1170 have similar behavior with slightly lower values, in comparison with Affinity 1880. This behavior is understandable because of the higher value of the flow melting point for this type of Affinity.

Keywords: extrusion, coextruded, multilayer films, metallocene

1. Introduction

The polyolefins processing is dependent on their molecular structure, especially the molecular weight distribution and branching structure and weight. A polyolefin with a wide distribution is easier to process than one with narrow distribution [1, 10, 11, 14, 15]. A long branch polymer flows more easily than a linear polymer.

The metallocene polyethylenes (mLLDPE) having a narrow molecular weight distribution, their rheological behavior will be different from the classical linear polyethylene, hovering above them as viscosity in the same range of shear rates. A rheological study could show the processing conditions for these types of polymers.

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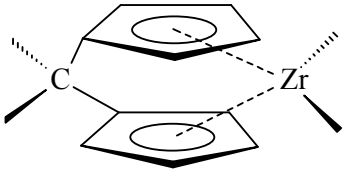
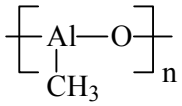
The ethene polymerization with metallocene catalysts takes place at low pressures and moderate temperatures, to about 80-100□C. Catalysts in this class are two-component systems consisting mainly from a metallocene compound Ti, Zr, Hf, noted I, and an alumoxan co-catalyst, noted II. The co-catalyst methyl-alumoxan, (MAO) is the metallocen key, which is obtained by controlled hydrolysis of tri-methyl-aluminum and is an oligomer with a molecular weight between 1000 and 1500 g / mol.



Metallocene compound (I)



Co-catalyst (II)

Starting from different metallocene catalysts the full range of linear or weakly branched polyethylene can be obtained similar to those with Ziegler-Natta catalysts.

Nowadays, polymerization with Ziegler-Natta catalysts is used to obtain a family of linear or weakly branched polyethylene: *Ultra Hight Molecular Weight Polyethylene* (UHMWPE), *Hight Density Polyethylene* (HDPE), *Medium Density Polyethylene* (MDPE), *Linear Low Density Polyethylene* (LLDPE) and *Very Low Density Polyethylene* (VLDPE) [1].

The change in density is achieved by copolymerization with propene, 1-butene, 1-hexene or 1-octene, with the specification that these metallocene catalysts lead to polymers with more uniform distribution of co-monomers in the polymer chain. In the propene co-polymerization the co-catalyst activity is much higher than that in ethene homo polymerization [1].

Linear low density polyethylene (LLDPE) is a linear polymer with density between 0.915 and 0.925 g/cm^3. This is due to a large number of short branches introduced in the polymer chain by copolymerization with α-olefins (1-butene, 1-hexene , 1-octene).

Very low density polyethylene (VLDPE) is a polymer with a density between 0.880 and 0.915 g/cm^3, which is obtained preferably, by

copolymerization of ethene with α-olefins, the metallocene catalysts providing a more uniform distribution of monomers in the polymer chain.

The polyethylene is used in manufacturing multilayer films in the form of bags or sacs for food packaging.

The capabilities for an adequate polyethylene processing are linear function of flow index and density, as shown in figure 1 [1].

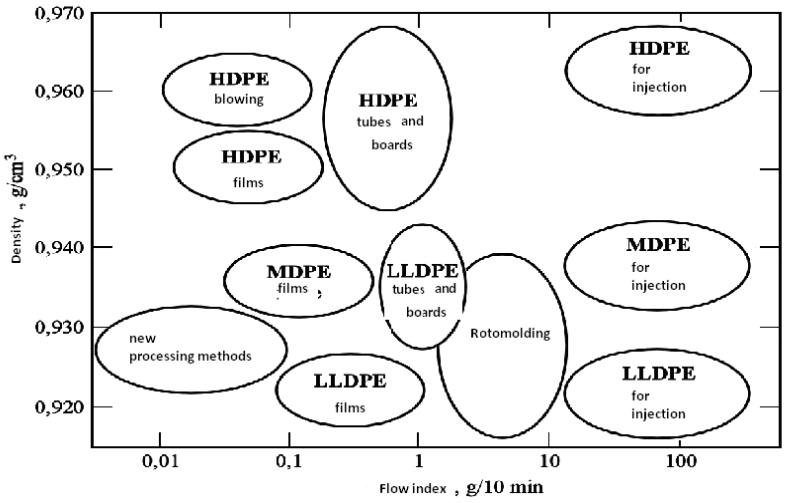


Fig.1. Relation flow index -density [1]

2. Experimental part

The studied metallocene polyethylenes come from the companies: BASF-Luflexen 0322 and Dow: Affinity 1170, Affinity 1880. Table 1 shows the main characteristics of these materials.

Table 1

Characteristics of the studied polyolefins

Metallocene Characteristics, Units	Luflexen 0322	Affinity 1170	Affinity 1880
Density (ISO 1183), (g/cm^3)	0.903	0.910-0.930	0.920-0.922

Index Flow, IMF (190°C, 2,16kg) (ISO 1133), g/10min	1.4	2.0	1.0

2.1. Equipment and procedure

Three types of *Metallocene Low Density Polyethylene* (mLLDPE) were tested on a Brabender extrusion device following the thermal regime recommended by the manufacturer for processing by extrusion-blowing and in blends with low density poly-ethylene in different proportions.[1]

The rheological study included determining the main rheological parameters: shearing stress τ (Pa), flow rate Q (g/cm^3 and cm^3/s), a developed polymer melt temperature T1 and T2 (° C), pressure difference Δ P (bar) [2, 3, 4, 9, 10, 13, 14].

From these parameters the rheological functions were calculated:

$$\gamma_{ap} = 4Q / \pi R^3, \tag{1}$$

$$\tau_{ap} = \Delta P / 2L, \tag{2}$$

$$\eta_{ap} = \tau / \gamma \tag{3}$$

$$\eta_{ap} = K\left(\gamma_{ap}\right)^{n-1} \tag{4}$$

$$\tau = K\left(\gamma_a\right)^n \tag{5}$$

In (1)-(5):
γ - shear rate, s^{-1}
γ_{ap}- apparent shear rate, s^{-1}
τ - shearing stress, Pa
τ_{ap}- apparent shearing stress, Pa
η_{ap}- apparent viscosity, Pa·s
n – power law index, adimensional
R – capillary radius, m,
K – consistency index, adimensional,
L – capillary length, m.

2.2.Evaluation of rheological behavior of metallocene polyolefins (mLLDPE)

2.2.1. Evaluation of rheological behavior of mLLDPE Luflexen 0322 0322

The thermal regime for rheological study was as follows:

T = 220° - 245°C for the extruder and 245°C for wide viscosimeter nozzle;

The compositions used in the test were as follow: Luflexen 0322/ LDPE (IMF = 1.4 g/10min): 100 / 0, 90/10, 80/20, 70/30, 60/40, 50/50 and Luflexen 0322 / LDPE (IMF=2 g/10min): 100 / 0, 90/10, 80/20, 70/30, 60/40, 50/50.

Processing row Luflexen 0322 was particularly difficult, because the screw torque range was very high and practically 30 rpm could not exceed. The screw torque range at this velocity exceeded 70Nm. Table 2 summarizes the apparent values of the parameters recorded by the screw velocity.

Table 2

Apparent values of the parameters depending on the screw velocity

Nr. crt.	Velocity screw (rot/min)	Pressure variation ΔP (bar)	Flow rate Q (g/min)	Velocity shear γ (s^{-1})	Shearing stress τ ($Pa \cdot 10^2$)	Viscosity η ($Pa \cdot s \cdot 10^{-3}$)
1	9	130	3.8	42	12.2	51.8
2	15	168	5.2	58	11.6	67.1
3	20	203	6.4	71	11.3	81.1
4	25	235	7.8	87	10.8	94.0
5	30	268	9.0	100	10.7	107.2

For Luflexen 0322 / LDPE (1.4 g/10min IMF) and Luflexen 0322 / LDPE (2g/10min IMF) statistical evaluations of the plots viscosity / shear rate are shown in Figure 2 and 3. It is noted that by increasing the LDPE content in the compound the shear stress decreases, in turn the velocity shear rate is less sensitive, so that the variation of viscosity is more depend on the shear stress, and the variation is more obvious at a lower revolution. The appearance of extruded product was rough with a tendency to break the melt and the opacity increased while the ratio of LDPE increased.

A best behavior was shown by the LDPE compound having an IMF = 2g/10min (scale 80/20 and 70/30).

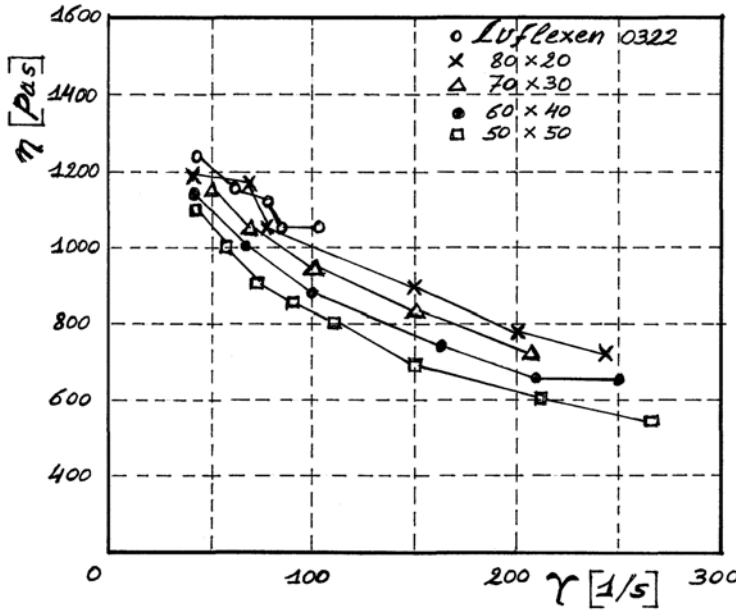


Fig. 2. Composition influence on compound rheological functions for Luflexen 0322 /LDPE (IMF = 1.4 g/10min)

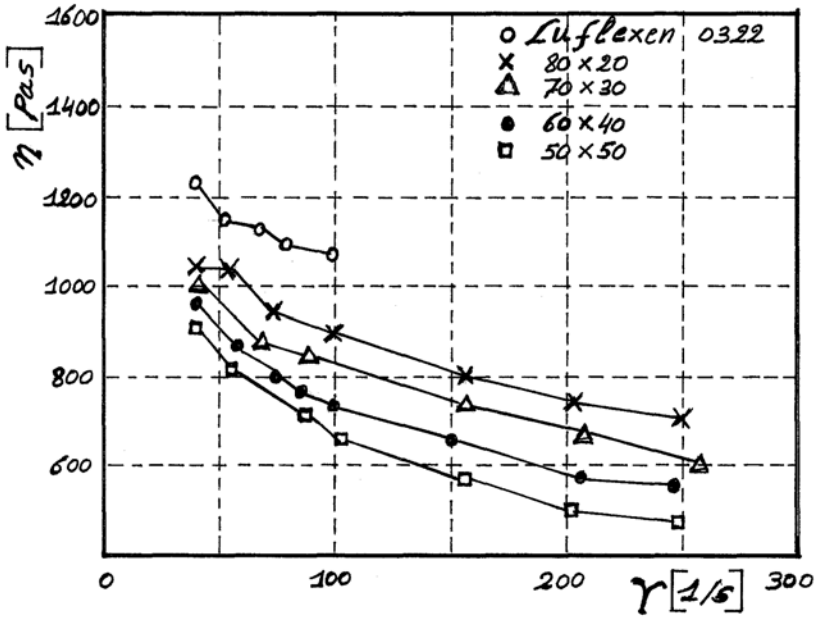


Fig. 3. Composition influence on compound rheological functions for Luflexen 0322 /LDPE (IMF = 2 g/10min)

2.2.2. Rheological behavior for mLLDPE Affinity 1770 and Affinity 1880

The thermal processing was identical to that chosen for Luflexen 0322. Test revolution velocities were as usually for LLDPE because these types of polyethylene were manufactured easily. In Table 3 there are given the apparent values of the rheological parameters versus screw velocity.

Table 3

Apparent values of the rheological parameters depending on the screw velocity

No. crt.	Screw velocity (rot/min)	Pressure variation ΔP (bar)		Flow Q (g/min)		Shear velocity γ (s^{-1})		Shearing stress τ (Pa x 10^2)		Viscosity η (Pa x s x 10^{-3})	
		Aff 1170	Aff 1880	Aff 1170	Aff 1880	Aff 1170	Aff 1880	Aff 1170	Aff 1880	Aff 1170	Aff 1880
1	30	165	172	9	9.4	88	105	66.1	68.8	752	656
2	50	225	236	15	14.0	146	156	90.1	94.5	615	605
3	70	272	288	18.5	19.2	181	214	109.0	115.1	603	537
4	90	312	330	22.5	23.4	220	261	125.0	132.0	568	505

Considering the obtained results for Luflexen 0322, only two compound options, namely Affinity 1880/ LDPE: 70/30 and 50/50 were made. As a second compound there were chosen: LDPE (IMF = 2g/10min) and LDPE (IMF = 1.0 g/10min) for Affinity 1880 and LDPE (IMF = 2g/10min) for Affinity 1170. The results are shown in Fig. 4 and fig.5.

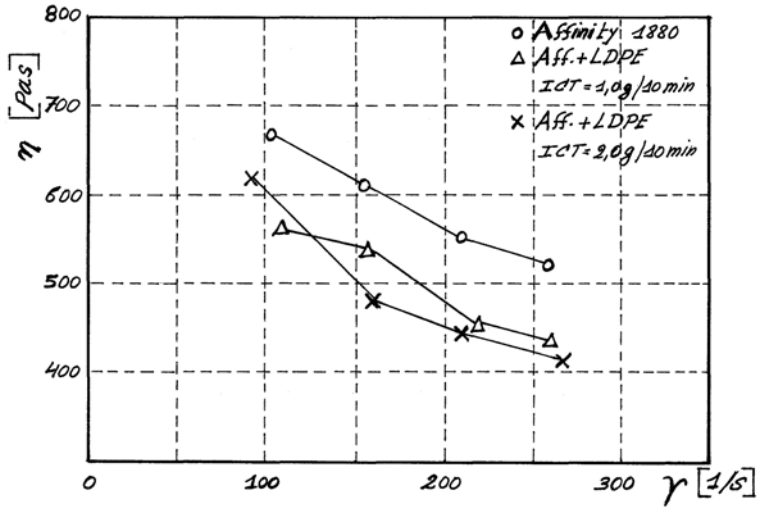


Fig.4. Variation of rheological functions on composition content (o Affinity 1880, Δ Affinity 1880+LDPE , x = Affinity 1170+LDPE)

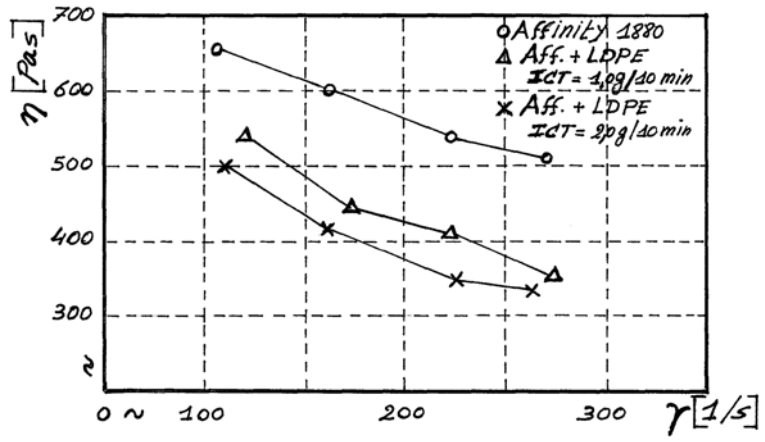


Fig.5. Variation of rheological functions on composition content (o Affinity 1880, Δ Affinity 1880+LDPE, x= Affinity 1170+LDPE)

3. Conclusions

Experimental measurements performed revealed higher rheological behavior for Affinity types related to Luflexen 0322.

All the compounds with Affinity 1880 have a dependence of the moment of the screw revolution. Largest differences occur in 50/50 compound, where a difference was observed by LDPE type. These close differences are reflected in the variation of strong narrow rheological functions. Compounds with Affinity 1170 have similar behavior with slightly lower values, which is understandable because the higher value of flow melt index, IMF, of 1.0 g/10min to 2.0 g/10min for this Affinity type.

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