Dynamically Vulcanized PP/EPDM Blends: Influence of Curing Agents on the Morphology Evolution

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ABSTRACT: Thermoplastic vulcanizates (TPE-Vs) are a special class of thermoplastic elastomers (TPEs), where the rubber phase is dynamically crosslinked in the presence of a thermoplastic matrix. The goal of this work is to compare the behavior of two curing agents systems, conventional peroxide named Peroximon and bismaleimide/dicumyl peroxide, in TPE-Vs based on PP/EPDM 35/65 w/w. It was also investigated the TPE-Vs morphological evolution and samples was collected at different times during the mixture and dynamic crosslinking. The materials were characterized by some techniques, which allowed investigating mechanical, morphological, hardness, and swelling properties. Considering the used curing agents contents, the TPE-Vs obtained by using Peroximon presented lower tensile strength, lower swelling degree, and remarkable lower deformation than those obtained with BMI/DCP system. The hardness properties were not significantly affected by the content of the curing agent, showing only a slight decrease when the Peroximon content was increased. The study of the evolution of morphology showed the rubber phase undergoes crosslinking after adding the curing agent. It could be observed by the increase of the torque and by the appearance of domains in the micrographs. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3093–3100, 2008

Key words: elastomers; thermoplastic; vulcanization; morphology

INTRODUCTION

Thermoplastics elastomers vulcanizates (TPE-Vs) are materials obtained by dynamical vulcanization, where the rubber is crosslinked in the presence of a molten thermoplastic phase. In this process larger proportions of rubber were used.[1] The morphology of the TPE-V is characterized by the presence of the crosslinked rubber domains finally dispersed in the thermoplastic phase.[2]

TPE-Vs based on polypropylene (PP) and ethylene-propylene-diene terpolymer rubber (EPDM) are the most representative example of this material class.[3–5] They are used mainly in the automotive industries to the manufacturing of profiles, hoses, and car bumpers, as well as in other segments as tooth brushes, handle tools, and covering wire.[6,7]

Some works have been realized to study the evolution of the morphology during the TPEs obtaining process. Machado and van Duin[8] have studied the morphological development of the TPE-Vs based on EPDM and polyethylene (EPDM/PE) at different compositions obtained in an extruder and crosslinked using a resol/$SnCl_2$ system. Coran et al.[9] studied the development of the morphology of natural rubber/polyethylene noncrosslinked blends. Radusch[10] analyzed the evolution of the morphology of the TPE-Vs based on ethylene-propylene rubber/polypropylene (40/60 wt %) crosslinked using peroxides, prepared in laboratory internal mixer.

Radusch[10] has proposed a scheme about the morphological evolution during the TPE-V obtaining process. In the initial state there is a mixture of the molten thermoplastic and the noncrosslinked rubber forming cocontinuous phase. As the curing agent is added the rubber phase becomes elongated until to reach a very deformed stage and then it breaks in small fragments. This process is called phase inversion, where the thermoplastic phase becomes the only continuous phase, even being the lower component. The final morphology of TPE-V is formed by crosslinked rubbers domains dispersed in a continuous thermoplastic phase.

Among several factors that can affect the morphology of TPE-Vs, such as composition (plastic/rubber), mixture conditions, and crosslinking density, the highlights are the type of curing agent used to crosslink the elastomeric phase. Different crosslinking systems have been used to obtain TPE-Vs and each on of them has advantages and disadvantages,

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TABLE I
Characteristics of the Materials Used

Materials/Trade name	Characteristics	
PP/CP191	MFI (230°C, 2.16 kg)	80 g/10 min
	Density (23°C)	0.895 g/cm^3
	T_m	164°C
EPDM/K 4703	Mooney viscosity ML (1+4) 125°C	65
	Ethylene content	48%
	Termonomer content	9%

depending on the chemical nature of the thermoplastic and the rubber selected to work.[11–17] The utilization of the peroxides in the obtaining of TPE-Vs can present, as a disadvantage, the degradation of the thermoplastic, because peroxides are not selective for unsaturated elastomers. A few number of works have been studied bismaleimides as curing agent,[18,19] although they are employed specifically to unsaturated elastomers.

In this article the results of two experimental studies are presented. First, a comparative study between two curing agents (conventional peroxide and bismaleimide) used to crosslink TPE-Vs based on PP/EPDM is presented with the main goal for to investigate the difference of the crosslinking obtained with each one of them. The second one presents a study about the morphological evolution with the mixing time of TPE-Vs, obtained with the both curing systems of interest in this work.

EXPERIMENTAL

Materials

The polymers used in this study are described in the Table I. Polypropylene copolymer and ethylene-propylene-diene terpolymer rubber (EPDM) with ethylidene norborene (ENB) as a termonomer, were kindly supplied by Braskem and DSM Elastomers, respectively, and were used as commercially available grades.

Two types of curing agents were used for the dynamic vulcanization: bismaleimide/dicumyl peroxide combination (BMI/DCP) and di(*tert*-butylperoxyisopropyl)benzene produced by Arkema under trade name Peroximon.

Blends preparation

The PP/EPDM ratio used was 35/65 w/w and the curing agent content (in parts of hundred of rubber, phr) was varied as described in Table II. The TPE-Vs obtained with the BMI/DCP system were named TB and those obtained by using Peroximon were named TP.

The TPE-Vs were prepared in a Haake internal mixer with a rotor speed of 75 rpm and temperature of 180°C, with a chamber volume of 69 cm^3. The PP (copolymer) was added in the beginning and 3 min later the EPDM was introduced. After 2.5 min of mixing, the curing agent was added. Considering the BMI/DCP system, first was introduced the BMI and 1 min later the DCP. The mixing was carried out during ~ 5 min. After mixing, the samples were compression molded at 190°C about 4 min and cooled down 100°C in a press Carver model G.

To study the morphology of the samples, the material was mixed during 20 min, the samples were taken out at different times and were quenched in liquid nitrogen to stop the cure reaction.

Characterization

Mechanical properties

Tensile tests were carried out in EMIC universal testing machine equipped with a 500 N load cell using dumb-bell specimens according to ASTM D 412.

Swelling measurements

The swelling degree was determined on the basis of equilibrium solvent-swelling measurements in toluene. The samples were submerged in the solvent and after the swelling equilibrium was reached, that means, no change in the weight of the swollen sample was observed, the mass of solvent was determined according to the ASTM D 471. The results were expressed as the mass of solvent absorbed per gram of TPE-V.

Hardness

The hardness, Shore A, was measured according to DIN 53505 using a durometer Teclock. Three samples were taking from each TPE-V and five measurements were made for each sample. The hardness value was taken as the median value of the 15 measurements. The statistical variation presented in the results is the standard deviation of the measurements.

Morphological studies

The morphology of the TPE-Vs was studied by using a scanning electron microscopy (SEM), model JEOL

TABLE II
Curing Agent Content in phr

Sample ID	TB1	TB2	TB3	TB4	TP1	TP2	TP3	TP4	TP5
BMI	2.0	2.5	3.0	3.5	–	–	–	–	–
DCP	0.20	0.25	0.35	0.35	–	–	–	–	–
Peroximon	–	–	–		1.2	1.5	2.0	3.0	4.0

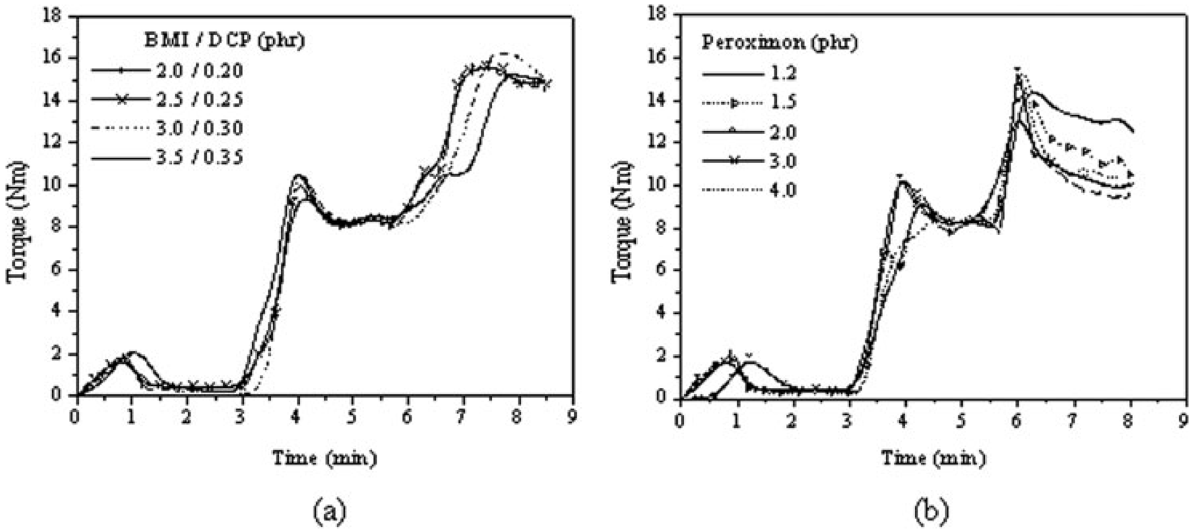


Figure 1 Mixing torque as a function of time to TPE-Vs PP/EPDM 35/65 cured with (a) BMI/DCP and (b) Peroximon.

JSM-5800 and JSM-6060 at Centro de Microscopia of the Universidade Federal do Rio Grande do Sul (UFRGS). The sample surface was etched with xylene during 30 min and then sputter-coated with gold. The images were obtained by secondary electrons (SEI).

RESULTS AND DISCUSSION

Influence of type and content of curing agents

Mixing torque behavior

The mixing torque behavior as a function of the mixture time are shown in Figure 1(a,b), considering two types of curing systems at different concentrations.

Considering that the mixing chamber has a temperature about 180°C, as the PP is added the torque goes down until practically zero, due to the melt of PP. In the third minute the rubber is introduced and it can be seen an increase in the torque curve until it reaches the stabilization when the curing agent is introduced initiating the cure reaction. With the beginning of the cure reaction, the crosslinking of the polymer chains starts to occur and there is an increase in the viscosity which can be seen by the arising of the torque.

After that it can be noted a decrease in the torque, what can be attributed to the break of the deformed rubber phase, the formation of the rubber cured domains and the dispersion in the low viscosity thermoplastic matrix.

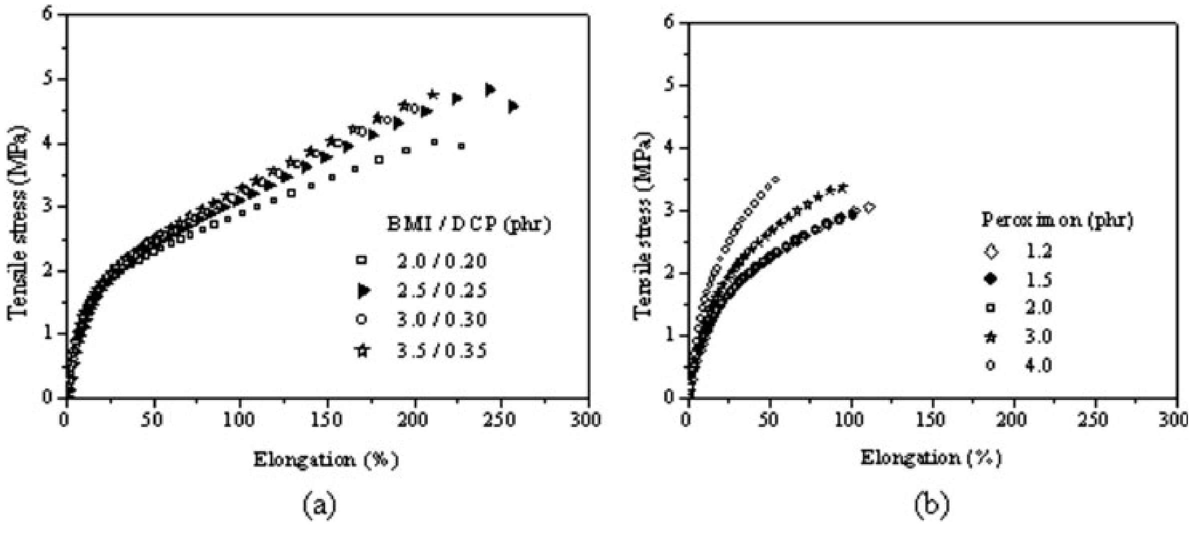


Figure 2 Tensile stress curves of TPE-Vs based on PP/EPDM (35/65 (w/w)), considering different contents of (a) BMI/DCP and (b) Peroximon.

TABLE III
Hardness of TPE-Vs

Cure system	Content of cure agent (phr)	Hardness (Shore A)
BMI/DCP	2.0/0.20	70 ± 4
	2.5/0.25	76 ± 2
	3.0/0.30	69 ± 5
	3.5/0.35	70 ± 4
Peroximon	1.2	76 ± 3
	1.5	75 ± 5
	2.0	75 ± 3
	3.0	70 ± 3
	4.0	71 ± 5

It can be observed in the Figure 1(a) that the final torque of the TPE-Vs obtained using BMI/DCP there were no significant changes in the torque considering different contents of curing agent. Analyzing the Figure 1(b) it can be clearly seen that the final torque of TPE-Vs undergo a pronounced decrease, probably due to the degradation of the polymer chain.

Mechanical properties

To evaluate the effect of the curing agent content in TPE-Vs based on PP/EPDM and to compare both curing agent systems (BMI/DCP and Peroximon), the mechanical properties were analyzed. In the Figure 2(a,b) are presented the results obtained by the tensile stress measurements.

Analyzing the results shown in the Figure 2, it can be seen that the type of the curing system influences greatly on the stress and deformation of the materials. The TPE-Vs obtained by curing with Peroximon, Figure 2(a), presented lower tensile strength. It can be due to the degradation of the PP polymer chain, as already mentioned previously. These TPE-Vs presented also remarkable lower deformation than those cured with BMI/DCP system. This behavior is a indication that the crosslinking density obtained by using peroxide should be higher than that obtained with BMI/DCP.

This behavior can be explained considering the difference in the chemical structure and in the performance mode of those cure systems. As the used peroxide presents two O—O bonds, its decomposition produces four radicals. Taking this into account the Peroximon can be considered more efficient than the bismaleimide (BMI), which is bifunctional. As the molecular weight of BMI (358 g/mol) and of Peroximon (338 g/mol) is similar, considering the same content in phr, the cure efficiency of the peroxide is much higher.

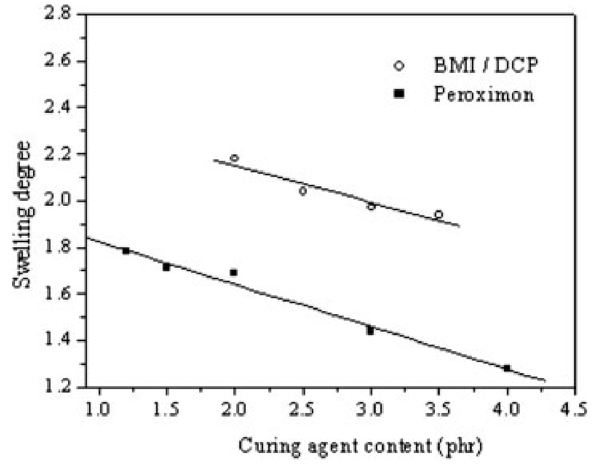


Figure 3 Influence of the curing agent content on the swelling degree for samples (PP/EPDM 35/65 w/w) cured with both cure systems.

Hardness

The TPE-Vs hardness was determined and the values are listed in Table III. It can be that this property does not undergo a significant influence considering the curing agent studied, showing only a slightly decrease as the content of Peroximon is increased. This behavior can occur because of a change in the thermoplastic phase, as decrease in the crystallinity.

Swelling degree

Figure 3 presents the results of swelling measurements in toluene of the TPE-Vs based on PP/EPDM (35/65 w/w) obtained with both curing systems studied. It can be observed, as expected, that as the curing agent content decreases the swelling degree

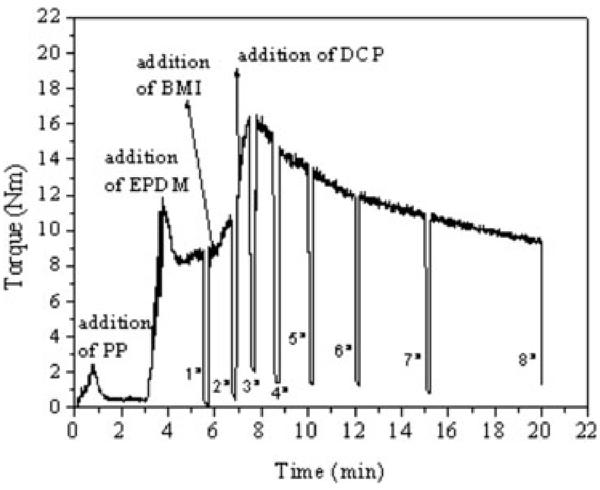
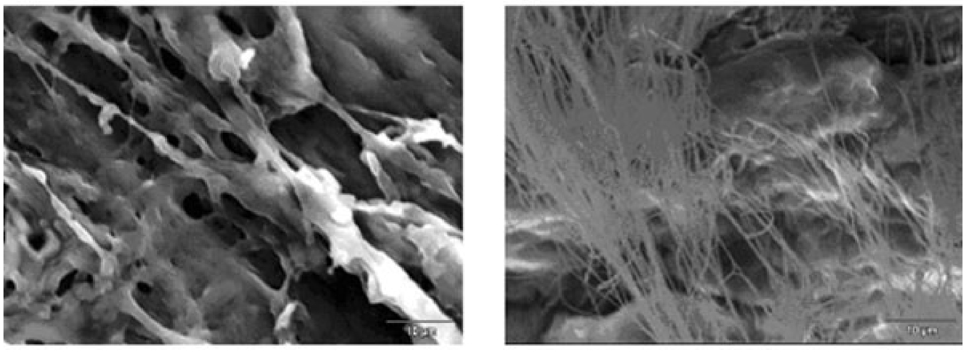
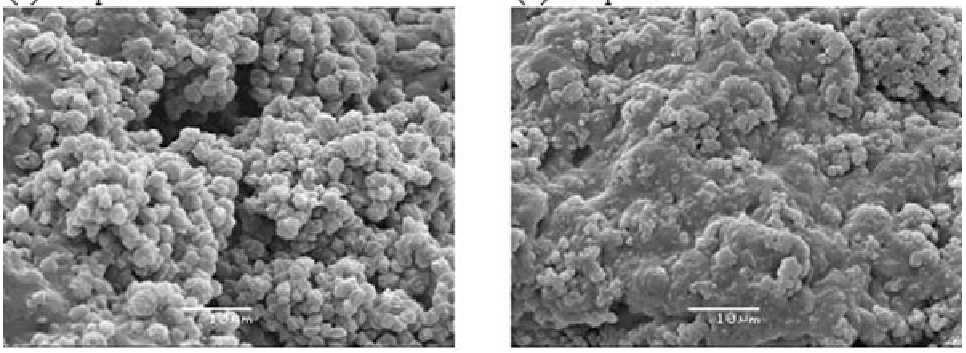
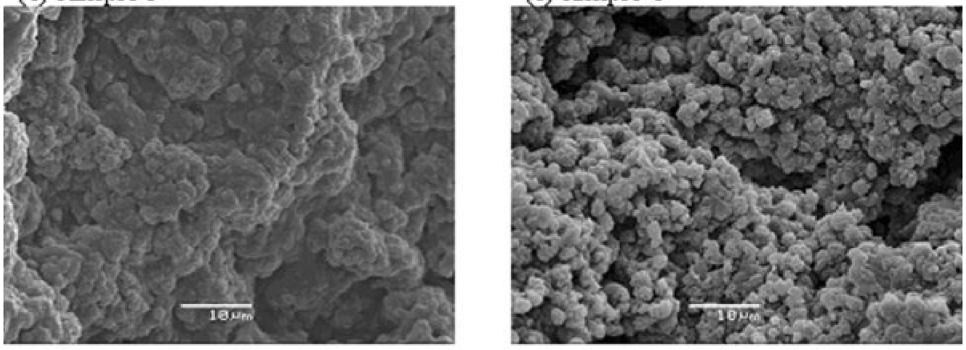


Figure 4 Torque behavior during the process of a TPE-V PP/EPDM obtained by curing with BMI/DCP.


(a) sample 1 (b) sample 2


(c) sample 3 (d) sample 4


(e) sample 5 (f) sample 6

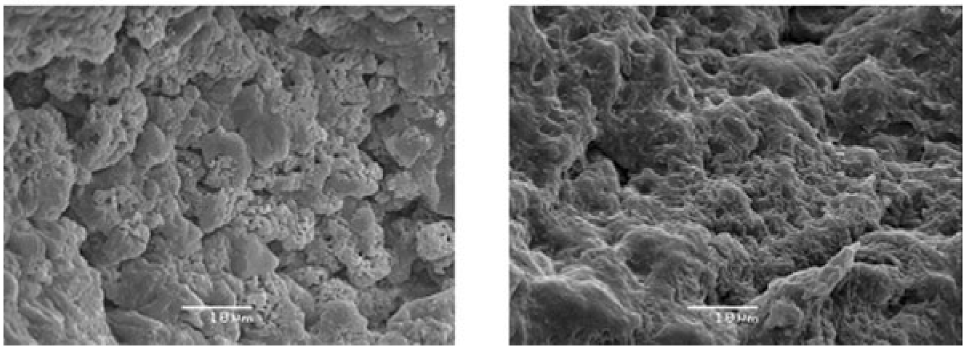

(g) sample 7 (h) sample 8

Figure 5 Micrographs of the collected samples to study of the morphology evolution of TPE-V based on PP/EPDM 35/65 mass fraction obtained by curing with BMI/DCP. Magnification ×2000.

increases. The TPE-Vs obtained by using the curing agent Peroximon, presented a swelling degree lower than that obtained with the BMI/DCP system, corroborating the idea that the crosslinking density is higher to the materials cured with peroxide.

Evolution of morphology

The morphology is developed during the processing and is dependent of the mixing conditions. To have a better understanding of the evolution of the morphology and to relate it with the final properties, it was carried out a study on the evolution of the morphology with two samples of TPE-Vs PP/EPDM 35/65 w/w: one cured with 2.5/0.25 phr of BMI/DCP and another one cured with 1.2 phr of Peroximon. These samples, TB2 and TP1, respectively, were chosen because of the better stress–strain performance. Higher contents of curing agent did not improve significantly the mechanical properties. Besides, the TPE-Vs obtained using higher content of Peroximon, TP2, TP3, TP4, and TP5, undergo an accentuated decrease of the final torque of the mixture, as already mentioned previously, due to the degradation.

During the mixing process (Fig. 4), the samples were taken out at different times, corresponding to different stages of mixing and different morphologies. The Figure 4 presents the torque evolution indicating the time when the TPE-Vs fractions obtained with 2.5/0.25 phr of BMI/DCP were collected. These fractions were immediately immersed in liquid nitrogen to interrupt the reaction.

The fractions were analyzed by scanning electron microscopy (SEM) to follow the changes in the morphology.

The evolution of the morphology of the TPV PP/EPDM 35/65 w/w can be seen in the scanning micrographs presented in the Figure 5 in a sequence of time.

The samples were immersed in hot xylene to extract the thermoplastic phase, with exception of the first and second samples, which are constituted only PP/EPDM, without curing agent and PP/EPDM only with BMI, respectively.

The sample 1 [Fig. 5(a)], which was obtained after mixing PP with EPDM, shows a cocontinuous phase. The sample 2 was taken out 1 min after the addition of the curing agent (BMI). This sample yet dissolves in xylene and so, it was not extracted. This sample for SEM was obtained only by cutting with a bistoury. It still has morphology where it is possible to see cocontinuous phase, without the rubber domains. Taking this into account it can be thought that the cure reaction should be activated after the addition of the peroxide. The fiber like material, observed in the Figure 5(b), is the deformed rubber strands softly cured. We cannot also discard the hypothesis of being the stretched thermoplastic phase covered by the rubber phase. The differentiation of the rubber and the thermoplastic phase is not possible by SEM, because both are hydrocarbons.

Immediately after the sample 2 was taken out of the mixing, the dicumyl peroxide was added and then, after 30 s the sample 3 was collected. As presented in the Figure 5(c) it can be observed the presence of domains of crosslinked rubber dispersed in a continuous thermoplastic matrix, represented in the micrographs by the cavities formed after the extraction.

Analyzing the micrographs obtained by collecting further samples during the mixing process [Fig. 5(d–h)] it can be seen that the TPE-V desired morphology, which presents rubber domains dispersed in the thermoplastic phase, was reached in the sample 3 [Fig. 5(c)], only 30 s after the addition of DCP, what is related to the maximum torque due to the high rubber viscosity. The smooth area in the Figure 5(d,e) can be an area of cocontinuous phase of rubber, which was not broken in domains. It is also possible that the extraction has not been so deep to visualize the rubber domains. So, the elastomeric phase can be still covered by the thermoplastic matrix. The Figure 5(f) shows the rubber domains in a more defined way.

The micrographs of the latest two samples, 7 and 8 [Fig. 5(g,h)] show the beginning of the coalescence of the elastomeric domains, what can occur due to a degradation of the material as a function of the increase in the mixing time and temperature.

A similar study was carried out using Peroximon as curing agent and the Figures 6 and 7 shows the results obtained.

The Figure 6 presents the torque evolution with the indication of the collect time of the fraction of TPE-V cured with 1.2 phr of Peroximon. Practically, the same profile of the torque obtained with BMI/DCP (Fig. 4) is observed, obtaining at the end of 20 min a final torque around 8 Nm, which is a little bit lower than that obtained with BMI/DCP.

As it has already been describe to TPE-V obtained with the curing system BMI/DCP (Fig. 5) the sample 1 [Fig. 7(a)], which was obtained after the mixture of

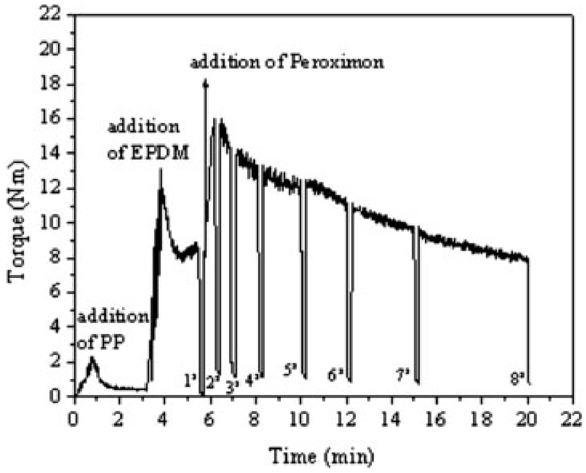


Figure 6 Torque behavior during the process of a TPE-V PP/EPDM obtained by curing with Peroximon.

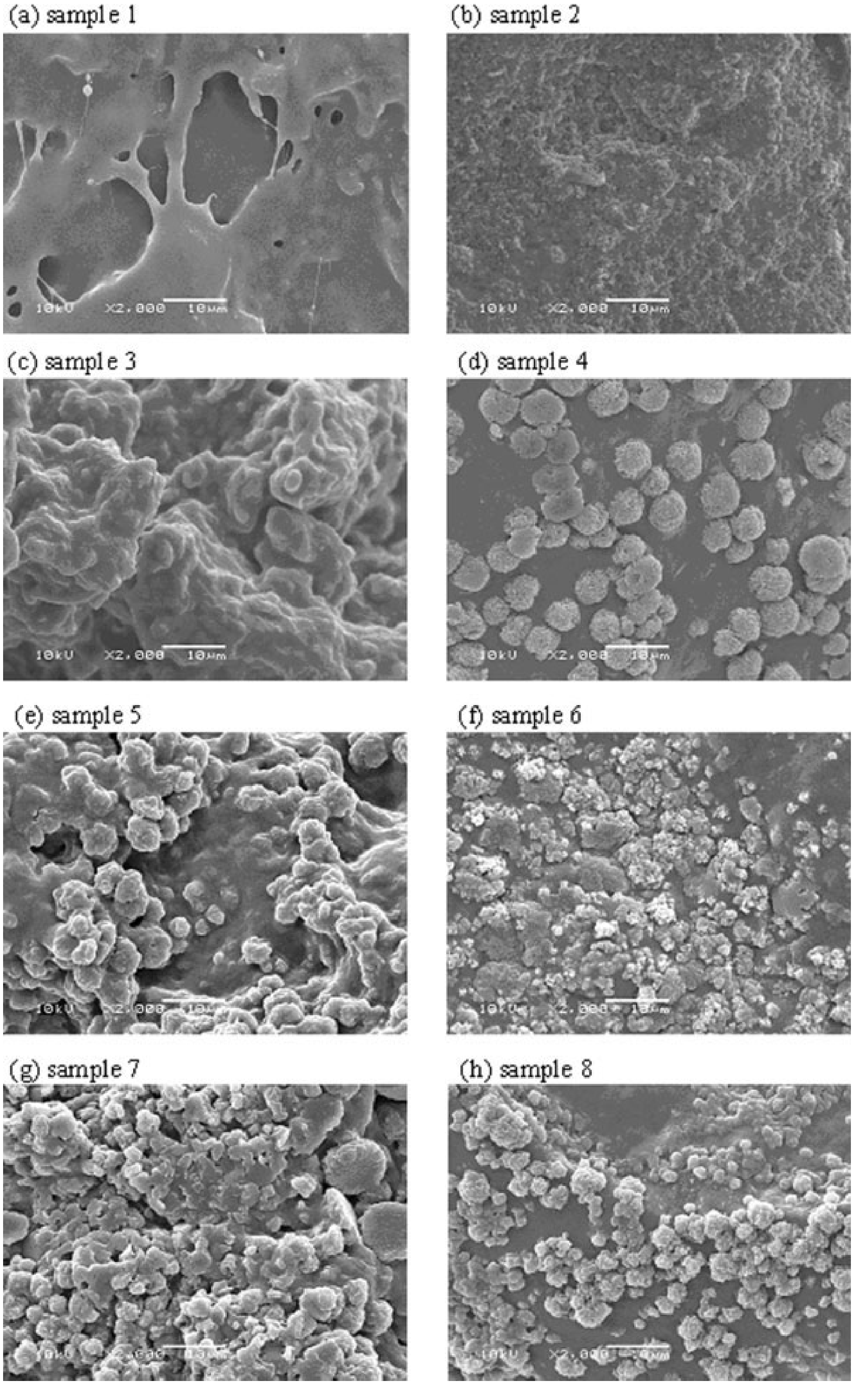

(a) sample 1
(b) sample 2
(c) sample 3
(d) sample 4
(e) sample 5
(f) sample 6
(g) sample 7
(h) sample 8

Figure 7 Micrographs of the collected samples to study of the morphology evolution of TPE-V based on PP/EPDM 35/65 mass fraction obtained by curing with Peroximon. Magnification ×2000.

PP with EPDM, shows morphology with cocontinuous phase. It is not possible to define very well the difference between the elastomeric and thermoplastic phases, probably due to the great affinity between both. Thirty seconds after the addition of Peroximon the sample 2 was collected [Fig. 7(b)] and it can be observed some changes in the morphology due to the beginning of the cure reaction. In the sample 4

[Fig. 7(d)], the morphology characterized by the elastomeric domains homogeneously dispersed in the thermoplastic phase, was reached. Analyzing the micrographs presented in Figure 7, it can be said that the better and more defined morphology was obtained with the sample 8 [Fig. 7(h)] where the domain size varies less than in the other samples and is minor than 5 μm.

These results are in agreement than that previously reported by Radusch,[10] where he has analyzed the morphology of TPE-Vs based on EPR/PP and verified that after the addition of the peroxide, at 30 s, the rubber was already dispersed, as small domains, in the thermoplastic matrix.

Considering this study of the morphological evolution and comparing the TPE-Vs obtained with the two different cure systems, BMI/DCP and Peroximon, it could be observed that the rubber domains are smaller and better defined when BMI/DCP was used as crosslinking system. This morphology is reflected in the mechanical properties. Besides this, BMI is a specific curing agent for polydienes. The small amount of dicumyl peroxide used with BMI is required to initiate the crosslink and probably is small to degrade the thermoplastic phase. The crosslinking with Peroximon is faster and not specific. Apparently, in this case, the rubber domains are not small and not so uniform. Consequently, the mechanical properties, as deformation, are smaller. The accentuated decrease of the final torque in the mixture presented by TPE-Vs obtained with Peroximon is indication that a degradation of the PP polymer chain was occurred.

CONCLUSIONS

As it can be clearly seen from the results obtained in this work the TPE-Vs based on PP/EPDM properties depend on the content of the crosslinking system. The use of the BMI/DCP leads to higher values of deformation and tensile strength than those obtained by using Peroximon. Considering the swelling measurements, which give information about the crosslink density, it was observed higher even content of BMI/DCP (2.5 phr) leads to lower crosslinking density than that obtained with 1.2 phr of Peroximon. The hardness properties were not significantly affected by the content of the curing agent.

Considering the study of the morphological evolution as a function of mixing time, it can be observed that the crosslinked elastomeric phase is dispersed in the spherical domains immediately after the addition of the curing agent. The rubber domains are smaller and better defined when the crosslinking system used is the BMI/DCP.

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