7º Congresso Brasileiro de Polímeros

9 a 13 de novembro de 2003
Centro de Convenções do Hotel Mercure
Belo Horizonte / MG

Promoção:

Associação Brasileira de Polímeros

COMISSÃO ORGANIZADORA

Roberto F. S. Freitas - Coordenador / Chairman (UFMG)
Cláudio Gouveia Santos (UFOP)
David Tabak (FIOCRUZ)
Domingos A. Jafelice (Polietilenos União)
Éder Domingos de Oliveira (UFMG)
Fernanda M. B. Coutinho (UERJ/UFRJ)
Kátia Monteiro Novack (UFOP)
Laura Hecker de Carvalho (UFPB)
Luiz Antonio Pessan (UFSCar)
Maria Elisa S. Ribeiro e Silva (UFMG)
Raquel S. Mauler (UFRGS)
Ricardo Baumhardt Neto (UFRGS)
Ricardo Geraldo de Sousa (UFMG)
Rodrigo Lambert Oréfice (UFMG)

COMISSÃO CIENTÍFICA

Raquel S. Mauler – presidente (UFRGS)
Ariosvaldo A. Barbosa Sobrinho (UFCG)
Bluma G. Soares (IMA/UFRJ)
Cesar L. Petzhold (UFRGS)
Cláudio Gouveia Santos (UFOP)
Cristiano P. Borges (COPPE/UFRJ)
David Tabak (FIOCRUZ)
Domingos A. Jafelice (Polietilenos União)
Éder D. de Oliveira (UFMG)
Fernanda M. B. Coutinho (UERJ/UFRJ)
Judith Feitosa (UFC)
Kátia Monteiro Novack (UFOP)
Laura Hecker de Carvalho (UFPB)
Luiz Antonio Pessan (UFSCar)
Márcia C. Delpech (UERJ)
Maria do Carmo Gonçalves (UNICAMP)
Maria Elisa S. Ribeiro e Silva (UFMG)
Maria Isabel Felisberti (UNICAMP)
Nicole R. Demarquette (EPUSP)
Ricardo Baumhardt Neto (UFRGS)
Ricardo Geraldo de Sousa (UFMG)
Rinaldo Gregório Filho (UFSCar)
Roberto F. S. Freitas (UFMG)
Rodrigo Lambert Oréfice (UFMG)
Thais H. Sydenstricker (UFPR)

Associação Brasileira de Polímeros
R. Geminiano Costa, 355 - Centro - CEP 13560-050 - São Carlos - SP
Telefax: (16) 274-3949 - abpol@linkway.com.br
www.abpol.com.br

MIXING AND PERFORMANCE STUDY OF EPDM PRODUCED VIA GAS-PHASE PROCESS USING METALLOCENE CATALYST TECHNOLOGY

Nei S. Domingues Jr.* [1,2], M. Steve Edmondson [1], Maria M. C. Forte[2]
[1] *Ethylene Elastomers R&D Center – DuPont Dow elastomers,L.L.C. – 2301, North Brazosport Blvd. – B1470C – Freeport, Texas 77541- USA.–* nei.domingues@dupont-dow.com*
[2] *Departamento de Materiais – Escola de Engenharia da UFRGS – mmforte@vortex.ufrgs.br*
The use and advantages of metallocene based catalyst technology for the production of EPDM and other ethylene-α-olefin copolymers in solution processes have been consolidate in the industry. Gas-phase EPDM production reached a significant advanced by combining the proven metallocene technology with the gas-phase process. This paper discusses the advantages in mixing performance in the new metallocene granular gas-phase EPDM. It also reviews the mechanical properties of one grade produced by this new process comparing with the traditional solution Ziegler-Natta and solution metallocene polymers.

Introduction

In the late 1990's a gas-phase EPDM produced via Ziegler-Natta catalysts with unique free-flowing granular form, demonstrated significant improvements in mix speed and quality over traditional polymers in internal batch mixers.[1,2] Recent advances in the metallocene based catalysts[3] combined with gas-phase process have allowed the successful production of high quality, consistent, granular EPDM for the thermoset rubber market (e.g. injection molded goods, extruded profiles)[4]. The new metallocene gas-phase EPDMs remain free flowing and retain the excellent mixing behaviour associated with its granular form. This paper discuss the mixing performance in the new granular EPDMs and point out its physical properties compared with the traditional solution Ziegler-Natta and solution metallocene EPDMs.

Experimental

Table 1 shows the properties of the three EPDM grades used in this study.

Table 1 – Polymer properties and characteristics.

	MG47085#	MS-70	ZN-S-60
Process-catalist	Gas Phase Metallocene	Solution Metallocene	Solution ZN
Form	Granular	Pellets	Bale
Viscosity *	85 **	70	60
% ethylene	69	70	69
% diene	4.5	5.0	4.5

30 phr carbon black as flow agent; * ML1+4 125°C; ** calculated;

The mixing performance was evaluated in a Haake Mixer with roller blades at 75 rpm and 69% fill factor using a basic recipe as seen in Table 2.

Table 2 – Mixing study formulation.

Ingredient	Phr
EPDM + X phr N650	100+X
N650 - X phr N650	80-X
Paraffinic Oil	50

X = 30 for MG47085 and zero for the solution grades

The compounds were cured using a standard sulfur donor package as reported elsewhere[5].
Oil addition under static condition on the granular gas-phase EPDM was examined in a Scanning Electronic Microscope Philips XL20 to check the particle morphology. Samples were gold coated to protect the surface.

Results and Discussion

Figure 1 shows the results of black incorporation time (BIT) and Mooney viscosity. The gas-phase MG47085 reaches BIT more quickly than the pelletized MS-70 sample and Ziegler-Natta ZN-S-60, even at higher polymer viscosity.

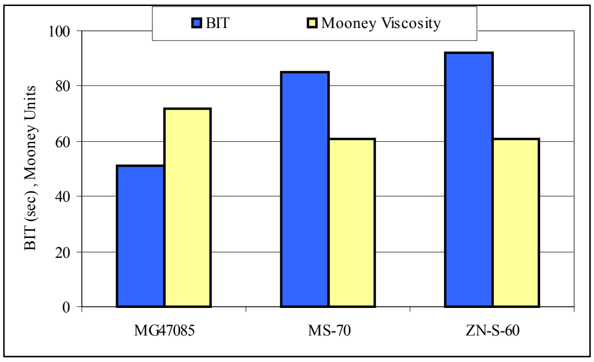


Figure 1 – Black Incorporation Time (BIT) in seconds and Mooney Viscosity (ML 1+4 125°C)

The higher Mooney of MG47085 than the solution polymers, is attributed to its higher molecular weight. Typically higher the viscosity more difficult to mix, taking longer to reach BIT and generating more heat. However at high shear rates MG47085 showed lower apparent viscosity and better processing[5].

In Figure 2 the physical properties are depicted, the metallocene gas-phase provided excellent tensile at break, slightly lower than the MS-70 partially due to the lower crystallinity level for the former. Metallocene solution MS-70 has higher crystallinity than both the gas-phase and the ZN-S polymers, which can be observed in the room temperature compression set results.

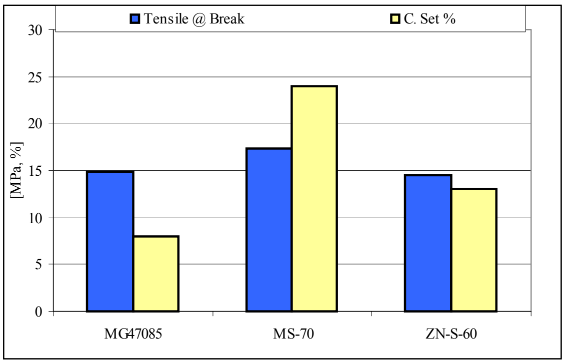
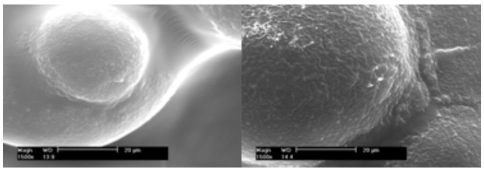
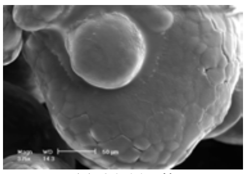


Figure 2 – Tensile at Break (MPa) and Compression Set % at 23 ^{o}C.

Overall the new metallocene gas-phase EPDM MG47085 provides comparable compounded properties to solution based EPDMs of similar composition.



(a) no oil (b) 10 % oil



(c) 30 % oil

Figure 3 – SEM images of MG47085 and parafinic oil

Figure 3 shows the effect of polymer swelling due to the absorption of paraffinic oil. The swelled polymer breaks up the original core-shell structure and favors the EPDM-filler interaction while still maintaining its free-flowing feature, contributing to shorter mixing times, and opening new compounding approaches with MG materials.

Conclusion

This paper highlighted the value of a granular metallocene gas-phase EPDM in mixing cycle and performance using a simple recipe. The unique granular form also allows for automated metering and feeding. The overall physical performance was comparable to solution based commercial EPDM grades.
The advent of this polymerization technology permitted the commercial production of a new EPDM family, which surely will lead the path towards continuous mixing in the rubber industry.

Acknowledgements

This work was supported by DuPont Dow Elastomers L.L.C. (N.S.D. and M.S.E.), and CNPq (M.M.C.F.). The authors wish to thank DuPont Dow Elastomers L.L.C. for the permission to publish this paper.

References

1 A. U. Paeglis and J.D. Collins, *Rubber World* **209**, 39 (1994)
2 E. T. Italiaander, Proceedings ACS – 151st Rubber Division, May 1997
3 D.R. Parikh, et. al. Proceedings ACS – 151st Rubber Division, May 1997.
4 A. U. Paeglis and E. T. Italiaander, Proceedings ACS – 158th Rubber Division, October 2000.
5 C.S. Grant, R.G. Vara and S.T. Tang Proceedings ACS – 162nd Rubber Division, October 2002.