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Rheometrical behavior and equilibrium swelling in NR/BR/CEL II composites

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Summary

Natural rubber/butadiene rubber/cellulose II blends (NR/BR/CEL II) have been obtained by coprecipitation of the rubber latex-cellulose xanthate mixtures through acidulation. The elastomer ratio NR/BR has been varied from 100/0 to 25/75 and the cellulose content from 0 to 25 phr. The cure behavior of the compositions has been investigated by a Monsanto Oscillating Disk Rheometer. The results are a function of cellulose filler, NR, and BR contents. Some compositions were also analysed by equilibrium swelling in order to investigate polymer-filler interaction. The results show that composites with higher BR contents exhibit higher elastomer-filler attachment.

Introduction

The use of elastomeric blends in the rubber industry is important because it is possible to obtain desired properties by using two or more elastomers in the composition. Classical examples are blends of natural rubber/butadiene rubber (NR/BR) with carbon black as reinforcing filler, extensively used in tire manufacture (1-4).

Rubber products cannot be made without vulcanization. Such systems usually contain sulphur and accelerator, and the use of zinc oxide and stearic acid as co-activator are also common (5). When sulphur is the vulcanizing agent, a crosslink may consist of one or more sulphur atoms. The process is usually carried out by heating the rubber together with vulcanizing agents in a mold (6). There are a wide range of accelerator systems available for elastomers, providing a range of cure rate, scorch time and final properties (7).

One of the most important facets of industrial use of elastomers is property enhancement and control by the use of fillers. With good reinforcing fillers the swelling of the polymeric matrix is restricted relative to the gum (8).

The extent of cure is measured as a function of cure time by using a curemeter. The crosslinks that reduce swelling in the filled vulcanizate come from a combination of several mechanisms and have been the subject of many studies (8).

In order to develop non black elastomeric compositions with enhanced mechanical properties, short fibers of cellulose have been used as filler (9-12). The purpose of this work is to investigate the rheometrical behavior of natural rubber/butadiene rubber/cellulose II (NR/BR/CEL II) compositions and to evaluate by equilibrium swelling the interaction between cellulose II and the elastomeric matrix in NR/BR blends of different ratios.

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Experimental

Blend Preparation

NR (Lemgruber S. A.) and BR (Nitriflex S. A. Indústria e Comércio) elastomers in latex form were mixed and the incorporation of cellulose II was carried out through coprecipitation of NR/BR - cellulose xanthate (Rhodia Indústrias Químicas e Têxteis) mixtures by gradual addition of $H_2SO_4/ZnSO_4$ 1:1 molar solution, with constant stirring and pH control. The cellulose II content in these blends was increased up to 25 phr and the NR/BR elastomer ratios were 100/0, 75/25, 50/50 and 25/75.

The compounds for vulcanization were processed in a 10 cm X 22,5 cm roll mill usually by ASTM D 3182. The formulation used was (in phr): 100 rubber(s); 5 zinc oxide; 2 stearic acid; 1 phenyl-β-naphthylamine; 3 sulphur; 0.7 N-cyclohexyl-2-benzothiazol sulfenamide (1,2).

Cure Parameters and Vulcanization

Cure parameters were determined at 150° C and 3° arc, using a Monsanto Oscillating Disk Rheometer (Model TM-100) according to ASTM D 2084, and are shown in Table 1. Vulcanization was carried out at 150° C, during cure times established previously in the rheometer, in an electrically heated hydraulic press.

From the resulting time-torque curve, one can obtain: (5)

- Minimum torque, representing the effective viscosity of the unvulcanized mix, M_L
- Scorch time, being the time to a fixed small rise above the minimum, ts_2
- Equilibrium torque, representing the elastic modulus of the fully vulcanized rubbers, M_H
- Time to an arbitrary "fractional modulus", commonly around 90% of the equilibrium modulus, and representing approximately a technical cure, $tc_{(90)}$
- Cure rate index (CRI), a parameter proportional to the average slope of the cure rate in the steep region ($100 / (tc_{(90)} - ts_2)$).

Equilibrium Swelling

Equilibrium swelling was carried out at room temperature in heptane. Small specimens (2 cm x 2 cm x 0.2 cm) dried to constant weight were allowed to swell in the dark in sealed bottles until no further swelling occured. The swollen samples were weighed after removal of excess swelling agent and dried to constant weight. The volume of imbibed heptane was calculated from the difference between the weights of the swollen and deswollen samples. The volume of the rubber network in the swollen rubber gel was measured by displacement in ethanol. The Vr (volume fraction of rubber in the swollen vulcanizate) values thus obtained can be used as indices of the crosslink densities in vulcanizates.

Polymer-filler interaction

Polymer-filler interaction was evaluated using the Kraus (equation (I)) and Cunneen and Russel (equation (II)) equations (13-19).

Equation (I): $\mathbf{Vro / Vrf = 1 - m\phi\,(1 - \phi\,)}$, where $\mathbf{m} = 3\,C\,(1 - Vro^{1/3}) + Vro - 1$,

where **Vro** represents the volume fraction of rubber in the gum vulcanizate; **Vrf** is the volume fraction of rubber in the filled vulcanizate (assuming that filler particles do not swell); ϕ is the volume fraction of filler in the vulcanizate and C is a constant characteristic for a particular filler, but independent of the polymer, the solvent, or the degree of vulcanization; and **m** is a parameter calculated from the slope of the curve.

$$\text{Equation (II): } \mathbf{Vro / Vrf = a\, e^{-z} + b},$$

where **Vro** and **Vrf** are the volume fraction of rubber in gum and in filled vulcanizates, respectively, swollen in a solvent, **z** is the weight fraction of filler in the vulcanizate, and **a** and **b** are constants characteristic for the system.

Results and Discussion

Figures 1 to 5 show typical rheographs for NR/BR blends at different loadings of cellulose II filler. The cure parameters are shown in Table 1.

Analysing the results for the elastomeric compositions in function of filler content (Figures 1 to 4), some conclusions can be drawn. It is generally observed that for all the compositions under analysis, the gradual addition of cellulose II increases the minimum torque, related to viscosity of the unvulcanized blends and the maximum torque, characteristic of the resistance values at small strain and in accordance with the cure state of the material.

The scorch time for compositions filled with cellulose II decreases considerably as compared to that of pure gum; this may demonstrate the influence of the filler on crosslinking. The optimum cure time also decreases with the incorporation of cellulose II in these systems.

Table 1 - Rheometric Parameters and Vr Values of NR/BR/CEL II Composites

Composition NR/BR/CEL II	M_L (dN.m)	M_H (dN.m)	ts_2 (min)	$tc_{(90)}$ (min)	CRI (min^{-1})	Vr
100/0/0	7.8	55.0	9.75	15.00	19.1	0.277
100/0/5	8.5	61.0	7.75	14.75	14.3	0.293
100/0/10	9.3	63.1	4.50	12.50	12.5	0.307
100/0/15	10.3	68.7	5.3	12.50	13.9	-
100/0/20	13.3	73.7	5.0	12.00	14.3	-
100/0/25	13.4	74.5	5.25	14.50	10.8	0.327
75/25/0	8.2	60.9	10.75	16.00	19.1	0.297
75/25/5	11.6	64.2	5.00	13.50	11.8	0.318
75/25/10	12.8	71.5	6.50	14.50	12.5	0.335
75/25/15	13.2	71.6	4.50	13.00	11.8	-
75/25/20	13.4	76.4	5.50	15.00	10.5	-
75/25/25	13.4	83.1	5.50	15.00	10.5	0.358
50/50/0	8.7	67.6	12.00	18.00	16.7	0.311
50/50/5	15.6	72.4	5.25	14.00	11.4	0.338
50/50/10	16.7	76.5	5.00	15.25	9.8	0.354
50/50/25	18.8	87.6	5.75	18.00	8.2	0.381
25/75/0	9.2	74.6	14.50	20.50	16.7	0.334
25/75/5	24.5	85.5	4.75	14.50	10.3	0.377
25/75/10	26.7	94.2	4.50	16.25	8.5	0.392
25/75/15	29.6	94.6	4.75	19.00	7.0	-
25/75/20	32.4	103.1	5.25	19.25	7.1	-
25/75/25	33.4	112.3	5.75	17.50	8.5	0.429

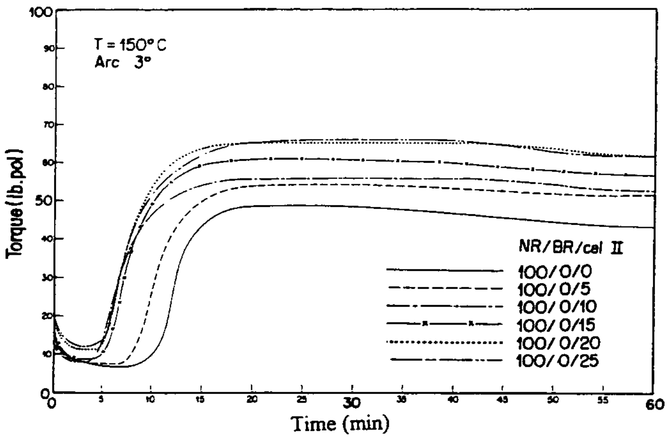

Fig. 1.- Rheographs of cellulose II filled NR/BR (100/0) blends at different cellulose II loadings

The cure rate index (CRI) is another parameter obtained from cure curves. The CRI values decrease for the various compositions when the cellulosic filler is added. The effect of the filler content in the vulcanization may be caused not only by the polymer-filler interaction but also by reactivity, leading to lower optimum cure times when cellulose is present, as compared to pure gum.

Analysing the rheometric data as a function of NR/BR pure gum rate (Figure 5), two types of behavior, inherent in the nature of each elastomer, are found: the one related to the reactivity to crosslinking, which is higher in NR than in BR, leads to lower values of optimum cure and scorch times and higher CRI when NR predomines, the other one related to the molecular rigidity, higher for this type of BR, as confirmed through minimum and maximum torque data, which is superior when BR predominates in the NR/BR system.

For the systems NR/BR/CEL II (Figures 1 to 4), at the same cellulose II content, the minimum torque, maximum torque, and optimum cure time increase as a function of increasing quantities of BR, and decrease in CRI, as seen previously for pure gum compositions.

Vr data are shown in Table 1. The **Vr** values depend on the swelling power of the solvent and on the crosslinking density. The **Vr** will be higher with the poorer solvent . With the same solvent, higher **Vr** values mean higher crosslinking density which results in less swelling.

In regard to **Vr** of either pure gum or filled compositions, **Vr** always increases with increasing cellulose II content, which shows that cellulose II also participates in crosslinking; this is in accord with rheometric analysis. As the ratio NR/BR is varied, it is observed that **Vr** rises with the increase of BR content in the system; this means that the BR phase presents a higher crosslinking density and this is also in agreement with cure parameters.

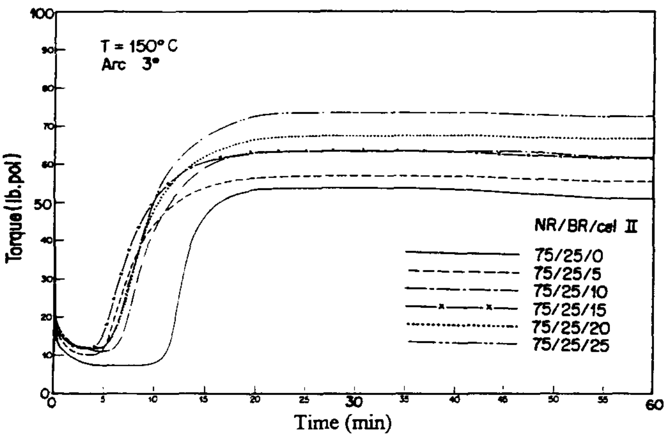

Fig. 2.- Rheographs of cellulose II filled NR/BR (75/25) blends at different cellulose II loadings

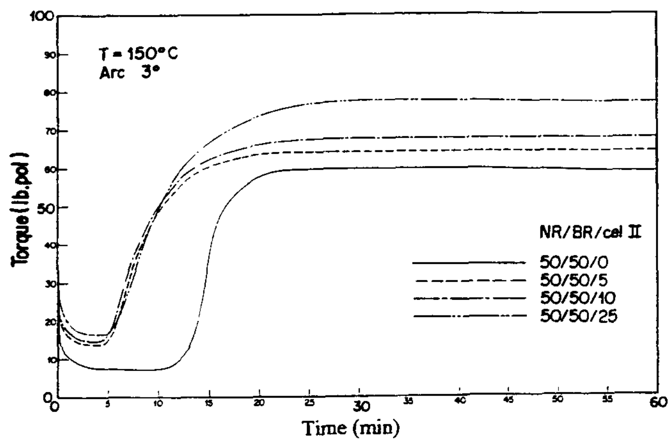

Fig. 3.- Rheographs of cellulose II filled NR/BR (50/50) blends at different cellulose II loadings

Kraus (13) has shown that swelling of a large number of vulcanizates containing highly reinforcing fillers follows a mathematical model as described in equation (I), that permits to evaluate the restriction to swelling a matrix, imposed by a filler.

The parameter **m** describes how much swelling is restricted due to a given volume fraction of filler and it is basically a measure of polymer-filler interaction during the swelling process. Similarly **Vro** is a measure of polymer-solvent interaction. When **m** = 0, the filler does not interfere in the degree of swelling of the vulcanizates.

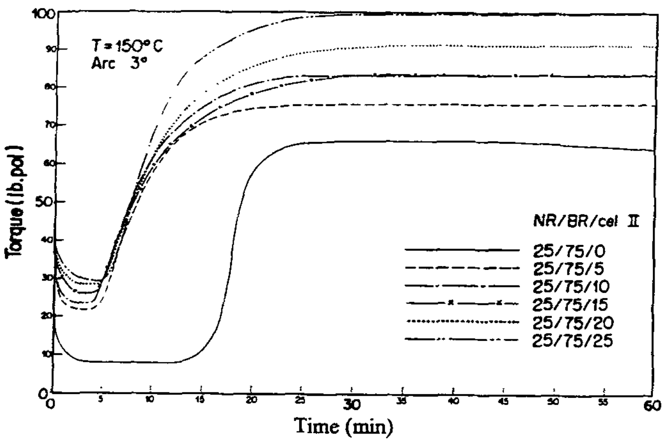

Fig. 4.- Rheographs of cellulose II filled NR/BR (25/75) blends at different cellulose II loadings

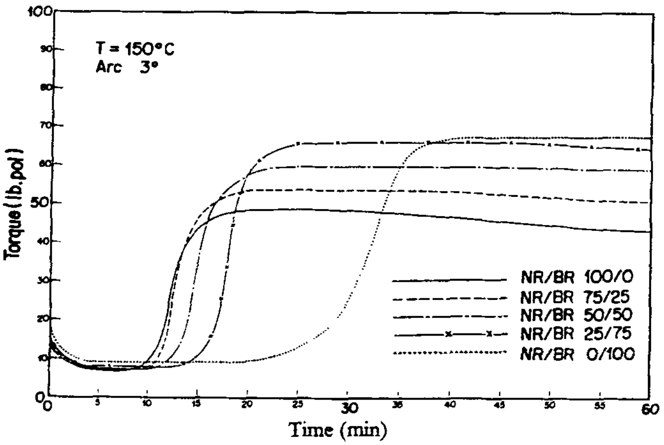

Fig. 5.- Rheographs of pure gum NR/BR blends

Figure 6 presents Kraus plots for different elastomer-filler compounds. It is shown that elastomer-cellulose II compositions obey equation (I) up to a certain volume fraction of cellulose II. There is a deviation from linearity at higher filler loadings. This behavior was also observed by Porter (14) in HAF-filled systems, by Mukhopadhyay and De (15) in NR systems with various carbon black types (ISAF, HAF, SRF, FT), and by Boonstra and Taylor (16) in carbon black filled SBR and BR systems. In our case, the degree of polymer-filler interaction follows the order (NR/BR): 25/75 > 50/50 > 25/75 > 100/0, suggesting that higher elastomer-cellulose II attachment takes place in systems with higher BR contents.

We also attempted to fit our data to the equation used by Cunneen and Russel (equation (II)) and it was observed that all compounds studied obey this mathematical model.

Figure 7 shows the plots for elastomer-cellulose II compositions. The constants **a** and **b** derived from such plots display the relative polymer-filler interaction, where high values of **a** and low values of **b** indicate strong polymer-filler attachment. Polymer-filler interaction increases as the proportion of BR in the composites rises, suggesting a better adhesion of this kind of filler with the BR phase.

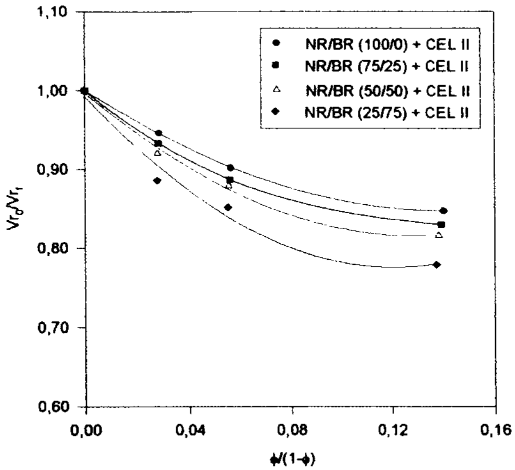

Fig. 6.- Relationship between concentration of cellulose II and equilibrium volume swelling in heptane of NR/BR network plotted in the form of Equation (I)

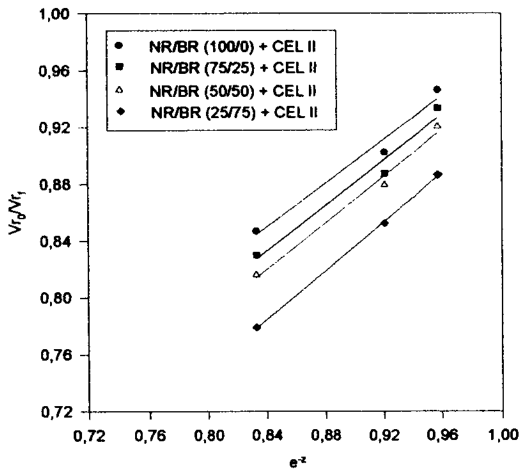

Fig. 7.- Relationship between concentration of cellulose II and equilibrium volume swelling in heptane of NR/BR network plotted in the form of Equation (II). • a = 0.7617, b = 0.2098; ■ a = 0.7920, b = 0.1673; △ a = 0.8109, b = 0.1386; ◆ a = 0.8512, b = 0.0695

Conclusions

The analysis of the experimental results obtained in this work allows the following conclusions:

- The observation of the various compositions having cellulose II as the filler has shown that this material effectively participates in crosslinking.
- For a given filler content or for pure gum compositions, higher proportions of NR, which is more reactive than BR in the rubber mixtures, lead to shorter cure times and higher CRI values.
- The maximum torque and Vr values increase with rising of BR content; this may be caused by a major crosslinking density in this phase.
- Swelling studies show that the degree of interaction between the elastomeric phase (NR and BR) and the filler (cellulose II) is improved by increasing the BR content in the elastomeric matrix.

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References

1. Joseph R, George K E, Francis D J, Thomas K T (1987) Int J Polym Mater 12:53
2. Joseph R, George K E, Francis D J (1988) Int J Polym Mater 12:111
3. Kurian T, George K E (1989) J Appl Polym Sci 37:987
4. Gharavi F, Katbab A A (1990) Prog Rubb Plast Technol 6:129
5. Blow C M, Hepburn C (1985) Rubber Technology and Manufacture, Butterworths, London
6. Coran A Y (1995) Rubber Chem Technol 68:351
7. Kreja M R, Koenig J L (1993) Rubber Chem Technol 66:376
8. Stickney P B, Mueller W J (1969) Rubber Chem Technol 42:604
9. Mano E B, Nunes R C R (1983) Eur Polym J 19: 919
10. Costa V G, Nunes R C R (1994) Eur Polym J 30: 1025
11. Affonso J E S, Nunes R C R (1995) Polym Bull 34: 669
12. Vieira A, Nunes R C R, Visconti L L Y (1996) Polym Bull 36:759
13. Kraus G (1963) J Appl Polym Sci 7:861
14. Porter M (1967) Rubber Chem Technol 40:866
15. Mukhopadhyay R, De S K (1979) Rubber Chem Technol 52:263
16. Boonstra B B, Taylor G L (1965) Rubber Chem Technol 38:943
17. Bhowmick A K, De S K (1979) Rubber Chem Technol 52:985
18. Bhowmick A K, De S K (1980) Rubber Chem Technol 53:960
19. Pranab K P, De S K (1983) J Appl Polym Sci 28: 3333