Polymer Bulletin 38, 701–705 (1997)

Polymer Bulletin

New thermoplastic polyolefins elastomers from the novel Multicatalysts Reactor Granule Technology: their relevant physical-mechanical properties after crosslinking

G. Collina, V. Braga, F. Sartori

Montell Italia, "G. Natta" R & D Center, P. le G. Donegani 12, I-44100 Ferrara, Italy

Received: 28 February 1997/Revised version: 11 April 1997/Accepted: 14 April 1997

Summary

A new process for the sequential copolymerization of olefins has been devised (Multicatalysts Reactor Granule Technology); it allows the synthesis of thermoplastic polyolefin elastomers having polypropylene from Ti-based catalysts and ethylene-propylene rubbers from metallocenes. Such new materials have been cured with peroxides an the relevant mechanical properties measured in comparison with those of heterophasic copolymers synthesized with traditional catalysts. It resulted that the new materials present an improved balance between strength and elasticity, especially at high temperature.

Introduction

Thermoplastic polyolefin elastomers (TPOs) are well known heterophasic materials having polypropylene (PP) and ethylene-propylene elastomeric copolymer (EPM) as main components(1,2). TPOs have been used in many applications as automotive parts, wire and cables insulation and jacketing, electric appliances, shoes, building industry, etc.(3). Further, the physical-mechanical properties of TPOs can be improved by curing under dynamic shear condition (i.e.: called TPVs after dynamic vulcanization); as a result the tensile strength, elastic modulus, tension set and compression set are improved(2). Their functional behaviour is similar to that of vulcanized rubbers (i.e.: thermosets), as they show good elasticity together with good strength, but they can be processed as simple thermoplastic polymers and they can be easily recycled(1,2).

At the beginning of the TPOs development, they have been produced through melt mixing of the components that, in turn have been synthesized with different catalysts and with different processes(4). Later on, it has been possible to manufacture these materials by direct synthesis in gas-phase multiple reactors, owing to the succesful development of high yield, porous, spherical form, heterogeneous Ziegler-Natta catalysts(5,6). In this way, the polyolefinic components are intimately mixed one each other, even in the polymer spheres that come from the reactor; so, the material performance resulted widened and improved. Further, cost savings have been possible as fewer manufacturing steps are required(5,6). However, it has been reported that Ti-based catalysts allow ethylene-propylene

copolymers that are crystalline at every composition, being 27-35 WT.% of ethylene the composition at which just small amount of crystallinity is detected(7); then, it is known that crystallinity is detrimental for the elastomeric properties(8). Recently, new catalysts (i.e.: the metallocenes) have been discovered and proven useful for the synthesis of amorphous EPM that shows good elastomeric behaviour(9); however, these catalysts lack of morphology control and can not be used with the existing technology operating in gas phase, unless they are put into suitable supports. So, it would be desirable to prepare a TPO combining the features of Ti-based catalysts (e.g.: good morphology, broad molecular mass distribution, high stereospecificity) with those of metallocenes (e.g.: EPM with good elasticity); this goal has been accomplished with the Multicatalyst Reactor Granule Technology(10-12)(MRGT). It is a process for the sequential copolymerization of olefins: in the first step propylene is polymerized with traditional Ti-based, porous, spherical form catalyst(13); then, the activated metallocene is put into the pores of the PP porous spheres after the deactivation of the Ti-based catalyst. Finally, the copolymerization of olefins is started by feeding the proper amount of monomers in gas phase; the TPO comes out from the reactor directly in free-flowing spherical form.
Thus, it seemed of interest to crosslink with peroxides these new heterophasic material and to measure their relevant physical-mechanical properties; the results have been compared with the properties of heterophasic copolymers synthesized with Ti-based catalysts.

Experimental

Catalysts: the catalyst named Ti-based is prepared by supporting TiCl4 on activated MgCl2 in the presence of diester as internal base. Triethylaluminum was used with a dialkydialkoxysilane as cocatalyst for the polymerization. The detailed procedure for the synthesis of the Ti-based catalyst is described in ref. 13. The metallocene racemic-ethylene-bis(4,5,6,7-tetrahydroindenyl)zirconiumdichloride was synthesized according to the procedure described in ref. 14. Tetraisobutylaluminoxane (TIBAO) was purchased from Schering.

Synthesis of TPO with MRGT: the procedure has been described in details elsewhere(10-12). Tipically, 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 activated metallocene 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 gas phase; the monomer composition is kept constant throughout the reaction.

Synthesis of TPO with traditional Ti-based catalysts: the detailed procedure is described in ref. 15. 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 tetrahydronaphtalene. 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 succesive recrystallization at 25°C. The ethylene content was determined by infrared spectroscopy using a NICOLET 20SXC spectrometer.

TPV formulation, crosslinking and characterization

The TPOs were added with paraffinic oil (extender) Flexon 876 and left at 70°C for 2 days; then, Zinc Oxide, liquid polybutadiene (tradename: Lithene PH), difurfuralaldazine (tradename: VP3), poly6- (1,1,3,3-tetramethylbutyl)-amine-1,3,5-triazine2,4-diyl-(2,2,6,6-tetramethyl-4-piperidinyl)-imine-1,6-hexanediyl- (2,2,6,6-tetramethyl-4-piperidinyl)-imine (tradename: Chimassorb 944, provided by Ciba-Geigy) (18) were added together with the TPOs into a Banbury internal mixer at 180°C and 60 rpm, mixing time was 2 minutes. Finally, the 2,5 dimethyl-2,5 di(ter-buthyl peroxy)hexane (tradename: Trigonox 101/40MD GR) was added to the melted mixture and the mixing was continued for further 6 minutes. Plaques with 120x120x2 mm were obtained through compression moulding at 220°C for 5 minutes without pressure then 5 minutes at 200 Bar of pressure and finally quickly cooled at r.t. under pressure of 200Bar. Hardness was measured according to ASTM D2240, Strength and Elongation at Break were measured according to ASTM D412 on microspecimens, Tension Set was measured according to ASTM D412 with a ASTM 1329 specimeme type, Compression Set was measured according to ASTM D395 (method B).

Results and Discussion

In tab. 1 the results of the molecular characterization are reported for the all the TPOs. The rubber composition of the materials prepared with MRGT has been set at around 65 Wt.% of ethylene in order to achieve the higher degree of crosslinking, related to the high comonomer content(16), together with an amorphous polyolefin. For a better comparison, the two heterophasic copolymers prepared with Ti-based catalysts have different ethylene content in the rubber: 29 Wt.% and 65 Wt.%; in this way, the first copolymer has the most amorphous rubber and the latter contains the rubber with the same ethylene content as the copolymers prepared with MRGT. It is worth noticing that the rubbers prepared with metallocenes are readly soluble in xylene, at least in the experimental conditions adopted, whereas the rubbers prepared with the traditional catalysis are partially solubles, being the solubility lower when the polymer is ethylene-rich. It suggests that the first polymers are nearly amorphous, whereas, the latters present some degree of crystallinity(7). Further, the MMD of the polymers prepared with metallocene is narrower than that of the rubber prepared with Ti-based catalysts; it is in good agreement with the present knowledge about heterogeneous and metallocene catalysis(17).

In tab.2 are reported the formulations of materials: the paraffinic oil has been used to control the hardness of TPVs, the peroxide has been used to promote the crosslinking of the rubber, the hindered amine has been used as stabilizer, the liquid polybutadiene and VP3 have been used as crosslinking coagents.

Then, all the materials have been compression moulded and specimens for mechanical measurements have been prepared. The results are presented in the table 3.

By comparing the samples A and B, it is worthwhile to note that the elastic behaviour of the latter is better; it may be due to the higher ethylene content in the rubber that afforded a better crosslinkability. As far as the new materials are concerned, they all behave better than the polymer references: they show higher tensile strength and lower tension and compression set (inverse measures of rubberlike behaviour). It may be accounted for by the nature of the rubber synthesized with metallocenes: it is nearly amorphous, with very low Tg (it allows good elasticity) together with high ethylene content (it allows good crosslinkability). Further, the good degree of crosslinking also turns into the better retention of elasticity at high temperature(2): as a result of the crosslinking process,

Tab. 1 - Molecular characteristics of the thermoplastic polyolefin elastomers.

Sample		1	2	3	4
Catalyst(1 step)		Ti-based	Ti-based	Ti-based	Ti-based
Catalyst(2 step)		Ti-based	Ti-based	r-EBTHI/TIBAO	r-EBTHI/TIBAO
Ethylene,whole	Wt.%	21	39	45,6	44,2
Plastomer	Wt.%	33	35	33,6	30,7
IV,plastomer	dl/g	1,4	1,65	1,6	2,1
Ethylene,plast.	Wt.%	3,2	Homopol.	Homopol.	Homopol.
EPM	Wt.%	67	65	66,4	69,3
Xylene Solubility	Wt.%	62	50	67,8	69
Ethylene,soluble	Wt.%	29	65	68,8	68,6
IV,soluble	dl/g	3,2	3,4	2,7	4,9
MMD,soluble		7	10	2,7	2,9

Tab. 2 - Formulations of thermoplastic polyolefin elastomers for the dynamic vulcanization.

	A	B	C	D	E
Formulation	phr	phr	phr	phr	phr
Sample 1	149				
Sample 2		166.7			
Sample 3			150.6		
Sample 4				144.3	144.3
Flexon 876	100	100	100	100	130
ZnO	5	5	5	5	5.4
Lithene PH	4	4	4	4	4.32
VP3	0.55	0.55	0.55	0.55	0.59
Chimassorb944	0.5	0.5	0.5	0.5	0.553
Trigonox 101/40	4	4	4	4	4.32

Tab. 3 - Relevant physico-mechanical properties of crosslinked TPOs.

Property	u.m.	A	B	C	D	E
Hardness	Shore A	56	65	58	65	60
Tensile Strength	MPa	4.7	5.3	6.4	5.7	5.2
Elong. at Break	%	800	630	650	610	750
Tension Set, 23°C	%	18	18	10	10	10
Tension Set, 100°C	%	44	36	16	16	15
Compression Set *	%	66	63	57	48	48

* at 100°C for 22 hours.

chemical bonds among rubber macromolecules have been established, i.e. a polymer network has been formed; so, the polymers disentanglement is prevented and the properties retained. Furthermore, it has already been reported(2) that TPVs perform similarly to thermosets, but process similarly to thermoplastics as the plastomer is the continuous phase, whereas the cured elastomer the dispersed phase, even for high amount of rubber; thus, also the materials prepared in the present work have the potentiality to be worked as common thermoplastic polymers.

Conclusions

New thermoplastic polyolefin elastomers (heterophasic copolymers) have been synthesized with a new process for the sequential copolymerization of olefins (MRGT). Such TPOs have been added with extenders, stabilizers and dynamically cured with peroxides in presence of suitable co-agents. The most relevant physico-mechanical properties have been measured in comparison with those of heterophasic copolymeres synthesized with traditional Ti-based, $MgCl_2$ supported catalysts. This work pointed out that the new copolymers have an improved balance of ultimate tensile properties and rubberlike elasticity, expecially at high temperature.

References

1) Legge N.R., Holden G., Schroeder H.E. eds. (1987) Thermoplastic Elastomers, Hanser Publishers, Munich, Vienna, New York
2) De S.K., Bhowmick A.K., Thermoplastic elastomers from rubber-plastic blends, Ellis Horwood series in Polymer Science and Technology,
3) Galli P., Foschini G., Moro A., Proc. from "Polymer Alloys: Structure and Properties", June, 4th-7th, 1984
4) Galli P., Milani F., Simonazzi T., Polymer Journal, (1985) 17:37
5) Galli P., Haylock J.C., Albizzati E., DeNicola A., Macromol. Symp. (1995) 98:1309
6) Cecchin G., Macromol. Symp. (1994) 78:213
7) Van Der Ven S. (1990) Polypropylene and other polyolefins. Elsevier, Amsterdam, Oxford, Tokyo, New York
8) (a)Gilbert M., Briggs J.E., Omana W., British Polymer Journal, Vol.11, June 1979. (b)Corbelli L., Martini E., Milani F., Proc. from. 9th Int. Rubber Conf., Gottwaldow, 1987
9) Galimberti M., Dall'Occo T., Piemontesi F., Camurati I., Collina G., Battisti M., proc. from MetCon '96, Houston (TX), USA, June 12th-13th, 1996
10) Collina G., Dall'Occo T., Galimberti M., Albizzati E., Noristi L., WO 96/11218 to Montell Technology Co. B.V.
11) Galli P., Collina G., Albizzati E., Sgarzi P., Baruzzi G., Marchetti E., submitted to Journal of Applied Polymer Science
12) Galli P., Albizzati E., Collina G., Sgarzi P., Marchetti E., proc. from IUPAC MACRO SEOUL '96, Seoul (Korea), August 4th-9th, 1996
13) Sacchetti M., Govoni G., Ciarrocchi A., EP 395083 to Montell Technology Co. B.V.
14) Brintzinger H.H., J. Organomet. Chem., (1985) 63:288
15) Cecchin G., Guglielmi F., Pelliconi A., Burgin E., EP 472946 to Montell Technology Co. B.V.
16) Chodak I., Prog. Polym. Sci., (1995) 20:1165
17) Albizzati E., Giannini U., Collina G., Noristi L., Resconi L., Catalysts and Polymerizations. In. Moore E.P. (ed) Polypropylene Handbook Hanser Publishers, Munich Vienna New York
18) Braga V., Zucchelli U., EP 0742257 to Montell Technology Co. B.V.