The Effect of Mercapto-Modified EVA on Rheological and Dynamic Mechanical Properties of NBR/EVA Blends

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ABSTRACT: The effect of mercapto-modified ethylene vinyl acetate copolymer (EVALSH) on the rheological and dynamic mechanical properties of acrylonitrile butadiene rubber (NBR) and ethylene vinyl acetate copolymer (EVA) blends was evaluated at different blend compositions. The addition of 5 phr of EVALSH in the blends resulted in an increase of the melt viscosity and a substantial decrease of the extrudate swell ratio. These results can be attributed to the interactions occurring between the double bond of the NBR phase and the mercapto groups along the EVALSH backbone. The power–law index also presents a slight increase in the presence of EVALSH, indicating a decrease in the pseudoplastic nature of the compatibilized blends. The reactive compatibilization of NBR/EVA blends with EVALSH was also confirmed by the decrease of damping values and an increase of glass transition temperature, in dynamic mechanical analysis. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 2335–2344, 2002

Key words: NBR/EVA blends; compatibilization; rheological properties; dynamic mechanical properties

INTRODUCTION

Elastomer–thermoplastic blends have become technologically important because they combine the excellent processing characteristics of thermoplastic materials at high temperature and the physical properties of elastomers at service temperature. Several researchers have reported useful rubber–plastic blends.[1–3]

Among several elastomers, nitrile rubber (NBR) is a very important rubber component in these systems because of its excellent oil resistance, abrasion resistance, and mechanical properties. Several thermoplastics were blended with NBR, such as poly(vinyl chloride) (PVC),[4–5] polyethylene,[6–8] polypropylene (PP),[9–11] nylon,[12] and poly(ethylene-*co*-vinyl acetate) (EVA).[13–15] NBR/PVC blends are miscible depending on the blend composition and are normally employed on the development of several flame-resistant materials.[4] The other NBR-based TPE blends are incompatible and present gross phase separation and poor interfacial adhesion, giving rise to materials with poor mechanical performance, in almost all cases.

An improvement of the physicomechanical properties can be normally achieved with the addition of appropriated interfacial agents, which act at the interface, thus, promoting an effective anchorage between the phases. Block and graft copolymers were extensively employed for the compatibilization.[16] However, the reactive compatibilization by the use of functional polymers or coupling agents is technologically more interesting because it is often less expensive. In these cases, the block or graft copolymer is formed *in situ* during blend processing. For example, Coran and Patel have successfully compatibilized NBR/PP blends by using PP modified with maleic anhydride.[11] The compatibilization was accomplished by the *in situ* formation of block copolymer resulted from the reaction between the amino end groups of the NBR component and the anhydride groups of the PP component. Thomas et al. also reported a series of studies concerning the compatibilization of NBR/polyolefin blends by using the corresponding polyolefin modified with phenolic or maleic anhydride groups.[7–8,10]

The compatibilization of NBR/EVA blends was also investigated in our laboratory by using mercapto-modified EVA (EVALSH) copolymer.[17] This functionalized copolymer was also employed in other EVA-based blends such as natural rubber (NR)/EVA[18–20] and styrene-butadiene rubber (SBR)/EVA blends.[21] In both systems, it is believed that an *in situ* reaction between the mercapto groups of the functionalized EVA copolymer and the double bond of the unsaturated rubber takes place during the melt processing. In fact, a substantial amount of insoluble material was obtained in nonvulcanized NR/EVA blends[18] and SBR/EVA blends[21] containing 5 phr of EVALSH. In addition, an improvement of the ultimate tensile strength was observed, indicating a reactive compatibilization. Concerning NBR/EVA blends, the addition of a low amount of EVALSH also resulted in an improvement of the ultimate tensile strength, mainly in blend composition containing a high amount of NBR.[17]

In addition to mechanical and morphological properties, it is well established that the compatibilization also affects the flow behavior of polymer blends.[10,22–26] Normally, the viscosity of the system increases with the reactive compatibilization as a consequence of chemical reactions occurring between the components of the blends. For example, the use of styrene-(ethylene-*co*-butylene)-styrene block copolymer grafted with maleic anhydride (SEBS-MA) in polypropylene/polyamide blends resulted in an increase in the viscosity of the blends as a consequence of the chemical reactions taking place between amine and anhydride groups.[22] Also, the compatibilization of NBR/PP blends by phenolic-modified PP increased the viscosity of the system.[10]

In this article, we examine the influence of the EVALSH on the flow characteristics and dynamic mechanical properties of nonvulcanized NBR/EVA blends.

EXPERIMENTAL

Materials

Nitrile rubber NBR615 (33 wt % of acrylonitrile; Mooney viscosity = 32) was kindly supplied by Nitriflex S.A., Rio de Janeiro, Brazil. EVA copolymer [18 wt % vinyl acetate; melt flow index (MFI) = 2.3 g/10 min at 120°C] was kindly supplied by Petroquimica Triunfo S.A., Triunfo, Brazil. Mercapto-modified EVA copolymer (EVALSH) was obtained in our laboratory by esterifying the hydrolyzed EVA copolymer with mercaptoacetic acid, according to literature.[27] The amount of mercapto groups in the functionalized copolymer corresponded to 62 mmol %, as determined by FTIR and TGA analysis.

Blend Preparation

The blends were prepared in a Berstoff two-roll mill at 110°C and 30 rpm. NBR was first masticated for 2 min and then compounded with EVALSH and EVA in this order. The total mixing time was 6 min in all blends.

Rheological Measurements

Rheological measurements were carried out in an Instron capillary rheometer (model 4204) at different plunger speeds. The plunger speed varied from 1.0 to 12 mm min^{-1}. The capillary used has an l/d ratio of 100. The samples were preheated for 3 min and extruded through the capillary at preselected speeds of the crosshead. The measurements were done at 120 and 150°C. The true shear rate was calculated from the apparent shear rate by using the Weissenberg–Rabinowish correction, assuming that the blend behaves as a power–law fluid. The power–law index was determined by regression analysis according to
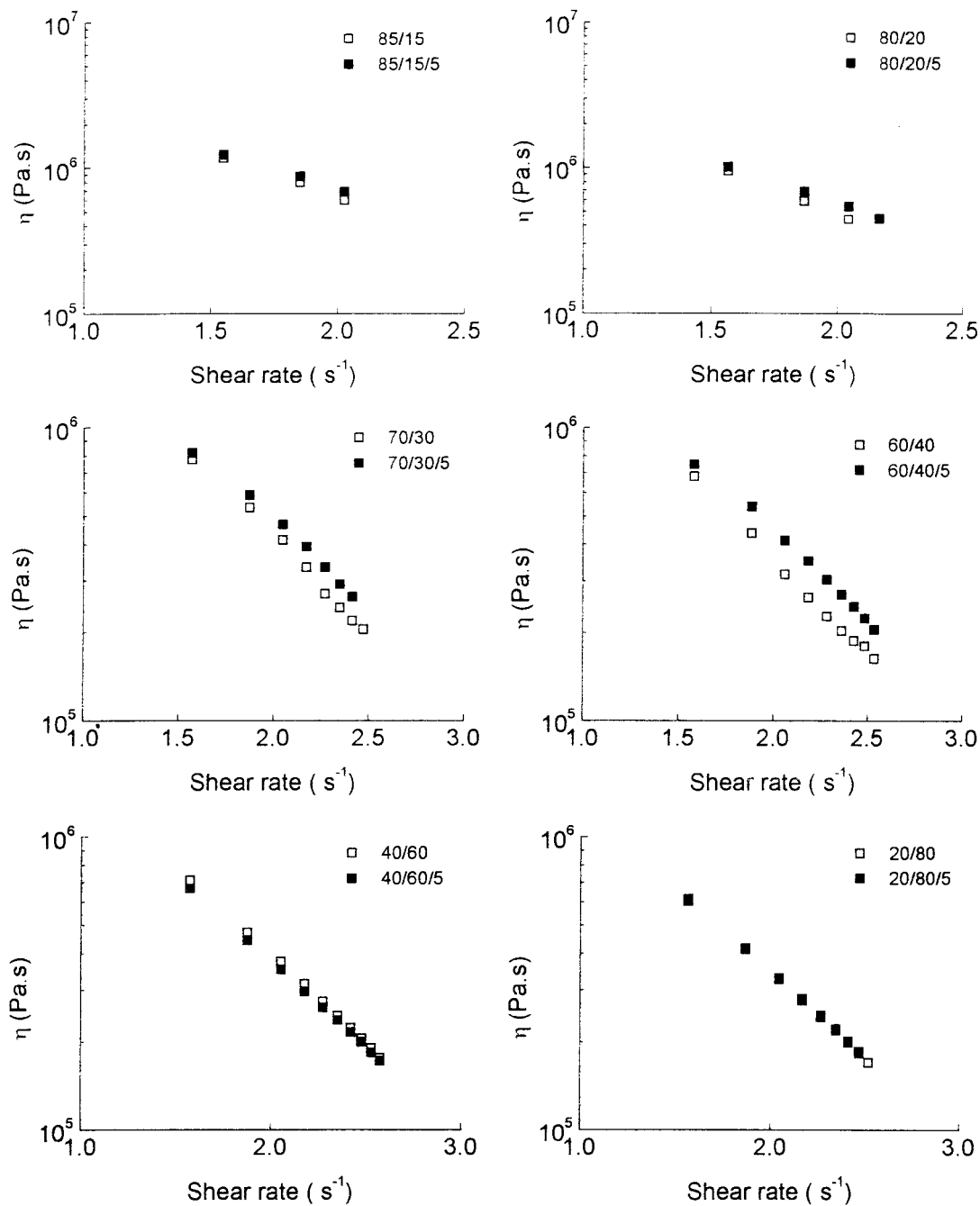
Figure 1 Variation of the melt viscosity with the shear rate of NBR/EVA blends as a function of the blend composition; ($\square$) without EVALSH; ($\blacksquare$) with 5 phr of EVALSH. (Experiments performed at 120°C.)

$$n' = \frac{d(\log \tau)}{d(\log \dot{\gamma})}$$

where τ is the shear stress and $\dot{\gamma}$ is the apparent shear rate. The shear viscosity, η, was calculated

from the ratio between shear stress and the true shear rate, obtained by the Weissenberg–Rabinowish correction.

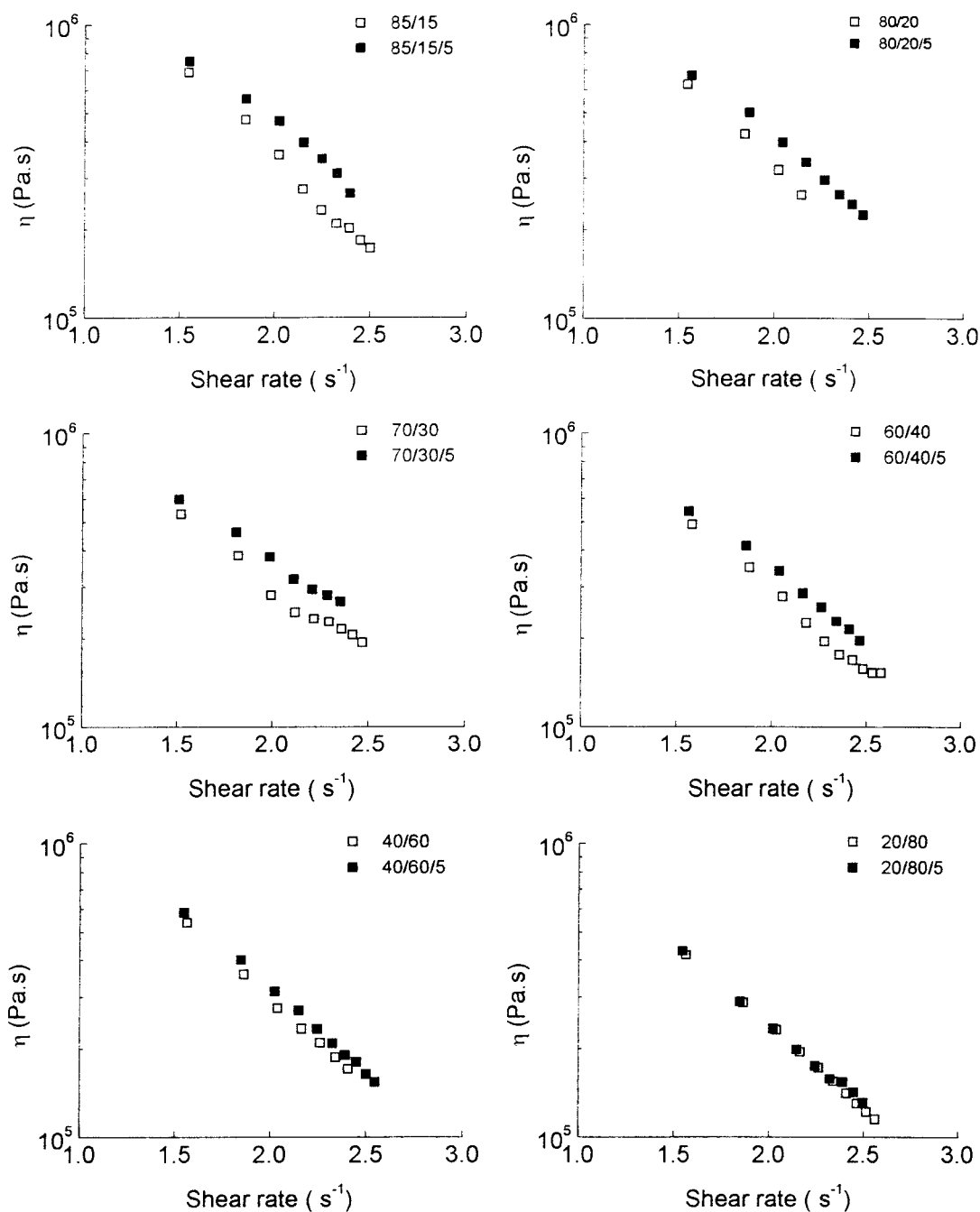For extrudate swell, the extrudates were carefully collected as they emerged out from the cap-

Figure 2 Variation of the melt viscosity with the shear rate of NBR/EVA blends as a function of the blend composition; (□) without EVALSH; (■) with 5 phr of EVALSH. (Experiments performed at 150°C.)

illary die, taking care to avoid any deformation. The diameter of the extrudate was measured after 48 h of extrusion. The die swell was calculated from d_e/d_c ratio, where d_e is the diameter of the extrudate and d_c is the diameter of the capillary.

Dynamic Mechanical Analysis

Dynamic mechanical analyses of the compatibilized, noncompatibilized, and individual polymers were performed on a Rheometric Scientific MKIII

DMTA. Samples of $50 \times 5 \times 0.5$ mm^3 were used for this study. The experiments were carried out at a frequency of 1 Hz over a temperature range of -50–$30°C$ in a bending mode. The tan δ and storage modulus were measured for each sample in this temperature range.

RESULTS AND DISCUSSION

Rheological Properties

Figures 1 and 2 compare the effect of the EVALSH on melt viscosity of NBR/EVA blends in experiments performed at 120 and 150°C, respectively. The viscosity of all blends decreased with the increase of the shear rate, indicating pseudoplastic behavior. The addition of 5 phr of EVALSH resulted in an increase of the melt viscosity, mainly in blends containing higher amounts of NBR. Such increase in viscosity on compatibilization of immiscible polymer blends was reported by several researchers.[10,24–26] This behavior is better illustrated in Figures 3 and 4, where the viscosity of the blends at different apparent shear rates is plotted as a function of the weight percentage of EVA.

During the mixing of EVALSH with NBR/EVA blends, the mercapto groups in the EVALSH are expected to react with the double bond of the NBR phase, as proposed in our previous article.[17] These reactions occurring inside the NBR phase should contribute to an increase of the viscosity of the blend. The effect is not so high, probably because of the low extent of grafting or crosslinking reactions between the EVALSH and NBR components as a consequence of the low amount of the mercapto groups along the EVASH backbone. The extension of the crosslink reaction was analyzed by submitting the NBR/EVA blends to a extraction with hot toluene for 48 h. Pure NBR/EVA blends without EVALSH were completely solubilized in hot toluene; that is, no insoluble material was present in these blends. Concerning blends containing 5 phr of EVALSH, a small amount of insoluble material was obtained after the extraction time, confirming the reaction between NBR and EVALSH. Such an amount was, however, small (only about 5–8 wt % of the whole sample) because of the low amount of mercapto groups in the EVALSH, as mentioned before. As reported in our previous studies,[17] the addition of EVALSH in nonvulcanized NBR/EVA blends improved the
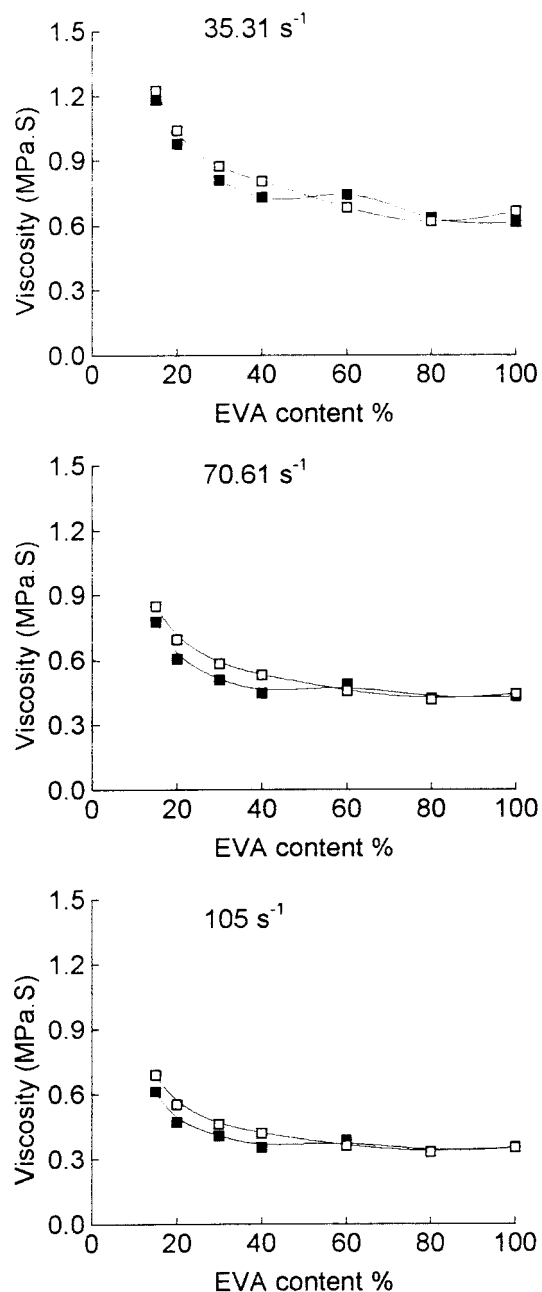

Figure 3 Variation of the melt viscosity with the composition of NBR/EVA blends at different shear rates; (■) without EVALSH; (□) with 5 phr of EVALSH. (Experiments performed at 120°C.)

ultimate tensile strength in blends containing higher amounts of NBR. From the mechanical and rheological results, one can confirm the efficiency of the reactive compatibilization, mainly in NBR-richer blends.

The effect of EVALSH on the power–law index of NBR/EVA blends is shown in Figure 5 for ex-
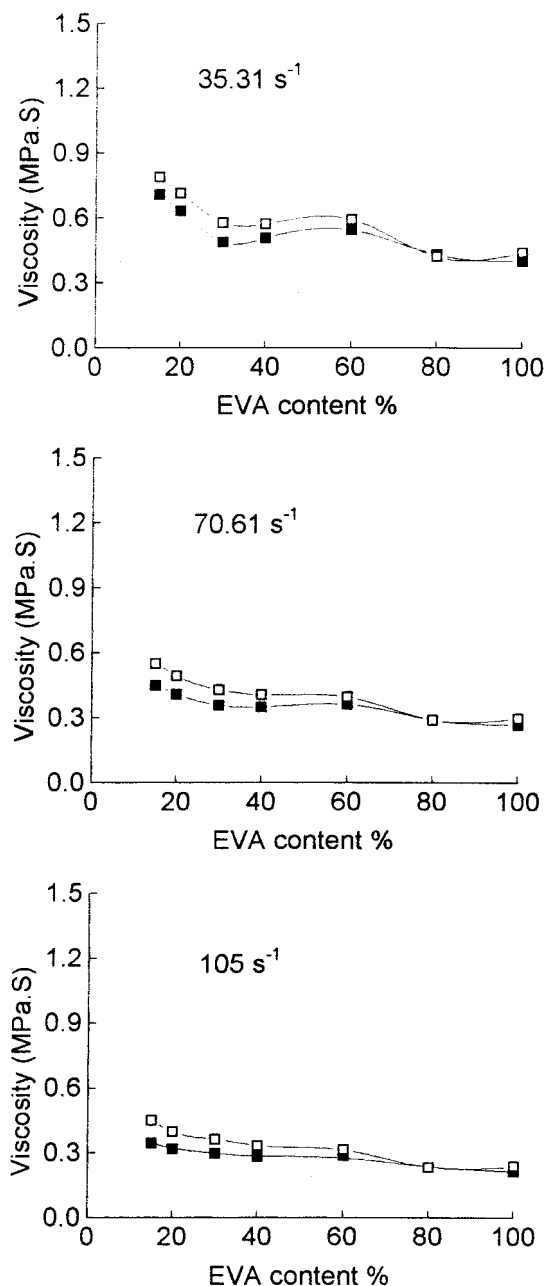
Figure 4 Variation of the melt viscosity with the composition of NBR/EVA blends at different shear rates; (■) without EVALSH; (□) with 5 phr of EVALSH. (Experiments performed at 150°C.)

periments performed at 120°C. The values of n' less than unity for NBR/EVA blends indicate pseudoplastic behavior, as normally observed in several polymer systems. It is interesting to observe that the presence of EVALSH resulted in a slight increase in the n' values in almost all

blends, suggesting an increase of the Newtonian behavior.

The presence of EVALSH in NBR/EVA blends exerts a strong influence on the melt elasticity of the blends. When a molten polymer flows through the capillary, the polymer chains undergo orientation due to shear. When the melt emerges from the die, the oriented macromolecules have a tendency to recoil, resulting in a lateral expansion. This phenomenon is known as die swell. The effect of blend composition and compatibilization on the extrudate swell at different apparent shear rate is illustrated in Figure 6 for experiments performed at 120°C. When EVA is the matrix, the extrudate swell ratio decreases with the addition of NBR in the blend until a composition corresponding to 40 wt % of NBR. Thomas et al. also reported similar behavior for PP/NBR blends, which was attributed to the elasticity of the rubber phase.[10] The presence of EVALSH does not exert significant influence on the extrudate swell ratio in this composition range probably because NBR is the dispersed phase and the interactions between EVALSH and this phase do not contribute for the changes in this property.

For blends containing a higher concentration of the NBR component, the extrudate swell ratio increases substantially as the concentration of the rubber phase increases. This phenomenon is more pronounced at higher shear rate because the residence time of the blend in the capillary decreases and more elastic energy is stored in the
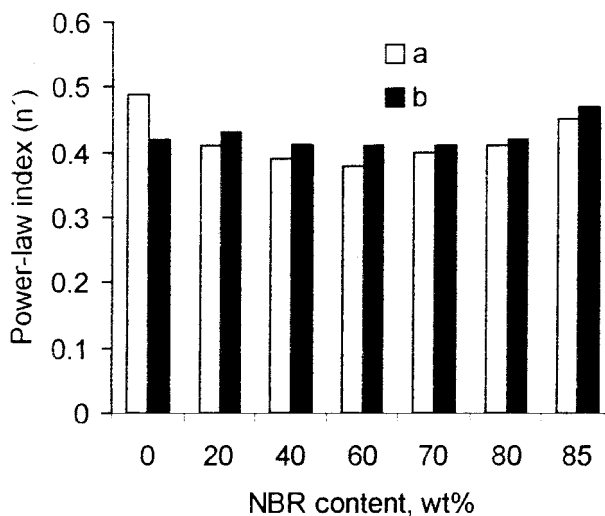

Figure 5 Effect of blend ratio and compatibilization on the power–law index (n'); (a) without EVALSH; (b) with 5 phr of EVALSH.
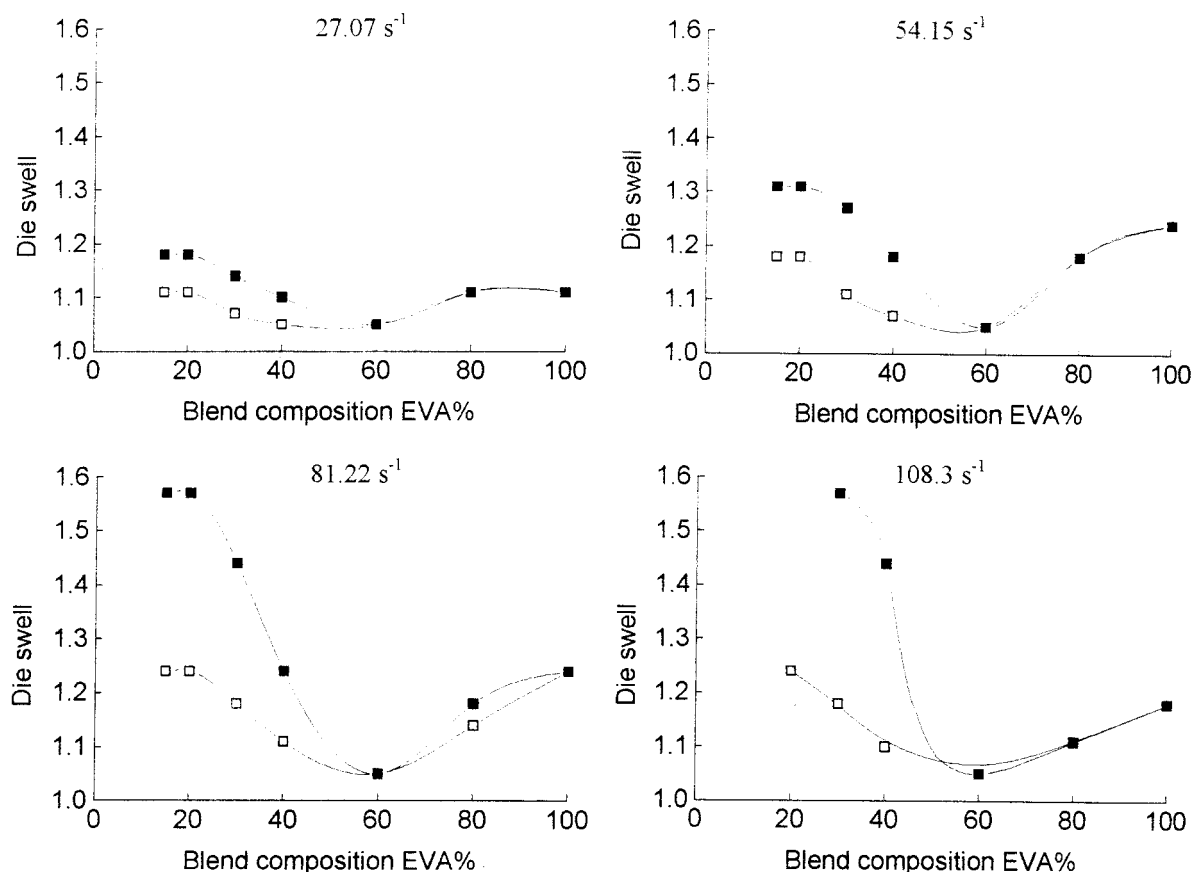
Figure 6 Variation of the extrudate swell ratio with the composition of NBR/EVA blends at different shear rates; (■) without EVALSH; (□) with 5 phr of EVALSH. (Experiments performed at 120°C.)

polymer. Similar behavior was also observed by Koshy et al. in nonvulcanized NR/EVA blends.[28] The presence of as low as 5 phr of EVALSH in the blends resulted in a substantial decrease on the extrudate swell ratio. In addition, the effect of the shear rate on the die swell is less pronounced in compatibilized blends. The results of the present study reveal that the interactions between the NBR phase and the EVALSH decrease the relaxation process of the blend and increase the elastic recovery of the NBR matrix.

Dynamic Mechanical Properties

Dynamic mechanical properties of polymers are highly dependent on the material structure. The dependence of tan δ of the pure components and the noncompatibilized blends on temperature is shown in Figure 7. NBR displays a sharp loss tangent peak at around −16°C [Fig. 7(a)],

which corresponds to the glass transition, whereas EVA displays two distinct peaks at around −23 and 20°C [Fig. 7(g)]. These EVA transitions are not clear in Figure 7 because the corresponding damping values are very low when compared to the damping of the rubber component. These results are also presented in Table I. The blends display a single transition, which is mainly related to the NBR phase. Its displacement toward lower temperature indicates an increase of the chain mobility of NBR caused by the presence of the EVA component by which the chain mobility of NBR is increased. The damping decreases as the EVA content in the blend increases, as expected, because this property is related to the volume fraction of the NBR in the blend. These results agree with those found by Thomas et al. in their studies concerning NBR/EVA blends.[13,15]
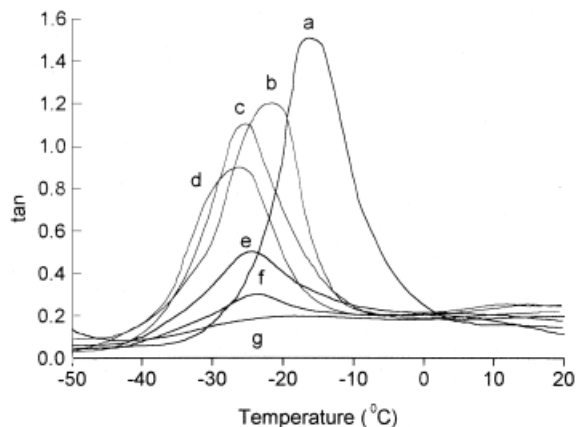
Figure 7 Variation of tan δ of noncompatibilized NBR/EVA blends with temperature; (a) pure NBR; (g) pure EVA; and their blends containing (b) 85%; (c) 80%; (d) 70%; (e) 60%; and (f) 40% NBR.

The effect of the EVALSH on loss tangent (tan δ) values of NBR/EVA blends as a function of temperature is illustrated in Figure 8. In all blend compositions studied, the addition of 5 phr of EVALSH resulted in a decrease of damping and a small displacement of the glass transition temperature toward higher values. These results are also summarized in Table I. The highest effect of the EVALSH on damping was observed for blends containing a greater amount of NBR. An increase of glass transition temperature associated with a decrease in damping indicate a decrease of the molecular mobility of the NBR phase, as a conse-

quence of the interactions between the rubber phase and the EVALSH. These results are in agreement with the rheological data.

Concerning the storage modulus E', the addition of EVALSH did not affect this property at lower temperatures (i.e., below the glass transition temperature). However, at higher temperatures [i.e., in the rubbery region (0 and 20°C)], the modulus slightly increases upon the addition of 5 phr of EVALSH (see Table I). These behaviors also confirm an increase in the phase interactions with the presence of the functionalized copolymer, EVALSH.

CONCLUSION

The addition of mercapto-modified EVA (EVALSH) in uncrosslinked NBR/EVA blends exerts a substantial influence on the rheological and dynamic mechanical properties. From rheological measurements, one can conclude that the presence of EVALSH increases slightly the viscosity of the blends but decreases significantly the extrudate swell ratio, indicating better dimensional stability of the extrudate. In addition, the flow behavior index of the blends increases with the compatibilization, indicating a decrease in the pseudoplastic nature.

Concerning the dynamic mechanical data, the addition of EVALSH also increases the glass transition temperature of the NBR phase and de-

Table I   Dynamic Mechanical Properties of NBR/EVA Blends as a Function of Blend Ratio and Compatibilization

| Blend Composition | | Log E' (Pa) | | | | | | | | T_g (°C) | | Maximum tan δ | |
| | | −40°C | | −20°C | | 0°C | | 10°C | | | | | |
NBR	EVA	a	b	a	b	a	b	a	b	a	b	a	b
0	100	9.09	—	8.68	—	8.22	—	7.78	—	−18.7	—	0.20	—
20	80	9.17	9.17	8.52	8.63	7.85	7.88	7.63	7.65	−21.8	−18.3	0.22	0.20
40	60	9.17	9.19	8.35	8.63	7.67	7.77	7.49	7.56	−23.8	−23.9	0.32	0.30
60	40	9.13	9.20	8.36	8.58	7.46	7.66	7.23	7.43	−23.9	−18.9	0.50	0.40
70	30	9.15	9.21	7.77	7.85	6.90	7.48	6.83	7.35	−24.4	−23.0	0.9	0.7
80	20	9.23	9.26	8.14	7.90	7.06	7.21	6.98	7.09	−24.7	−23.5	1.1	1.0
85	15	8.86	9.12	7.68	7.74	7.21	7.40	7.04	7.23	−21.2	−19.9	1.2	1.1
100	0	9.12	9.10	7.44	7.68	6.30	6.64	6.27	6.54	−16.0	−14.3	1.5	1.4

[a] Blends without EVALSH.
[b] Blends with 5 phr of EVALSH.
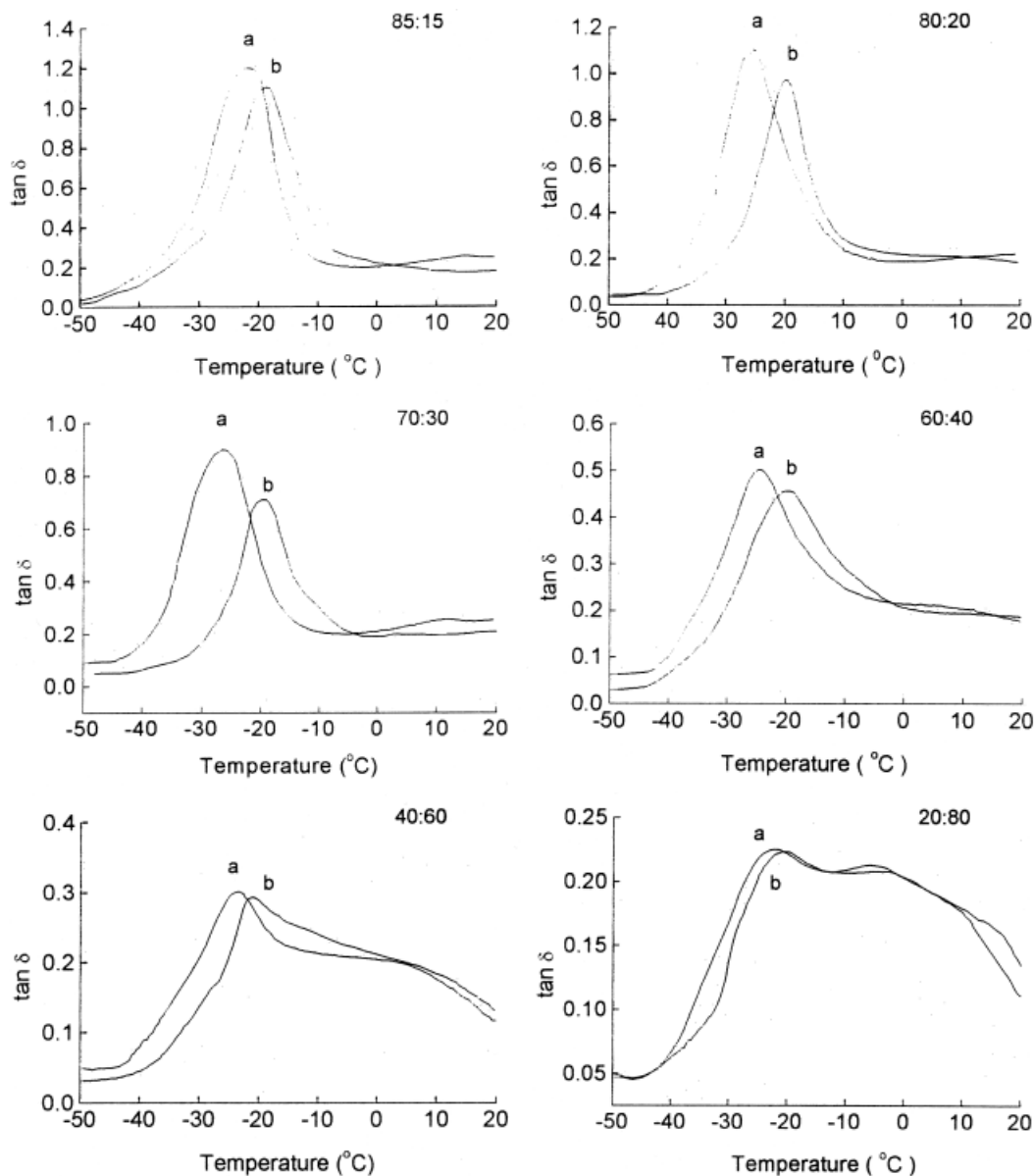
Figure 8 The variation of tan δ of compatibilized and noncompatibilized blends as a function of temperature; (a) without EVALSH and (b) with 5 phr of EVALSH.

creases the damping values. During mixing, the mercapto groups along the EVALSH backbone are able to react with the double bond of the elastomer phase, thus forming interactions between the phases. These interactions are responsible for the better performance in ultimate tensile strength, reported in a previous article, and also for the peculiar behaviors found in dynamic mechanical and rheological properties of the compatibilized blends. It is important to emphasize that the influence of EVALSH on the melt viscos-

ity is not so pronounced because the extent of the interaction between the NBR phase and the functionalized copolymer is low because of the low amount of the mercapto group along the EVALSH backbone.

REFERENCES

1. Dellens, G. in Thermoplastic Elastomers—A Comprehensive Review; Legge, N. R.; Holden, G.; Schroeder, H. T., Eds.; Hanser Publishers: New York, 1987; Chapter 7.

2. Legge, N. R. Rubber Chem Technol 1989, 62, 529.

3. Kresge, E. N. Rubber Chem Technol 1991, 64, 469.

4. Hay, D.; Pfisterer, H. A.; Storey E. B. Rubber Age 1955, 94, 77.

5. O'Connor, G. E. Thermoplastic Elastomers, Future Market Opportunities; in Handbook of Thermoplastic Elastomers, 2nd ed.; Walker, B. M.; Rader, C. P., Eds.; Van Nostrand Reinhold: New York, 1988; Chapter 15, p 399.

6. George, J.; Varughese, K. T.; Thomas, S. Polymer 2000, 41, 1507.

7. George, J.; Joseph, R.; Thomas, S.; Varughese, K. T. J Appl Polym Sci 1995, 57, 449.

8. George, J.; Ramamurthy, K.; Varughese, K. T.; Thomas, S. J Polym Sci, Part B: Polym Phys 2000, 38, 1104.

9. George, S.; Varughese, K. T.; Thomas, S. Polymer 2000, 41, 579.

10. George, S.; Ramamurthy, K.; Anand, J. S.; Groeninckx, G.; Varughese, K. T.; Thomas, S. Polymer 1999, 40, 4325.

11. Coran, A. Y.; Patel, R. Rubber Chem Technol 1983, 56, 1045.

12. Kumar, C. R.; George, K. E.; Thomas, S. J Appl Polym Sci, 1996, 61, 2383.

13. Varghese, H.; Bhagawan, S. S.; Rao, S. S.; Thomas, S. Eur Polym J 1995, 31, 957.

14. Varghese, H.; Bhagawan, S. S.; Thomas, S. J Polym Sci, Part B: Polym Phys 1999, 37, 1815.

15. Bandyopadhyay, G. G.; Bhagawan, S. S.; Ninan, K. N.; Thomas, S. Rubber Chem Technol. 1997, 70, 650.

16. Koning, C.; Duin, V. M.; Pagnoulle, C. Jerome, R. Prog Polym Sci 1998, 23, 757.

17. Jansen, P.; Soares, B. G. J Appl Polym Sci 2001, 79, 193.

18. Jansen, P.; Amorim, M.; Gomes, A. S.; Soares, B. G. J Appl Polym Sci 1995, 58,101.

19. Soares, B. G.; Jansen, P.; Gomes, A. S. J Appl Polym Sci 1996, 61, 591.

20. Tavares, M. I. B.; Jansen, P.; Soares, B. G. Polym Bull 1996, 37, 215.

21. Soares, B. G.; Alves, F. F.; Oliveira, M. G.; Moreira, A. C. F.; Garcia, F. G.; Lopes. M. F. S. Eur Polym J 2001, 37, 1577.

22. Miettinen, R. M. H.; Seppala, J. V.; Ikkala, O. T.; Reima, I. T. Polym Eng Sci 1994, 34, 395.

23. Valenza, A.; Acierno, D. Eur Polym J 1994, 30, 1121.

24. Oommen, Z.; Premalatha, C. K.; Kuriakose, B.; Thomas, S. Polymer 1997, 38, 5611.

25. Kim, J. K.; Lee, H. Polymer 1996, 37, 305.

26. Ju, M. Y.; Chang, F. C. Polymer 2000, 41, 1719.

27. Dutra, R. C. L.; Lourenço, V. L.; Diniz, M. F.; Azevedo, M. F. P.; Barbosa, R. V.; Soares, B. G. Polym Bull 1996, 36, 593.

28. Koshy, A. T.; Kuriakose, B.; Thomas, S.; Premalatha, C. K.; Varghese, S. J Appl Polym Sci 1993, 49, 901.