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Citation: AIP Conference Proceedings **1593**, 526 (2014); doi: 10.1063/1.4873836
View online: http://dx.doi.org/10.1063/1.4873836
View Table of Contents: http://scitation.aip.org/content/aip/proceeding/aipcp/1593?ver=pdfcov
Published by the AIP Publishing

Influence of Different Components in a TPV PP/EPDM Based with Low Hardness

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Abstract

Thermoplastic vulcanizates (TPVs) are a class of polymeric material obtained by dynamic vulcanization of an elastomer in a melted thermoplastic matrix. This work intend to evaluate different variables in the production of low hardness TPVs made of polypropylene (PP) and ethylene propylene rubber (EPDM), as well the optimization of the variables looking for TPVs with improved performance. In the Study I the influence of PP crystallinity were evaluated, in the Study II the effects of different amounts of dicumyl peroxide (DCP) were evaluated and in the Study III the amount of the phenolic resin were evaluated. This extended abstract presents, in a more detailed way, the results considering the curative phenolic resin content (Study III). The others results and discussions are briefly described in the results and discussions section. The compounds were obtained in a closed mixing chamber and their processability properties, swelling, hardness and tensile strength were evaluated. With the results obtained were possible to evaluate the influence of different ingredients in the TPVs properties. The results were discussed and presented looking for a better understanding of the influence of this variable in the final product, as well the correlation between then.

Keywords: TPV, phenolic resin, dynamic vulcanization

INTRODUCTION

Thermoplastic vulcanizates (TPVs), are a special class of thermoplastic elastomers (TPEs) where the rubber phase is dynamic vulcanized in the presence of a melted plastic phase. The cure procedure produces a significant increment in the properties like temperature resistance, swelling resistance in organic fluids, better compression set and fatigue resistance, lower stress relaxation of the TPV when compared with an equivalent not cured blend, a thermoplastic polyolefin (TPOs) [1].

In a TPV the cured rubber phase is dispersed in the thermoplastic phase as small domains. The TPV morphology is defined during the dynamic vulcanization and it influences significantly in the final properties of the material. The key is a higher crosslink density of the rubber phase and the small size of the rubber domains [2].

The TPVs production in twin screw extrudes is a very known and studied process (and also a kind of art). In the other way, the TPV production in a discontinue process, like closed mixing chambers, until now is not so much studied.

Different cure systems were already described for polypropylene/ethylene norbornene diene (PP/EPDM) TPV`s: peroxides, peroxides with coagents, phenolic resins, hidrosilanes catalyzed by platine and vinyl-trialcoxi-silanes [3,4]. Each system exhibit theirs own advantage and disadvantages.

TPVs cured with peroxide, usually shows lower properties with the ones cured with phenolic resin.

According to Naskar and Noordermeer [4,5] the TPVs PP/EPDM peroxide cure with the coagent triallylcyanurate (TAC) result in optimized final properties, mainly in the tensile strength.

In the other way, the phenolic resins as curing agents for TPV`s has been growing in importance considering the good properties in the final product, as the temperature resistance of these materials [6-8].

In this work 03 studies were performed. In the Study I the influence of PP crystallinity were evaluated, in the Study II and III the nature and the amount of the curing agents were evaluated. This extended abstract presents, in a more detailed way, the influence of the content of the phenolic resin like curative was analyzed (Study III). The others results are briefly described in the results and discussions section.

EXPERIMENTAL

Experiments were performed with different TPV`s compositions, according to the formulas described in Tab. 1, 2 and 3. The amounts of each ingredient were defined in function of the total polymer content and expressed as per hundred of polymer (php). In all mixtures the oil content was fixed in 40php.

The 03 PPs used were produced by Braskem S.A with the following properties: homopolymer PP H103 (PPH1), copolymers PCD0810 (PPC1) and CP241 (PPC2), with a crystallinity degree of 63%, 43% and 37%, respectively.

The elastomer used was an EPDM 4703Z produced by Lanxess Elastomer Brazil, with an ethylene content of 48% and the phenolic resin SP1045 was produced by Schnectady S.A.

Proceedings of PPS-29
AIP Conf. Proc. 1593, 526-529 (2014); doi: 10.1063/1.4873836
2014 AIP Publishing LLC 978-0-7354-1227-9/$30.00

TABLE 1. TPVs compositions with different PPs (Study I)

Ingredientes	PPH 40/ EPDM1 60	PPC1 40/ EPDM1 60	PPC2 40/ EPDM1 60
PPH[1]	**40,0**	-	-
PPC 1[1]	-	**40,0**	-
PPC 2[1]	-	-	**40,0**
EPDM 1	60,0	60,0	60,0
Antioxidant[2]	3,0	3,0	3,0
Parafinic oil	40,0	40,0	40,0
Dicumil peroxide	4,0	4,0	4,0
Coagent TAC	2,0	2,0	2,0
Total	**149,0**	**149,0**	**149,0**

(1) Melt flow index (230ºC/2,16kg): PPH = 40g/10min; PPC1 = 12g/10min e PPC2 = 20g/10min
(2) Irganox 1076 and Irgafos 168 (1:1)

TABLE 2. TPVs compositions with different DCP content (Study II)

Ingredients	PPH/ EPDM1 (blend)	PPH/ EPDM1 PER 1	PPH/ EPDM1 /PER 2	PPH/ EPDM1 /PER 4	PPH/ EPDM1 /PER 6
PPH	40,0	40,0	40,0	40,0	40,0
EPDM 1	60,0	60,0	60,0	60,0	60,0
Paraffinic oil	60,0	60,0	60,0	60,0	60,0
Dicumil peroxide[1]	-	1,0	2,0	4,0	6,0
Coagent TAC	2,0	2,0	2,0	2,0	2,0
Total	162,0	163,0	164,0	166,0	168,0

(1) Considering only the EPDM content, the resin content is 0; 1,7; 3,0; 6,7 e 10,0php, respectively

TABLE 3. TPVs compositions with different phenolic resin content (Study III)

Ingredients	PPH/ EPDM1 (blend)	PPH/ EPDM1 RES1,25	PPH/ EPDM1 /RES2,5	PPH/ EPDM1 /RES 5	PPH/ EPDM1 /RES 10
PPH	40,0	40,0	40,0	40,0	40,0
EPDM 1	60,0	60,0	60,0	60,0	60,0
Paraffinic oil	40,0	40,0	40,0	40,0	40,0
Phenolic Resin[1]	-	1,25	2,5	5,0	10,0
Stannous chloride	-	1,0	1,0	1,0	1,0
Total	140,0	142,3	143,5	146,0	151,0

(1) Considering only the EPDM content, the resin content is 0; 2,1; 4,2; 8,3 e 16,7php, respectively

The mixtures were prepared in a Haake closed mixing chamber with roller rotors. The following conditions were used: rotor speed 80rpm, initial temperature 180^{0}C, piston pressure of 8,1kgf/cm^2 and filling factor of 65%.
The test samples were produced by direct compression in a press with a controlled cooling system.
The Shore A hardness was obtained according to the ASTM D2240 (2005). The tensile properties were determined according to ASTM D 412, test type C. The swelling properties (Q) were done in toluene. The tested sample were firstly extracted, to extract the oil and other extractables, than dried, weighted (M_i) and immersed in toluene by 48h at 23^{0}C, and then weighted again (M_f). The swelling was calculated according to the Eq. 1.

$$Q = \frac{M_f - M_i}{M_i} \times 100 \qquad \text{Equation 1}$$

The morphology of the samples were evaluated by scanning electronic microscopy (SEM, Shimadzu SSX-550), with the samples firstly washed in hot xylene by 2 minutes in order to extract the uncured thermoplastic phase.
The size of the elastomeric domains was defined with the software AnalySIS Starter Olympus 5.1 and the results are a median of different measurement.

RESULTS AND DISCUSSION

The final torque evolution as function of time to the PPH/EPDM1 blend and TPVs with different phenolic resin as cure agent is presented in Fig. 1. In the graphic is possible to observe the highest final torque to the TPV with 5php phenolic resin content. Considering that just the cure content was changed, the final mixture with higher torque (and also higher viscosity) can be considered the one with higher crosslink density.

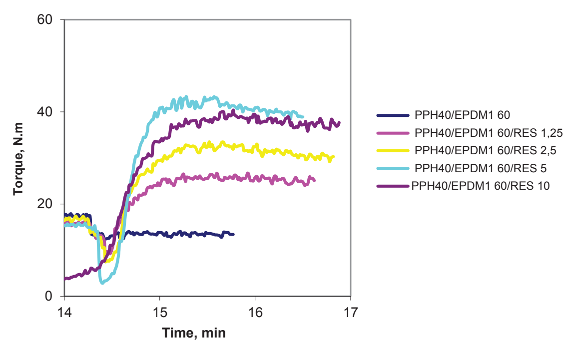


FIGURE 1. Evolution of the torque as function of time for PP/EPDM TPVs prepared with different amount of phenolic resin

The tensile strength results to the TPV`s with different cure systems are presented in Fig. 2 where is possible to observe an increment in the modulus with the increase of phenolic resin content. The TPV with 5php phenolic resin content can be considered the one with the better relation between crosslink content and tensile strength properties. The Shore A hardness of the TPV`s increase with the phenolic resin content, mainly when compared with the PP/EPDM blend (Tab. 4).

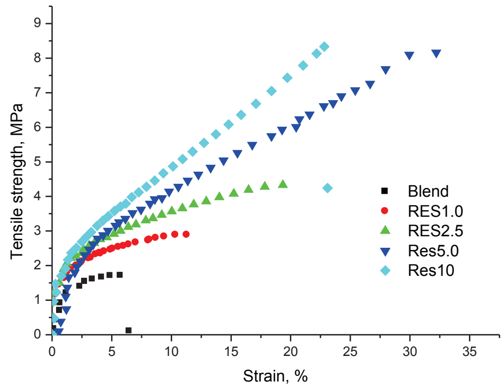


FIGURE 2. Tensile strength x strain of the blend and TPV`s with different phenolic resin content

TABLE 4. Shore A hardenss of TPVs with different phenolic resin content

	PPH/ EPDM1 (blend)	PPH/ EPDM1 /RES 1,25	PPH/ EPDM1 /RES 2,5	PPH/ EPDM1 /RES 5	PPH/ EPDM1 /RES 10
Shore A hardness	61	75	77	79	79

In a cured polymer with a high crosslink density the length of the elastomeric chains will be smaller, the size of the network mesh will be smaller and, as a result, a lower swelling degree in organic fluids is expected. According to Mark [9] as lower is the crosslink density of a rubber as higher will be the solvent absorbed by the polymer, considering that the chain crosslink segments distance are higher in this systems.

The Fig. 3 presents the swelling behavior in toluene of the five TPVs as function of the phenolic resin content where is possible to observe that amounts of phenolic resin higher than 5php didn`t result in lower swelling index.

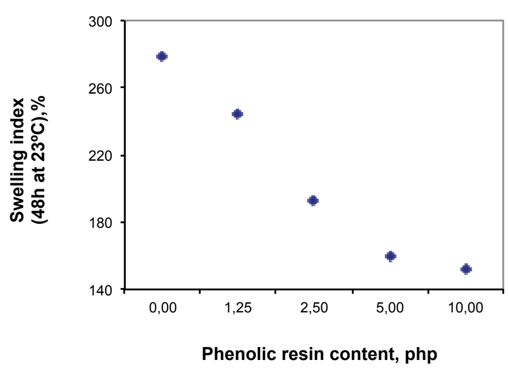
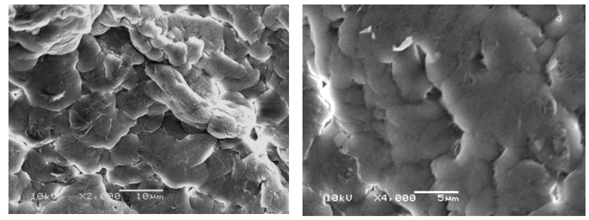
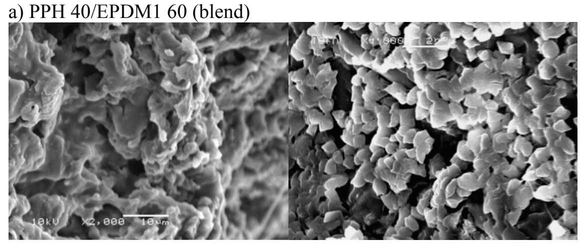


FIGURE 3. Swelling index to TPV`s with different phenolic resin content

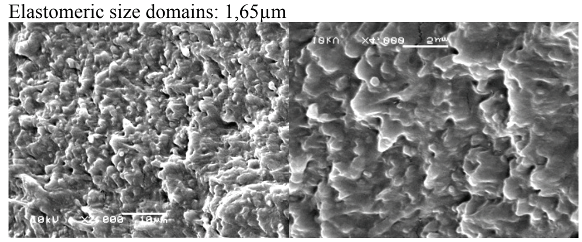
The morphology of the five compounds evaluated is presented in Fig. 4. Different elastomeric size domains can be observed. In the PPH 40/EPDM1 60 blend a co-continuous phase can be observed. In the TPV`s it was possible to identify clearly the elastomeric domains and their respective sizes. The TPV with phenolic resin content of 2,5php presented the smaller elastomeric domains (Fig 4c).



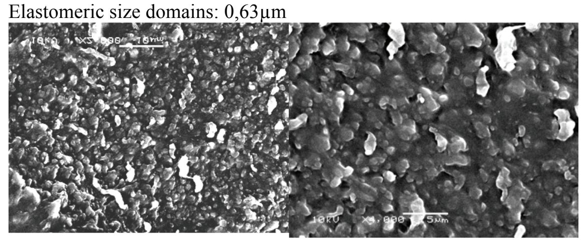
a) PPH 40/EPDM1 60 (blend)



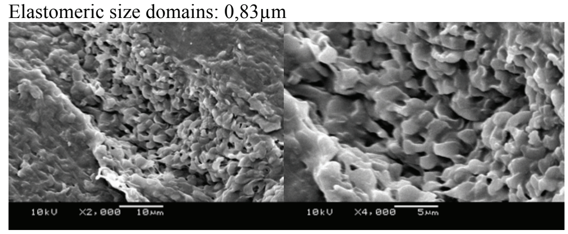
b) PPH 40/EPDM1 60/RES 1,25
Elastomeric size domains: 1,65μm



c) PPH 40/EPDM1 60/RES 2,5
Elastomeric size domains: 0,63μm



d) PPH 40/EPDM1 60/RES 5
Elastomeric size domains: 0,83μm



e) PPH 40/EPDM1 60/RES 10
Elastomeric size domains: 1,8μm

FIGURE 4. Morphology of the five compounds with 2.000 and 4.000X magnification

With the SEM results was possible to conclude that the elastomeric size domains became small until 5php of resin content, over this value, the size of the domains started to increase again.

When the microstructure and size domains are correlated with the tensile properties in the TPV with 10php is possible to observe an increment in the size domains and a decrease in the tensile strength resistance

Regarding to the other studies (I, II), the following results were obtained:

- Study I: the hardness and tensile strength increase with increasing of the PP cristalinity. At the same time, lower hardness TPVs were obtained with EPDM with lower cristalinity, and ethylene content;
- Study II: with a DCP content of 4php the TPVs presented a good balance between processability and physical mechanical properties. The torque observed during the curing in the dynamic vulcanization didn`t change with DCP amounts of 2php or more. The tensile strength of the TPV with 4php of DCP was superior to the others TPVs.

CONCLUSION

It was possible to produce TPV`s with low hardness in a closed mixing chamber. The size domains decrease until 2,5php of phenolic resin when back to increase with the increment in the phenolic resin content. The better results in the physical mechanical properties of the TPV`s were found in the compound with 5php of phenolic resin. This TPV also was the one that presented the higher torque in the torque x time curve produced by the mixture in the closed mixing chamber.

REFERENCES

1. Radusch, H. J. Phase Morphology of Dynamically Vulcanized Thermoplastic Vulcanizates. In: THOMAS, Sabu; GROENINCKX, Gabriel; HARRATS, Charef (Ed.) Micro- and Nanostructured Multiphase Polymer Blend Systems: phase morphology and interfaces. Toronto: CRC; Taylor & Francis, 2005
2. RODGERS, Brendan. *Rubber Compounding Chemistry and Applications*, Marcel Dekker, New York, 2004
3. ABDOU-SABET, S.; PUYDAK, R. C.; RADER, C. P., *Dynamically Vulcanized Thermoplastic Elastomers*. Rubber Chemistry and Technology, Akron, v. 69, n. 3, p. 476-494, 1996
4. NASKAR, Kinsuk; NOORDERMEER, Jacques W. M.; *Dynamically Vulcanized PP/EPDM blends: Multifunctional Peroxides as Crosslinking Agents – Part I*. Rubber Chemistry and Technology, Akron, v. 77, p. 955, 2004
5. NASKAR, Kinsuk; NOORDERMEER, Jacques W. M.; *Dynamically Vulcanized PP/EPDM blends: Effects of Different Types of Peroxides on the Properties*. Rubber Chemistry and Technology, Akron, v. 76, p. 1001-1018 2003
6. BHOWMICK, Anil K.; STEHPENS, Howard L. Handbook of Elastomers: new developments and technology. New Cork: New York and Basel, 1988.
7. REID, Ch. G.; CAI, K. G.; TRAN, H. Polyolefin TPV for Automotive Interior Applications. KGK Katschuk Gummi Kuntstoffe, v. 57, nº 5, p. 227, 2004
8. ANTUNES, C. F.; MACHADO, A. V.; DUIN, M. Van. Degradation of the Rubber Network during Dynamic Vulcanization of EPDM/PP Blends Using Phenolic Resol. Rubber Chemistry and Technology, Akron, v. 82, n. 5, p. 492-505, nov. 2009
9. MARK, James. Experimental Determinations of Crosslink Densities. Rubber Chemistry and Techonology, Akron, v. 55, p. 762, 1982