Acrylic Rubber/Nitrile Rubber Blends: The Effect of Curatives on the Mechanical, Morphological, and Dynamic Mechanical Properties

Micheli L. Celestino,[1] Marlucy de Oliveira,[1] Alex S. Sirqueira,[2] Bluma G. Soares[1]

[1]*Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro, Centro de Tecnologia, Bloco J, Ilha do Fundão, 21945-970, Rio de Janeiro, RJ, Brazil*
[2]*Universidade Estadual da Zona Oeste, 23070-200 Rio de Janeiro, RJ, Brazil*

ABSTRACT: The curing characteristics and mechanical properties of blends constituted by acrylic rubber (ACM) and nitrile rubber (NBR) were investigated. The curing process was performed by a combination of curing systems specific for each rubber component. The curing system for the ACM phase consisted of hexamethylene diamine carbamate/sodium stearate, whereas the NBR phase was cured with different systems: accelerated sulfur or bismaleimide/peroxide. In all of the curing systems employed, the blends presented more outstanding ultimate tensile properties than the individual rubbers, which indicated a compatibilization effect of the curing systems. Dynamic mechanical analysis of the blends revealed a broadening of tan δ peak and a shift in the glass-transition temperature of the ACM phase in the direction of the NBR transition in most of the systems studied and an increase in the storage modulus, which was also an indication of a compatibilization effect. Scanning electron microscopy also revealed a very thin rubber phase, which confirmed the compatibilization. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 721–729, 2009

Key words: blends; compatibilization; elastomers; vulcanization

INTRODUCTION

Acrylic rubber (ACM) is considered a very important rubber for manufacturing seals and gaskets used in high-performance automotive engines because of its outstanding oil and temperature resistance.[1] These unique characteristics make this rubber a good candidate for blending with many other polymers. Thermoplastic elastomer blends based on ACM and nylon,[2–5] poly(vinyl chloride),[6,7] poly(ethylene-*co*-vinyl acetate),[8] and polypropylene[9] have been reported in the literature with the aim of developing oil- and temperature-resistant elastomeric materials with the processability of the thermoplastics. The blending of ACM with other elastomers has not been extensively studied, probably because of the incompatibility between the rubber components and because of the different types of curatives required for each rubber in a blend. ACM is a saturated rubber, usually commercialized with different types of cure-site monomers, introduced into the polymer chain during the polymerization process.[10,11] The most common cure-site monomers include those containing a labile chlorine atom, a carboxyl group, or an epoxide moiety, which require different curing systems.[10,11] ACMs containing chlorine groups are usually cured with a soap–sulfur system, whereas those containing carboxyl or epoxide groups are better cured with quaternary ammonium salts.[10] Therefore, the crucial step for the processing of ACM-based elastomer blends is to find a suitable curing system for both rubber components. Recently, Kader and coworkers[12–16] published a series of articles related to ACM–fluorocarbon rubber. They employed ACM containing epoxide as the cure-site monomer for ACM and suggested that the best curing system for the blend was a combination of hexamethylene diamine carbamate (HMDAC; DIAK #1) and ammonium benzoate. Improved tensile and tear properties were observed for the 50 : 50 wt % ACM–fluorocarbon blends, when compared

to the pure rubbers, which indicated the presence of some interaction between the rubbers.[14]

Wootthikanokkhan and coworkers[17–19] studied the main properties of gum and filled natural rubber–ACM blends. For these studies, they employed ACM with chlorine as the active cure site, which was cured with a system that consisted of sodium stearate and sulfur in the presence of the usual accelerator (2-mercaptobenzothiazole) and activators (zinc oxide and stearic acid) for the curing of unsaturated rubbers. They also developed a compatibilizing system based on a block copolymer to improve the mechanical properties of these dissimilar blends.[18]

Blending ACM with nitrile rubber (NBR) is also an interesting approach for the development of improved oil- and temperature-resistant elastomeric materials. NBR is cheaper than ACM and also presents good oil and fuel resistance, which is imparted by the polar groups along the backbone. However, the presence of unsaturation in the chain limits its application at higher temperatures. Despite the potential applications, studies involving such blends have been scarce. One of the few publications in this field is a patent invented by Coran[20] almost 20 years ago. In that procedure, Coran described a methodology that involved first the vulcanization of ACM in the presence of NBR, followed by the vulcanization of the NBR. After this patent, no important reports in the accessible literature were found.

Our main target in this study was to find the best curing system for both the ACM and NBR rubber components, which would be added simultaneously during rubber formulation in a Banbury or two-roll mill. The ACM used in this study was produced by Petroflex Industria e Comercio S.A. (Rio de Janeiro, Brazil) and contained double-active cure sites based on chlorine and carboxyl groups. According to the manufacturer suggestion, the curing system used for this ACM grade was a combination of sodium stearate and a blocked diamine, namely, HMDAC.

The aim of this study to examine the influence of different curing systems, based on accelerated sulfur or peroxide, on the curing process and mechanical properties of the corresponding ACM/NBR blends.

EXPERIMENTAL

Materials

NBR [33 wt % acrylonitrile; Mooney viscosity (ML 1+4 at 100°C) = 60] and ACM Hicryl 1540 [derived from the polymerization of ethyl acrylate and containing carboxyl and chlorine as the double cure-site groups; Mooney viscosity (ML 1+4 at 100°C) = 40] were kindly supplied by Petroflex Industria e Comercio S.A. WB 222, a processing agent based on aliphatic fatty acid esters, used for the ACM, was

supplied by Struktol (Stow, OH). Chemac Park 50, a HMDAC was supplied by Chemicon Industria Química S.A. (São Paulo, Brazil). N,N'-m-Phenylene-bis-maleimide (BMI; HVA-2) was purchased by Dupont Dow Elastomers (Freeport, TX). Other ingredients, such as zinc oxide, stearic acid, sulfur, tetramethylthiuram disulfide (TMTD), dicumyl peroxide (DCP), and sodium stearate (Na stearate), were laboratory reagent grade.

Blend preparation

The blends were prepared in a two-roll mill operating at room temperature, with a friction ratio of 1 : 1.1. NBR was masticated for 3 min and blended with ACM together with the processing aids for the ACM component (WB 222 and stearic acid). After the homogenization of the rubber blend (for about 5 min), the other ingredients were added. The basic formulations are listed in Table I, obeying the addition sequence. The processing time after each component addition was about 2 min.

After mixing, the samples were compression-molded between pieces of aluminum foil in a two-plate hydraulic press at 170°C at a pressure of 5 MPa. The molding time was adjusted according to the optimum cure time (t_{90}; ASTM D 2084-81 method) as determined from an oscillating disk rheometer (ODR; Tecnologia Industrial, model T100, Buenos Aires, Argentina) with an oscillating angle of 1°. t_{90} was established as the time to reach 90% of the maximum torque.

The cure rate index (CRI) is calculated as follows:

$$CRI = \frac{100}{t_{90} - t_{s1}}$$

where t_2 is the scorch time.

The test specimens for the tensile measurements and dynamic mechanical analysis (DMA) were cut from molded slabs approximately 2.0 mm thick.

Testing

Tensile testing of the samples was done at 25°C with dumb bell-shaped test specimens according to the DIN 53504 type S2 method. The measurements were performed in a universal testing machine (Instron model 5569, Boston, MA) at a crosshead speed of 200 mm/min. The average value of five tests for each sample is reported here.

The compression set test was done under a constant strain of 25% according to ASTM D 395-85 at 100°C for 70 h. The specimens for this test were compression-molded for $2t_{90}$ to obtain circular disk samples 6.0 mm thick and 12.5 mm in diameter.

TABLE I
Formulations, Cure Characteristics, and Physical Properties of ACM, NBR, and Their Blends as a Function of the Curing System

		Peroxide-based system			Sulfur-based system		
	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6	Mix 7
Ingredients (phr)							
ACM	100	—	50	50	—	50	50
NBR33	—	100	50	50	100	50	50
Stearic acid	1.0	—	—	0.5	0.5	0.5	0.5
WB 222	2.0	—	—	1.0	1.0	1.0	1.0
Sodium stearate	4.0	—	—	2.0	—	—	2.0
Chemac Park50	1.5	—	—	0.75	—	—	0.75
BMI	—	3.0	3.0	1.5	—	—	—
DCP	—	0.3	0.3	0.15	—	—	—
Sulfur	—	—	—	—	0.3	0.3	0.15
TMTD	—	—	—	—	1.5	1.5	0.75
Zinc oxide					2.5	2.5	1.25
Cure characteristics from ODR							
t_{S1} (min)	2.0	1.6	1.4	1.6	2.6	2.6	2.5
t_{90} (min)	16	7.5	8.5	16	5.5	17	14
M_L (dN m)	2.3	2.9	2.3	2.4	2.3	1.6	2.1
M_H (dN m)	11.5	31	12	15.4	13.8	13	9.4
CRI	7.0	17	14	6.9	35	6.9	8.5
Physical properties							
Tensile strength at 100% deformation (MPa)	0.77	2.8	1.94	2.2	0.82	0.80	0.53
Tensile strength (MPa)	1.66	3.84	5.3	6.7	4.0	4.9	7.6
Elongation at break (%)	347	148	417	470	1180	1080	1680
Compression set (%)	17	18	40	25	35	36	58
Swelling in mineral oil (%)	7.8	12	9.2	8.1	32	12	11

t_{s1}, scorch time; t_{90}, optimum cure time; M_L, minimum torque; M_H, maximum torque.

Oil resistance

The test specimens were immersed in a mineral oil at 100°C for 22 h. The test specimens were then removed from the oil, wiped with tissue paper to remove the excess oil from the surface, and weighed. The percentage mass swell was then calculated as follows:

$$\text{Change in mass} = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 and W_2 are the weights of the samples before and after immersion, respectively.

DMA

The DMAs of the blends were obtained by with a DMA analyzer (Q800; TA Instruments, New Castle, DE). The sample specimens ($25 \times 12 \times 2$ mm^3) were analyzed in single-cantilever mode at a constant frequency of 10 Hz, a strain amplitude of 30 μm, and a temperature ranging from -60 to $+40$°C, with a heating rate of 3°C/min. The temperature corresponding to the peak in the loss tangent (tan δ) versus temperature plot was taken as the glass-transition temperature (T_g).

RESULTS AND DISCUSSION

Curing characteristics and physicomechanical properties

Table I presents the curing characteristics and mechanical properties of ACM, NBR, and their blends as a function of the curing system. ACM was cured with a combination of a HMDAC and sodium stearate, whereas NBR was cured either with an accelerated sulfur or peroxide system. Peroxide was used together with BMI because it was reported to be an effective crosslinking agent in the presence of an organic peroxide.[21] The ACM/NBR blends were cured with the systems employed for the NBR phase (sulfur- or peroxide-based systems) either alone or combined with the curing system employed for the ACM phase. The rheograph curves obtained from ODR measurements are illustrated in Figure 1 as a function of the NBR-based curing system. The BMI/DCP system promoted a very fast cure of the NBR (mix 2) and ACM/NBR blend (mix 3). By using a combination of the BMI/DCP–HMDAC dual curing system (mix 4), we observed a delay of the curing process, as indicated by the higher t_{90} value. The delay of the curing process in mix 4 may have been due to the consumption of part of the BMI by the decomposition product of HMDAC, an aliphatic diamine, which occurred at higher temperatures, as
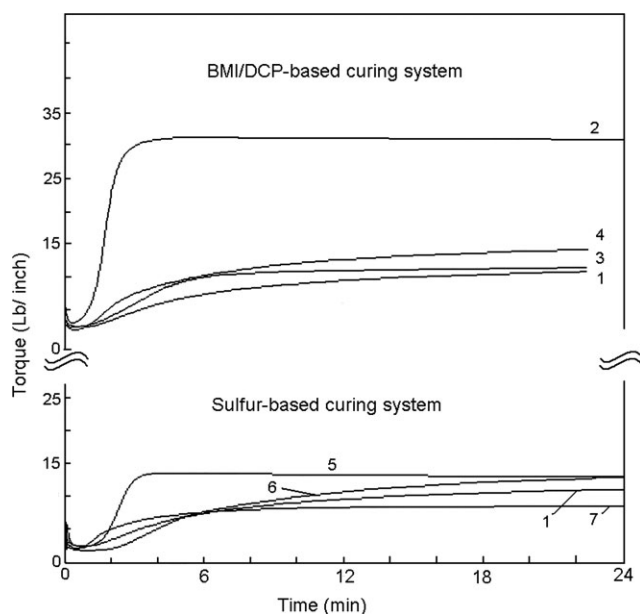
Figure 1 Rheograph curves of ACM, NBR, and their blends as a function of the curing system (the numbers on the curves refer to the formulations listed in Table I).

discussed later. With BMI/DCP system alone in the blend (mix 3), the curing time for the blend was significantly shorter, which confirmed the interference of HMDAC on the curing process of NBR phase. The maximum torque values of the blends (mixes 3 and 4) were significantly lower than that of pure NBR, which suggested a decrease in the overall crosslink density.

The ACM/NBR blends cured with the accelerated sulfur system (mix 6) displayed a longer curing time than pure NBR (mix 5). Sulfur has been reported to be an effective curing agent for ACM containing chloride as the reactive cure site[17–19] and is also extensively used in NBR formulations. Therefore, there is a competition of the sulfur toward the allylic hydrogen of the unsaturated NBR rubber and the chloride groups of ACM, which contributes to the delay of the curing process. The maximum torque found in mix 6 was higher than that in the other blend (mix 7) and achieved a similar value as that found for the pure NBR.

The stress–strain curves of NBR, ACM, and their blends are illustrated in Figure 2 as a function of the curing system. The ultimate tensile properties and other physicomechanical properties are also summarized in Table I. The ACM/NBR blends cured with BMI/DCP and BMI/DCP–HMDAC displayed significantly better ultimate tensile properties, which indicated an important compatibilization effect exerted by the curing agents. These additives could react with both rubber phases and contribute to the formation of a network at the interface involving both rubber components. This process is known as

covulcanization. In addition, this phenomenon may be related to better curative migration and better crosslink distribution in each phase of the rubber blend, probably because of the polarity of both rubber components. The better crosslink distribution may explain the lower maximum torque observed in these blends, when compared to the pure NBR vulcanizate. The effectiveness of the curing system for both rubber phases was confirmed from extraction experiments in tetrahydrofuran. The vulcanized blend did not present any extractable material after 7 days of extraction in THF, which confirmed that all rubber phases were vulcanized. These results suggest that the curing systems also acted as interfacial agents. The probable reactions that occurred during the curing process in the blends cured with peroxide-based curing systems are illustrated in Figure 3. In the absence of HMDAC, the free radical formed by the action between DCP and the rubbers may have reacted with BMI, which formed a bridge between the phases. Additionally, the carboxyl groups of the ACM phase may have added to the double bond of BMI and contributed to the interfacial adhesion. The combined curing system BMI/DCP/HMDAC also imparted interfacial adhesion because the hexamethylene diamine (HMDA) formed by the decomposition of HMDAC was able
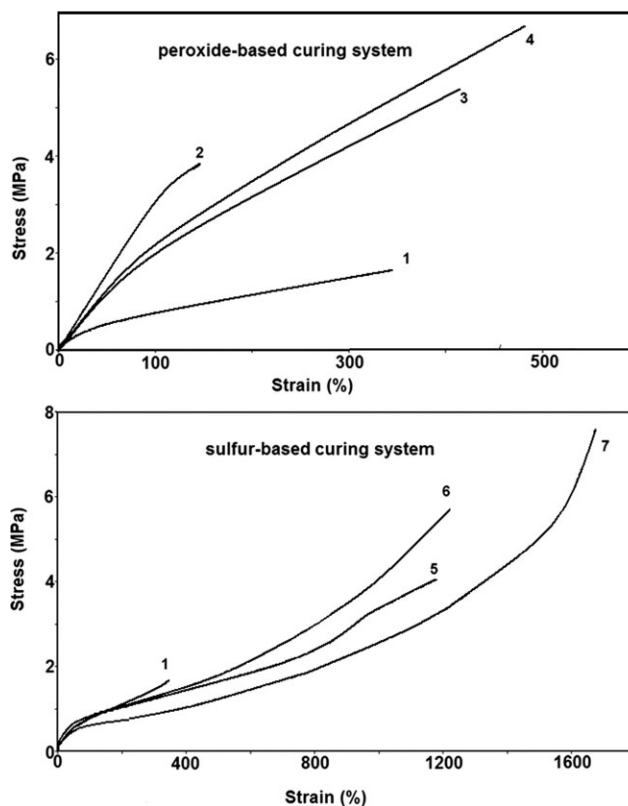

Figure 2 Stress–strain curves of ACM, NBR, and their blends as a function of the curing system (the numbers on the curves refer to the formulations listed in Table I).
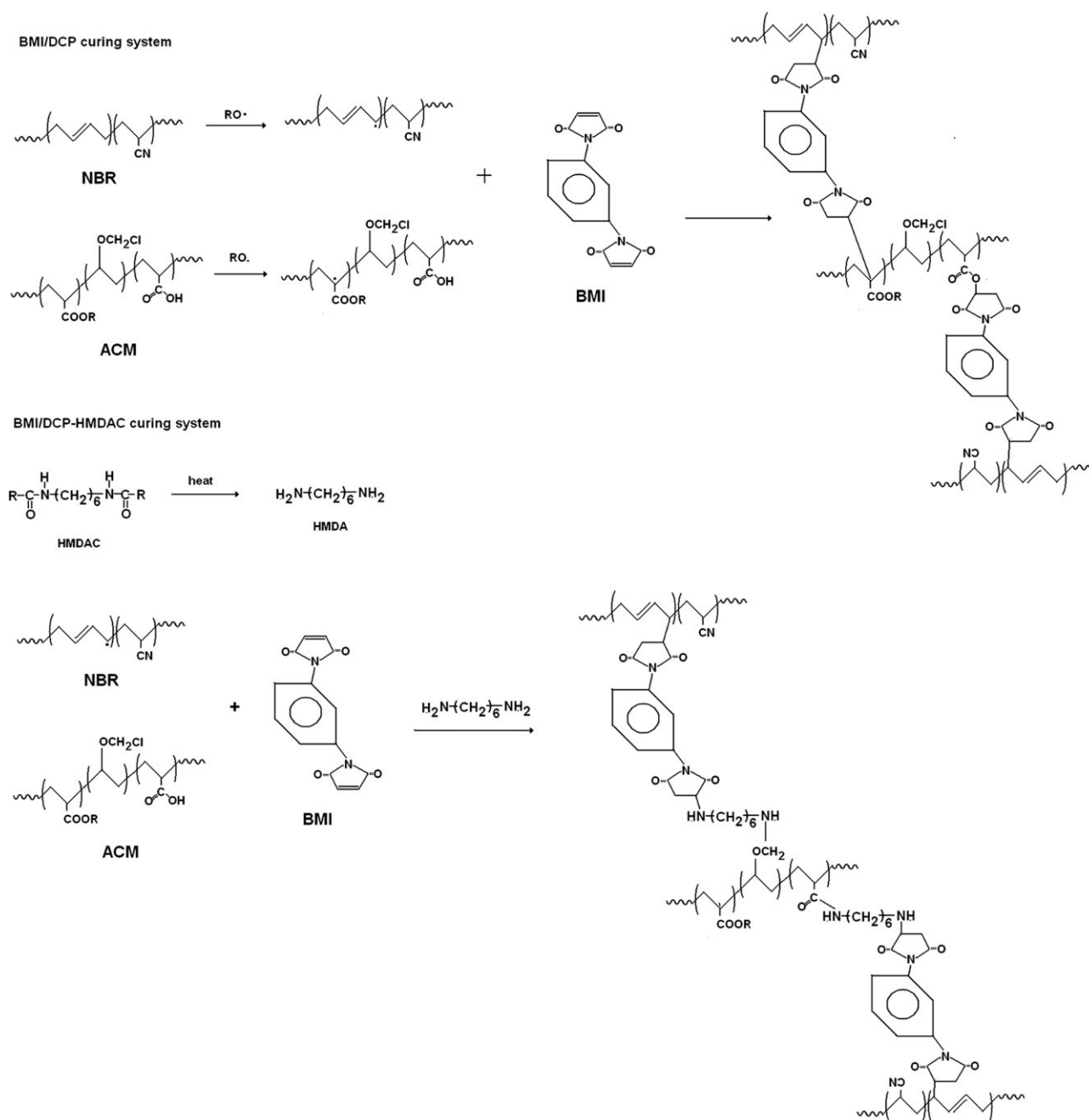
Figure 3 Probable reactions taking place during the curing processes of the ACM/NBR blends with the BMI/DCP and HMDAC curing systems.

to react with BMI via Michael addition and also with the chlorine and/or carboxyl groups of the ACM phase.

Blends cured with accelerated sulfur system presented superior ultimate properties, when compared to those of the ACM or NBR rubbers, and this phenomenon was more pronounced when sulfur was used together with the HMDAC;/sodium stearate curing system. This synergism in tensile properties may have been due to a compatibilizing effect of the curing agents. The compatibilization should have

occurred through reactions that may have taken place during the curing process, as illustrated in Figure 4. It is well known from organic chemistry that sulfur is able to react with the chlorine cure site of the ACM through nucleophilic substitution and also with the double bond of the NBR phase, which promotes the crosslinking of both phases. This nucleophilic substitution of chlorine by the sulfur is assisted by sodium stearate, as already pointed out in other studies involving ACM containing chlorine as the cure-site monomer.[10] This explains the
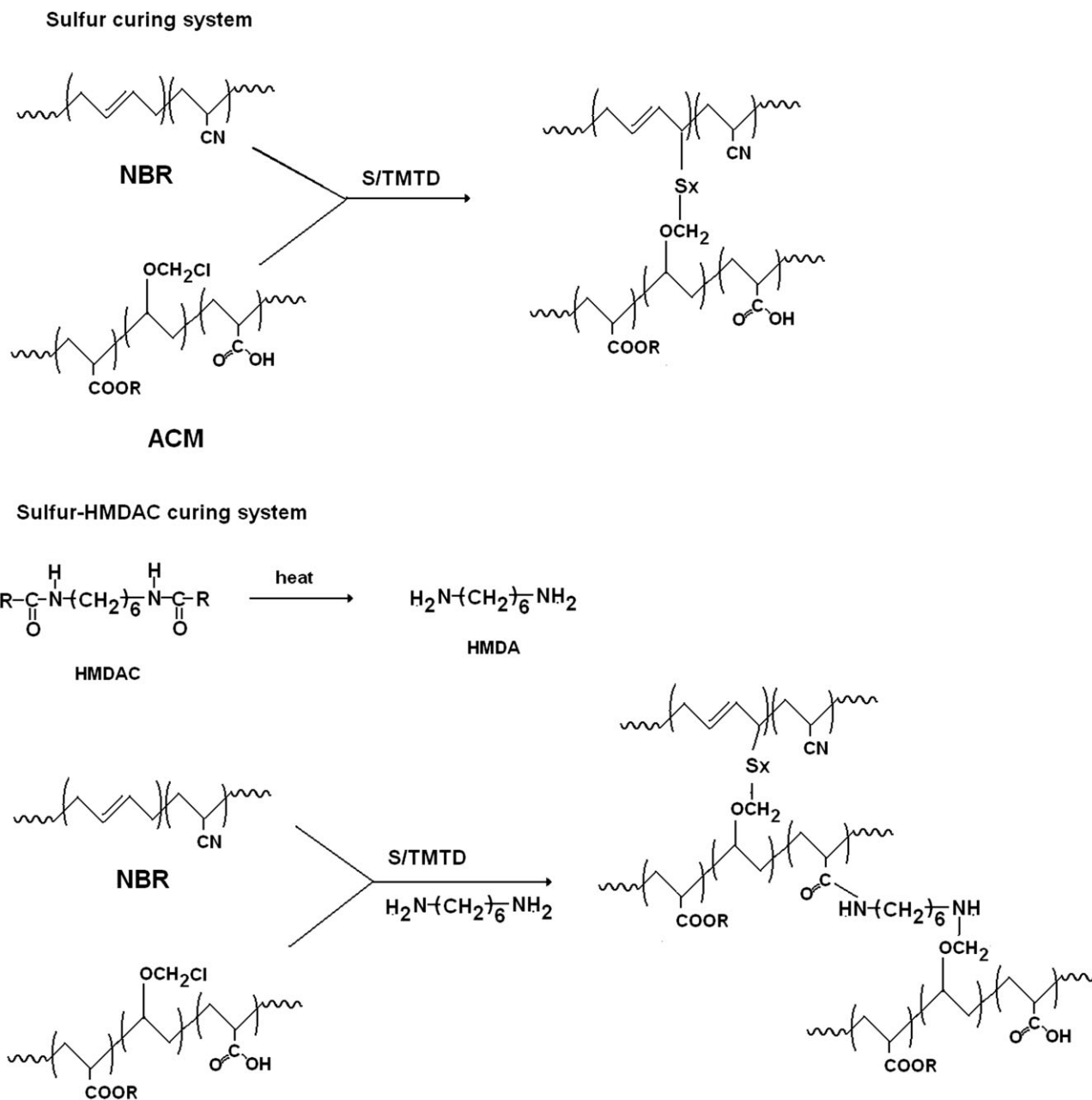
Figure 4 Probable reactions involved during the curing processes of the ACM/NBR blends with the accelerated sulfur–HMDAC curing system.

outstanding mechanical performance of the blend cured with the combined sulfur/HMDAC sodium stearate system.

The swelling data of the rubbers and their blends shown in Table I were obtained in mineral oil. ACM presented the best oil resistance, as expected. The rubbers (NBR or the corresponding blends) cured with the BMI/DCP system presented outstanding oil resistance, which indicated that peroxide is more indicated when oil resistance is required. In both curing systems, the ACM/NBR blends presented oil resistance better than pure NBR and, in the case of mix 4, comparable to the oil resistance of pure

ACM. This result is very important for application purposes because NBR is cheaper than ACM rubber.

DMA

DMA constitutes an important tool for investigating the compatibility/miscibility of polymer blends. The dependence of tan δ and the storage modulus with temperature for ACM (cured with HMDAC system) and NBR and their blends cured with peroxide-based systems is illustrated in Figure 5. T_g was taken as the temperature corresponding to the maximum of the tan δ peak. The ACM transition occurred
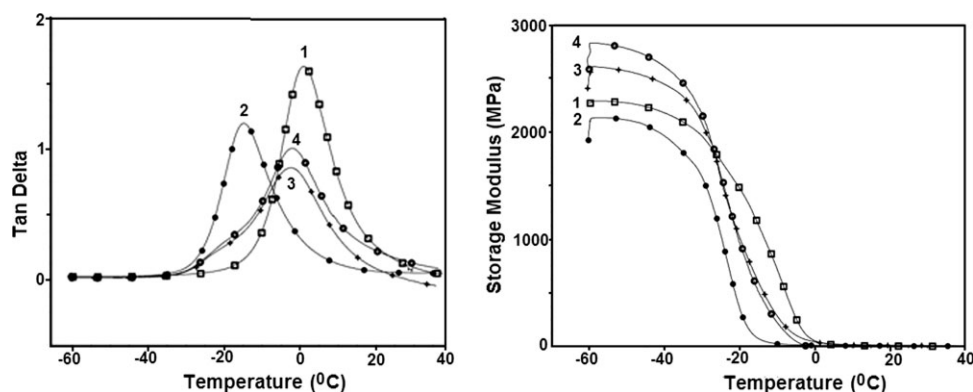
Figure 5 Dynamic mechanical properties of ACM, NBR, and their blends cured with the peroxide-based system (the numbers on the curves refer to the formulations listed in Table I).

around 1°C, and the transition of NBR appeared around −15°C. The ACM/NBR blends cured with BMI/DCP (mix 3) and BMI/DCP–HMDAC (mix 4) presented broad transitions with maxima at −2.5 and −2.2°C, respectively. The transition related to the NBR phase was significantly reduced, appearing as a shoulder at lower temperature. The absence of two well-defined transitions in the blends cured with both peroxide-based curing systems suggested that the transitions of each rubber phases overlapped as a consequence of an increase in the molecular intermixing of both components. The broadening of the transition region could be estimated by the evaluation of the width at half height of the peak. Table II presents the main dynamic mechanical parameters, including the half width values of the tan δ peaks. As we can see, there was a significant broadening of the transition peak of the blends, when compared to the pure rubber components. According to several other authors, the broadness of the transition peak is an indication of the formation of an interphase, constituted by both rubber components, as a consequence of a strong interaction between them,[22,23] which characterizes the interfacial action of these curing systems. Blends cured with a BMI/DCP system (mix 3) presented a decrease in the tan δ peak, which was also an indication of a decrease in the mobility of the macromolecular chain

segments.[24,25] This phenomenon may be explained by the rigid network formed by the peroxide system together with BMI. The DMA data were in agreement with the tensile properties and suggested that the curing systems acted as interfacial agents, promoting the vulcanization and the compatibilization between the phases, through the reactions illustrated in Figure 3. The storage modulus values of the blends were significantly higher than the pure rubbers in the region below T_g, which indicated strong interactions between the phases, which was also in agreement with the tensile data.

The dynamic mechanical properties of the blends cured with sulfur systems are illustrated in Figure 6. A significant broadening of the tan δ peak in the blend cured with the sulfur–HMDAC combined system (mix 7) and the shift of the peak related to the ACM transition toward a lower temperature also indicated the formation of an interphase as a consequence of a strong interaction between the components;[22,23] this characterized the interfacial action of these curing systems. The blend cured with the sulfur system (mix 6) presented two distinct transition peaks, which indicated that the compatibilization was less efficient, as also suggested from the tensile properties. The storage modulus of mix 7 (cured with the sulfur–HMDAC combined system) presented the highest value below T_g, which was also

TABLE II
Dynamic Mechanical Parameters of ACM, NBR, and Their Blends as a Function of the Curing System

Dynamic mechanical properties	ACM	Peroxide-based system			Sulfur-based system		
	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6	Mix 7
Storage modulus at −50°C (MPa)	2300	2100	2550	2830	2680	2530	3230
Storage modulus at 20°C (MPa)	6.6	7.9	11.6	11.8	12.9	6.6	7.3
Tan δ	1.64	1.20	0.85	1.1	1.24	0.9	1.0
T_g (°C)	0.9	−15	−2.5	−2.2	−15	0.5	−2.1
Width at half height (mm)	2.6	2.3	3.5	3.2	2.9	2.9	3.9

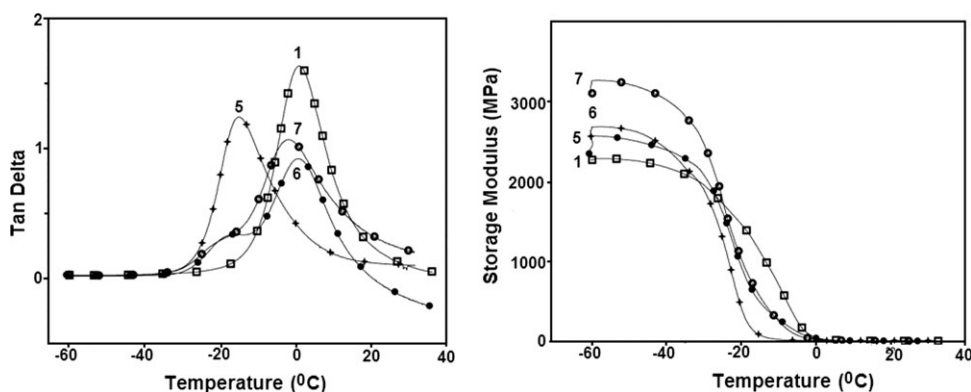The mix formulations are listed in Table I.

Figure 6 Dynamic mechanical properties of ACM, NBR, and their blends cured with the sulfur-based system (the numbers on the curves refer to the formulations listed in Table I).

an indication of an excellent interaction between the phases.

SEM microscopy

The reactive compatibilization of the ACM/NBR blends promoted by the curing agents based on the peroxide or sulfur system was confirmed by scanning electron micrographs. Figure 7 illustrates the SEM micrographs of mixes 4 and 7. The white

Figure 7 SEM micrographs of the ACM/NBR blends: (a) mix 7 and (b) mix 4 (the mix numbers refer to the formulations listed in Table I).

region corresponds to the NBR phase, which was selectively stained with osmium tetroxide. All blends presented a dual-phase morphology, which indicated that the rubbers were not miscible. However, the domain size of the rubber, specially the ACM phase (black region), was very small, which was an indication of blend compatibilization. The smaller domain phase of the ACM rubber may have been due to its lower viscosity because of the higher crosslink density of the NBR phase achieved with these curing systems. The cocontinuous morphology was more evident in blends cured with the BMI/DCP–HMDAC system [Fig. 7(b)].

CONCLUSIONS

ACM/NBR blends were investigated for the first time with different curing systems. The vulcanization of each phases was performed simultaneously with curing systems indicated for NBR rubber, or a double curing system, which involved a combination of the ACM-based curing system (HMDAC/sodium stearate) and NBR-based curing systems (peroxide or accelerated sulfur system). In all systems studied, the ultimate tensile properties of the blends were superior to those found for the individual rubbers, which indicated a compatibilization effect. This compatibilizing effect was also suggested from the dynamic mechanical properties and SEM micrographs. From the dynamic mechanical properties, it was possible to observe that blends cured with the peroxide-based curing systems displayed only one broad transition, which indicated a compatibilization effect. Similar behavior was also observed in the blend cured with accelerated sulfur in combination with HMDAC. The storage moduli of these blends also displayed higher values than the pure rubber components, which indicated strong interaction between the phases. Such interactions were also confirmed by the morphologies obtained by SEM microscopy. In all curing systems, it was not
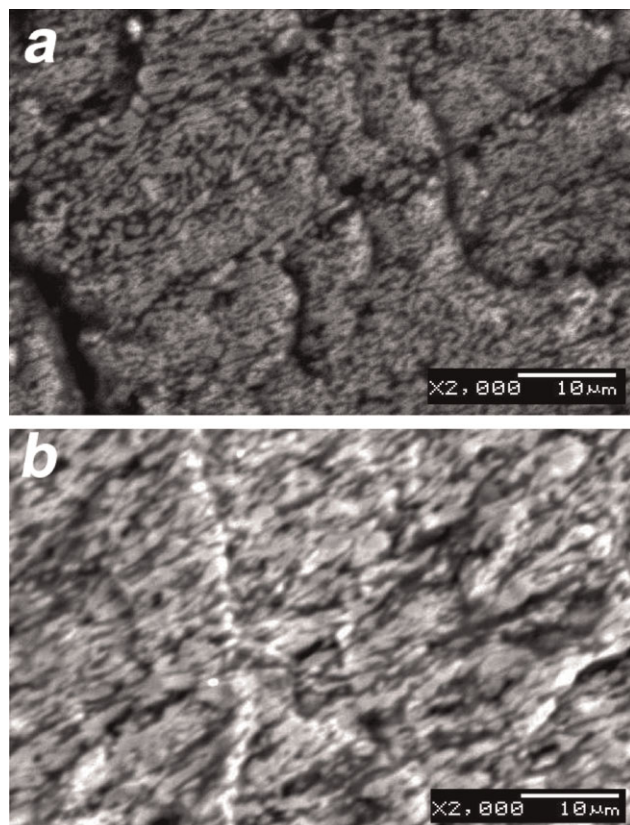
observed any insoluble material, which indicated that all rubber phases were cured. From the results obtained in this study, we conclude that BMI/DCP alone or in combination with the curing system for ACM could also act as the compatibilizing system. Similar feature were also evidenced with the sulfur–HMDAC combined system.

References

1. Nakajima, N.; DeMarco, R. D. J Elast Plast 2001, 33, 114.
2. Jha, A.; Bhowmick, A. K. Polym Degrad Stab 1998, 6, 575.
3. Ding, X.; Xu, R.; Yu, D.; Chen, H.; Fan, R. J Appl Polym Sci 2003, 90, 3503.
4. Jha, A.; Bhowmick, A. K. J Appl Polym Sci 1998, 69, 2331.
5. Jha, A.; Dutta, B.; Bhowmick, A. K. J Appl Polym Sci 1999, 74, 1490.
6. Wimolmala, E.; Wootthikanokkhan, J.; Sombatsompop, N. J Appl Polym Sci 2001, 80, 2523.
7. Wong-On, J.; Wootthikanokkhan, J. J Appl Polym Sci 2003, 88, 2657.
8. Chowdhury, S. R.; Das, C. K. J Appl Polym Sci 2000, 77, 2088.
9. Soares, B. G.; Santos, D. M.; Sirqueira, A. S.; Soares, B. G. Express Polym Lett 2008, 2, 602.
10. Vial, T. M. Rubber Chem Technol 1971, 44, 344.
11. Giannetti, E.; Mazzocchi, R.; Fiore, L.; Crespi, E. Rubber Chem Technol 1983, 56, 21.
12. Kader, M. A.; Bhowmick, A. K. J Appl Polym Sci 2003, 90, 278.
13. Kader, M. A.; Bhattacharyya, A. K.; Bhowmick, A. K. Polym Polym Compos 2001, 9, 263.
14. Kader, M. A.; Bhowmick, A. K. J Appl Polym Sci 2003, 89, 1442.
15. Kader, M. A.; Bhowmick, A. K. Rubber Chem Technol 2000, 73, 889.
16. Kader, M. A.; Bhowmick, A. K. Rubber Chem Technol 2001, 74, 662.
17. Wootthikanokkhan, J.; Tongrubbai, B. J Appl Polym Sci 2002, 86, 1532.
18. Wootthikanokkhan, J.; Tongrubbai, B. J Appl Polym Sci 2003, 88, 921.
19. Wootthikanokkhan, J.; Rattanathamwat, N. J Appl Polym Sci 2006, 102, 248.
20. Coran, A. Y. U.S. Pat. 5,053,450 (1991).
21. Halimatuddahliana, H. I.; Akil, H. M. J Elast Plast 2005, 37, 55.
22. Mathai, A. E.; Thomas, S. J Appl Polym Sci 2005, 97, 1561.
23. Rocha, T. L. A. C.; Rosca, C.; Schuster, R. H.; Jacobi, M. M. J Appl Polym Sci 2007, 104, 2377.
24. Perera, M. C. S.; Ishiaku, U. S.; Ishak, Z. A. M. Eur Polym J 2001, 37, 167.
25. Stephen, R.; Raju, K. V. S. N.; Nair, S. V.; Varguese, S.; Oommen, Z.; Thomas, S. J Appl Polym Sci 2003, 88, 2639.