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Highly flexible heterophasic copolymers through the novel multicatalysts reactor granule technology

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Summary

New heterophasic copolymers with high rubber content have been synthesized by combining heterogeneous Ti-based catalysts with metallocenes. The molecular, morphological and mechanical features of these materials were evaluated: it was pointed out that the new copolymers, having more than 60Wt.% of rubber, perform as reinforced elastomers whereas traditional ones show a more plastomeric behaviour. This suggests that new polyolefin materials can augment rather than compete with the traditional ones.

Introduction

In the past ten years the fast development of process and catalysts has created many opportunities to broaden the range of properties of propylene-based polymers(1). The most important results have been achieved with the synthesis of thermoplastic polyolefin elastomers (TPO), that are heterophasic copolymers having at least 50 Wt.% of an elastomeric ethylene-propylene copolymer (EPM) mixed with semicrystalline isotactic polypropylene (PP). This result has been obtained through the combination of the features (porosity, stereospecificity, high activity, controlled shape and size) of $MgCl_2$- supported, $TiCl_4$-based catalysts with the gas phase polymerization technology (CATALLOY)(2). It allows the polymerization of the rubber directly into the pores of the PP spheres and such a technology has been recognized as the only reliable way to synthesize TPOs (Reactor Blends). This technology affords costs reduction and a wider properties range with respect to the PP/EPR mechanical blends; indeed, the reactor blends show a finer rubber dispersion arising from the fact that PP and EPM grow on the same granules; therefore, it is possible to mix PP and EPM with largely different molecular mass(3), broadening the range of properties. An important feature of reactor TPOs is observed when the amount of the rubber, being mostly amorphous, exceeds 60 Wt.%: very low elastic modulus, high elongation at break together with considerable strain hardening(4). These properties are believed to be the consequence of the particular morphology observed: a cocontinuous and interpenetrated structure of amorphous and semicrystalline olefinic copolymers(4). Further, it has been described the synthesis of polypropylene, having isotactic-atactic stereoblock structure, with "oscillating metallocenes"(5); it has been reported to behave as an elastomeric polymer. Furthermore, it has also been described the synthesis of random ethylene-propylene copolymers(6) that show very good elastomeric properties with metallocene catalysts; the low glass transition temperature of such copolymers should allow good performance even at temperatures below 0°C. So, to exploit the potentialities offered by metallocene catalysis, a new technology for the sequential polymerization of olefins has been devised(7-9) and named Multicatalysts Reactor Granule Technology (MRGT): in the first step of this process propylene is polymerized with a superactive, porous, Ziegler-Natta (ZN) catalyst having spherical form; the activated metallocene is introduced in the pores of the PP spheres after the deactivation of the Ti; then, ethylene and propylene are copolymerized by the metallocene and the resulting copolymers are prepared directly in spherical form. Therefore, this new technology allows the synthesis of new heterophasic copolymers in which PP, from Ti, and EPM, produced with metallocene complexes as catalysts, are intimately mixed together, already in the spheres coming from the reactor(10); further it was possible to synthesize copolymers having around 70 WT.% of EPM (8,9). Thus, it seemed of interest to the authors to investigate around the stress-strain behaviour of these new materials compared with similar copolymers synthesized with traditional $MgCl_2$-supported, $TiCl_4$-based, catalysts; mechanical properties have been related with the morphology of the specimens.

Experimental

Synthesis of heterophasic copolymers with MRGT: the procedure has been described in details elsewhere(7-10). Typically, in the first step propylene is polymerized at 70°C for two hours in liquid phase with the traditional Ti-based catalyst; hydrogen is used as molecular weight regulator. In the second step the active sites are deactivated, then the racemic-ethylene-bis(4,5,6,7-tetrahydroindenyl)zirconiumdichloride, previously activated with the mixture of tris-2,4,4-methylpentylaluminum and water (Al/H2O=2 molar), is introduced in the pores of PP spheres through an in-situ impregnation/drying step and finally the copolymerization is started by feeding into the reactor the proper amount of ethylene and propylene in the gas phase; the monomer composition is kept constant throughout the reaction.

Synthesis of heterophasic copolymers with traditional Ti-based catalysts: the detailed procedure is described in ref. 11. Typically, in the first step propylene is polymerized at 70 °C for two hours in liquid phase with the traditional Ti-based catalyst; hydrogen is used as molecular weight regulator. Then, the monomer is flashed off and the proper amount of ethylene and propylene is admitted into the reactor. The copolymerization is performed at 60°C until the desired amount of rubber is produced; the monomer composition is kept constant throughout the reaction.

Molecular characterization: intrinsic viscosity was measured at 135°C in tetrahydronaphthalene. Molecular mass distribution was measured in o-dichlorobenzene at 135°C with GPC WATERS mod. 150. Universal calibration was made using polystyrene monodisperse fractions. Xylene solubility was determined through dissolution of the sample in o-xylene at 135°C and successive recrystallization at 25°C. The ethylene content was determined by infrared spectroscopy using a NICOLET 20SXC spectrometer.

Specimens preparation and mechanical characterization: 120x120x1mm plaques were prepared by compression moulding the copolymers at 220°C and quickly cooling at room temperature with circulating water. 50x6x1 mm, with 30 mm span, were cut from the plaques and used for the characterization. Strength at yield, strength at break and elongations were measured at a crosshead speed of 500 mm/min; hardness was measured according to ASTM D2240; DMTA was performed according to ASTM D5026. Melt flow rate was measured according to ASTM D 1238 L

Transmission electron microscopy: ultrathin sections of the specimens were cut by using an ultramicrotome Reichert ULTRACUT-S equipped with a cryo device FCS. The samples were at -130°C and the knife was at -60°C, to avoid plastic deformations. Then,

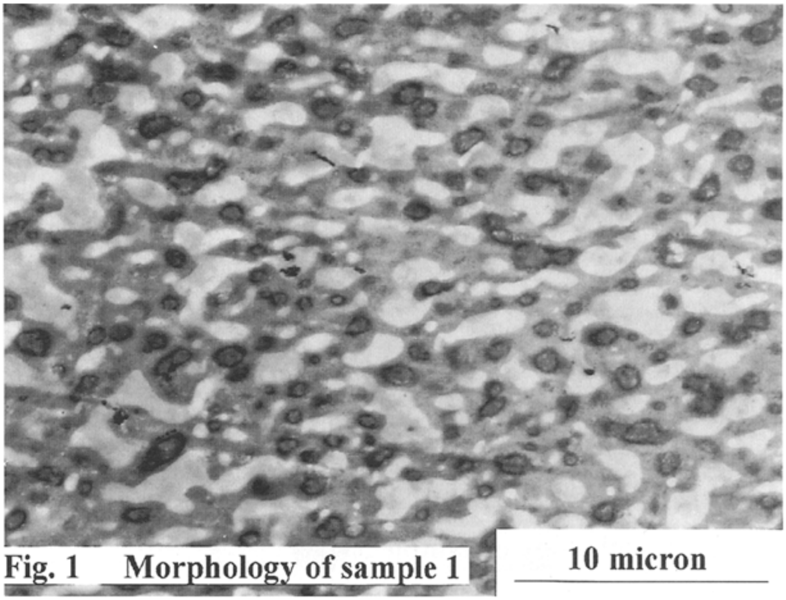

Fig. 1 Morphology of sample 1

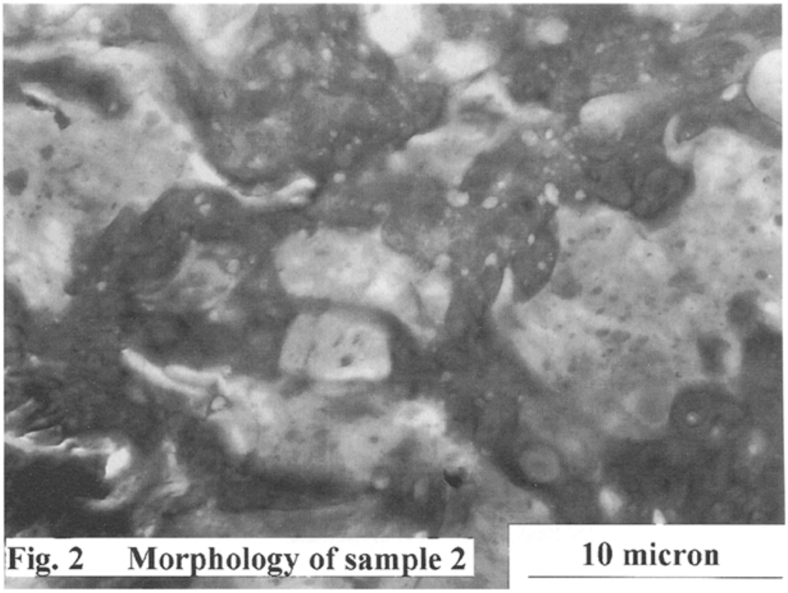

Fig. 2 Morphology of sample 2

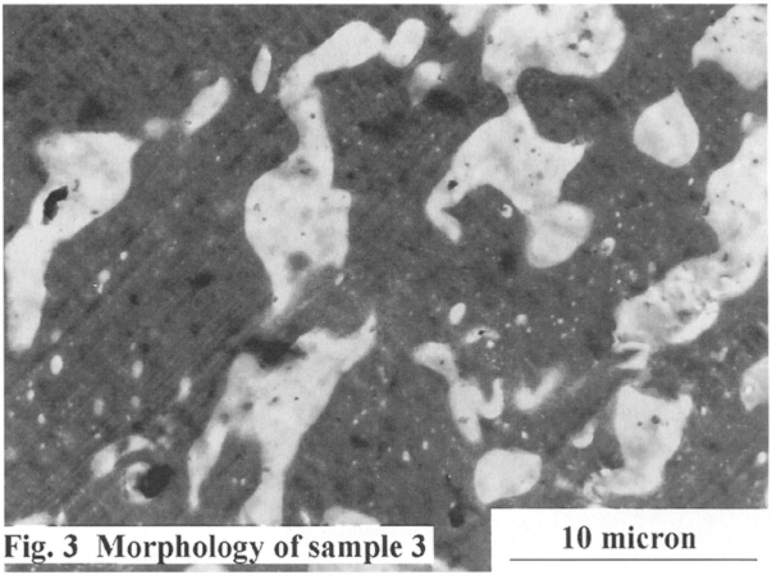

Fig. 3 Morphology of sample 3

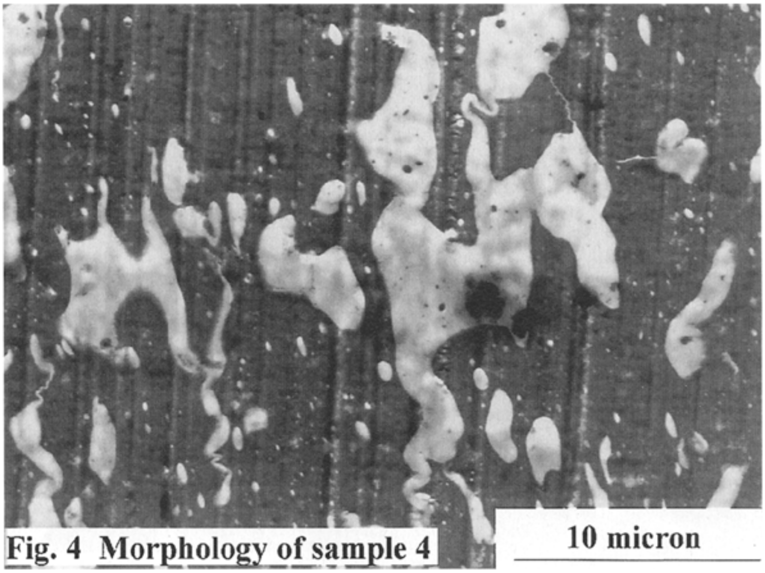

Fig. 4 Morphology of sample 4

the thin sections were put on copper grids and examined with a Philips 301 TEM at 80 kV.

Results and Discussion

Two heterophasic copolymers were synthesized with the MRGT(samples 3,4): they contain almost 70 Wt.% of EPM and they have different rubber composition, being almost similar the other molecular parameters; the copolymers were compression moulded and some mechanical properties were evaluated. They were compared with two heterophasic copolymers, having similar molecular structure, prepared with traditional $MgCl_2$ supported, Ti-based catalyst (samples 1,2). The results of the characterization are reported in tab. 1. It is worthwhile to note that the rubbers synthesized with metallocenes are readily soluble in xylene at room temperature, at least for the experimental conditions adopted. Therefore, the characteristics determined on the soluble fractions can be considered representative of whole rubber: the ethylene content in the rubber changes from 37 Wt.% to 63 Wt.%

Tab. 1- Molecular and mechanical characterization of the heterophasic copolymers.

Run		1	2	3	4
Matrix		Homo- PP	Homo- PP	Homo- PP	Homo- PP
IV	dl/g	1.4	1.65	1.55	1.5
XI	Wt.%	97	97	96.8	96.7
EPM	Wt.%	65	60	66.2	69.7
C_2	Wt.%	19.4	39	24.7	44.6
IV	dl/g	2.4	3.0	2.85	2.81
XS	Wt.%	57.6	43	65.2	69.3
XS,epm	Wt.%	88	72	97	98
C_2,sol.	Wt.%	26.7	56	37.8	62.8
IV,sol.	dl/g	2.8	3.2	3.3	3.5
Mw/Mn,sol.		8	10	2.9	2.9
MFR(L)	dg/min	1.1	0.8	0.6	0.4
Hardness	°Shore D	38	38	30	33
Elastic modulus	MPa	180	360	130	80
Tensile yield	MPa	6.7	7.1	4.2	3.8
Tensile strength	MPa	16.1	6.6	3.8	8.2
Elong. at yield	%	35	10	15	46
Elong. at break	%	1000	140	55	850
Tg	°C	-25	-52	-47	-48

sol.= measured on the fractions soluble in xylene.

and the molecular mass distribution is quite narrow, as it would be expected on the base of the present knowledge around metallocene catalysis(12); the intrinsic viscosity is almost unchanged.The EPM prepared with Ti-based catalysts is partially insoluble: indeed, it has already been reported that ZN catalysts allow ethylene-propylene copolymers that are semicrystalline at every composition, being 27-35 Wt.% of ethylene the composition at which just small amount of crystallinity is detected(13). As a consequence the ethylene content of the soluble fractions is less than that of the whole EPM; in any case, it is possible to calculate it on the base of the amount of rubber and the composition of the heterophasic material. Therefore, EPM of sample 1 contains around 30 Wt.% of ethylene and EPM of sample 2 contains around 65 Wt.% of ethylene. Further, the crystallinity of the rubber synthesized with ZN catalysts stems from the broad composition distribution(13). As far as the mechanical characterization is concerned, it is worth observing that sample 1 is more flexible than sample 2; this behaviour likely arises from the higher crystallinity of the EPM of sample 2. Further, sample 1 shows strain-hardening phenomenon, as the tensile strength is higher than tensile yield, together with higher elongation at break. It may stem from both the rubber composition (propylene-rich) and the broad composition distribution that lead to better compatibility with PP. Looking at the samples synthesized with MGRT, it is possible to observe that the stress-strain behaviour definitely improves on going from the copolymer with C_2=37 Wt.% up to C_2=63 Wt.%: tensile strength is higher than tensile yield for sample 4, suggesting that strain-hardening occurred also for this material. Further, the elastic modulus decreases upon the increase of ethylene in the rubber and it is far lower than that of both the materials prepared with traditional catalysts. In fig. 1-4 the morphological details are presented of the specimens prepared by compression moulding and used to determine the stress-strain performance. The copolymers prepared with ZN catalyst have a multyphase morphology; in particular, the sample 1 shows a fine cocontinuous morphology where olefinic polymers with different degree of crystallinity are mixed together. Sample 2 presents a coarse morphology, where large PP particles, sometimes containing small rubbery globules, are mixed with the rubber. The new materials show a two phase morphology where the rubber tends to be the continuous phase and PP the dispersed polymer. So, the behaviour of the new materials is determined mainly by the characteristics of the rubber; indeed, it has been known that strength and elongation decrease when the ethylene content of the rubber goes below 60 Wt.%(14). Therefore, the first copolymers can be considered as plastomers softened with EPM , having broad composition distribution and broad molecular mass distribution; it likely originates the multiphase morphology and it explain the plastomer-like performance. The latters may be considered as rubbers, having narrow molecular mass and composition distribution, reinforced with PP; it may account for the elastomer-like performance. Finally, sample 3 has Tg far lower than that of sample 1, whereas sample 4 shows Tg higher than sample 2, despite the composition of the rubbers do not differ so much. This finding has not been fully understood yet; however, different composition distribution and the sequences distribution might account for this result.

Conclusions

New highly flexible heterophasic copolymers were synthesized with MRGT: the preliminar physical-mechanical characterization pointed out that they perform as reinforced elastomers; it likely stems from the morphological structure where the rubber tends to be the continuous phase and PP the dispersed one. As both mechanical and morphological features of these materials are different from those copolymers allowed by ZN catalysis, it can be suggested that they will not be competitive, but synergistic materials.

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