Polymer Bulletin 34, 669–675 (1995)

Polymer Bulletin

Influence of the filler and monomer quantities in the rheometrical behaviour and crosslink density of the NBR-cellulose II composites

José Eduardo de Sena Affonso*, Regina Célia Reis Nunes

Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro,
Cidade Universitária, PO Box 68525, 21945-970 Rio de Janeiro, RJ, Brazil

Received: 13 November 1994/Accepted: 20 December 1994

ABSTRACT

Cellulose II (the structural component) was incorporated into latex of butadiene-acrylonitrile copolymer (the matrixial component) by coprecipitation of nitrilic latex-cellulose xanthate mixture, according procedure developed in this Institute. According to different types of elastomeric compositions with 26%, 33% and 45% of acrylonitrile (monomers) and cellulose II up to 25 phr were evaluated. This study tries to correlate the rheometrical behaviour, which was estimated by cure parameters, with crosslink density values, which were obtained by swelling method using organic solvent. It was found that the amounts of both acrylonitrile and cellulose present in these several composites affect the cure results, and this fact suggests the presence of a rubber-filler interaction.

INTRODUCTION

The addition of certain compounds to polymeric compositions has striking influence on the artifact properties, and amongst these additives, the fillers especially those acting as reinforcing agents, have an outstanding importance. The use of fillers in synthetic elastomer compositions is essencial in order to the obtain materials with low cost, better processability and mechanical performance. Several definitions for reinforcement can be found in the literature (1-4), but usually, it can be thought of as the responsible for an improvement in the service life and in some properties for elastomeric composites, as increase in hardness, rupture energy, tear strength, tensile strength, and fatigue and abrasion resistance (5).

The use of cellulose I and II as reinforcement in mixture of natural and synthetic rubbers has been investigated by some researchers (6-9), and in these elastomeric systems, cellulose II was used as the structural component while the nitrile rubber was the matrixial one.

The cure or vulcanization can be defined as a process that promoves an increase in the retrative force and reduces the amount of permanent deformation remaining after

---

* Corresponding author

removal of the deforming force. Thus, the cure process increases elasticity while plasticity decreases. It is generally accomplished by the formation of a cross-linked molecular network (10).

The swelling measurement of vulcanized rubbers in contact with organic solvents is widely used to determine experimentally the crosslink density, which generally improves and can be related to changes in physical properties (11-13). A high degree of swelling of an elastomeric matrix immersed in a given solvent indicates that the product can not be placed in such environment because the contact between the solvent and the elastomeric matrix would cause a deleterious effect in the resistance of the cured product (13).

In this work, three differents grades of nitrile elastomers containing 26%, 33% and 45% of acrylonitrile and 0-25 phr of regenerated cellulose or cellulose II were studied. Cellulose II was incorporated into the elastomeric matrix by coprecipitation of nitrile latex-cellulose xanthate mixture. Cure parameters such as minimum torque (M_L), maximum torque (M_H), optimum cure time (t90) and cure rate index (CRI) were determinated on an oscillating disk rheometer. These properties can be related with the crosslink density, which was obtained using the swelling method in the equilibrium in organic solvents such as toluene. The correlation between swelling in equilibrium and crosslink density was achieved by the Flory-Rehner`s equation.

EXPERIMENTAL

Preparation of NBR-cellulose II composites

The incorporation of cellulose II into NBR was carried out by coprecipitation of cellulose xanthate (Rhodia Ind. Quím. e Têxteis) and NBR latex (Nitriflex SA Ind. e Com.), in acid solution (H_2SO_4 $ZnSO_4$ 1:1 molar solution), with pH control and constant mechanical stirring. After coagulation, the products were filtrated, washed and dried at 50° C for 24 hours.

Preparation of vulcanized NBR-cellulose II compositions

Dried NBR-cellulose II composites were mixed in a roll mill, according to the following formulation (14): Elastomer (100 phr), zinc oxide - Uniroyal do Brasil SA Ind. Quím. (3,0 phr), stearic acid - Companhia Estearina Paranaense (1,0 phr), N-t-butyl-2-benzothiazole sulfenamide [TBBS] - Indústria Monsanto (0,07 phr) and cellulose II (0-25 phr).

Determination of vulcanization or cure parameters

The cure parameters were determined according to ASTM method (15), by means of a Monsanto oscillating disk rheometer model 100S. The tests were carried out at 150°C (423 K), arc +/- 3° for 60 minutes. From the rheometric curves obtained for each compositions, minimum and maximum torques (M_L and M_H) and scorch time (t_s2) were evaluated, the optimum cure time (t90) was calculated from both the 90% vulcanization torque value (M90) and the cure rate index (CRI).

Determination of crosslink density

Samples of vulcanized NBR-cellulose II with 1,5X1,5X0,2 cm were immersed in toluene (Reagen-Quimibrás Ind. Quím. SA) until a thermodynamic equilibrium was reached. After that, from data of polymer-solvent interaction parameters (χ), molar volume of the solvent (Vo), volume fraction of polymer in the swollen mass (Vr) and density of polymer (d), the crosslink density values (ν) were calculated as:

$$\nu = [\ln(1-Vr) + Vr + \chi Vr^2] / Vo[(Vr)^{1/3} - Vr/2]$$

RESULTS AND DISCUSSION

Table 1 shows crosslink density values and some rheometric parameters for the cure of the NBR-cellulose II composites, with 26%, 33% and 45% acrylonitrile and 0-25 phr of cellulose II.

Table 1
Crosslink density values and rheometric parameters of NBR-cell II composites

properties→ compounds↓	crosslink density (mol/cm^3)x10^6	min. torque ML(dN.m)	max. torque MH(dN.m)	cure optimum time (min.)	cure rate index (min^{-1})
NBR26/pure	200.2	8.8	46.3	21.0	6.3
NBR26/10phr cell II	341.4	15.7	98.6	12.5	9.5
NBR26/15phr cell II	326.1	16.3	100.6	10.5	11.5
NBR26/20phr cell II	363.7	24.9	110.7	7.5	19.6
NBR26/25phr cell II	411.7	30.3	121.4	9.5	13.3
NBR33/pure	226.1	5.7	38.8	32.0	3.8
NBR33/10phr cell II	380.4	11.1	63.8	23.0	5.3
NBR33/15phr cell II	517.9	15.7	94.8	15.5	9.1
NBR33/20phr cell II	522.2	16.6	105.1	12.0	12.5
NBR33/25phr cell II	526.5	18.6	115.8	19.0	6.6
NBR45/.pure	393.5	5.9	35.0	43.0	2.8
NBR45/10phr cell II	866.9	8.8	100.6	33.5	3.3
NBR45/15phr cell II	960.0	12.2	101.6	25.0	4.5
NBR45/20phr cell II	995.6	12.2	116.4	33.0	3.3
NBR45/25phr cell II	1004.7	11.8	131.8	25.0	4.4

Figure 1 shows the influence of cellulose II and acrylomtrile quantities on the crosslink density values for the composites.

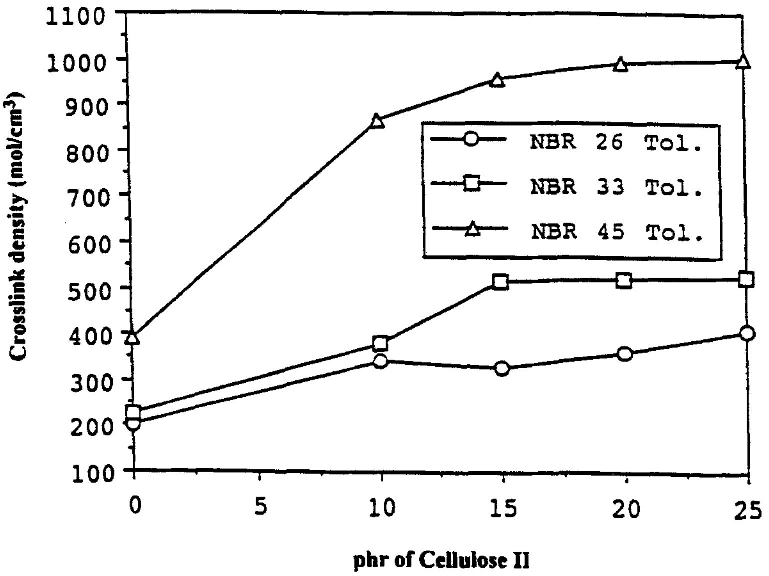

Figure 1- Crosslink density values for the NBR-cellulose II composites

According to the obtained results, it can be seen that cellulose II causes an increase in the crosslink density values, for each compositions. It is known that, the minimum swelling of a rubber or any other polymer in organic solvents is a consequence of high network; from these observations it is evident the importance of the amount of cellulose in the composite, i.e., compositions with 25 phr of cellulose II are less swollen than those with 20, 15, 10 or 0 phr.

It is interesting to observe that the amount of acrylonitrile in the NBR affects significantly the crosslink density values, i.e., composites with equal quantities of incorporated cellulose in the elastomeric matrix with increasing high acrylonitrile amounts, present higher crosslink density values. This behaviour can be related to the NBR polarity.

Figures 2, 3 and 4, show rheometric curves for NBR-cellulose II compositions with 26, 33 and 45 % acrylonitrile and 0-25 phr of cellulose II.

The rise in maximum torque value with the increasing crosslink density is remarkable all over the NBR-cellulose II composites. The highest values of maximum torque and crosslink density, i.e., 131 dN.m 1004,7 mol/cm^3, were found for the NBR 45/25 phr of cellulose II, which could explain the influence of NBR polarity and cellulose II quantity, in the studied systems.

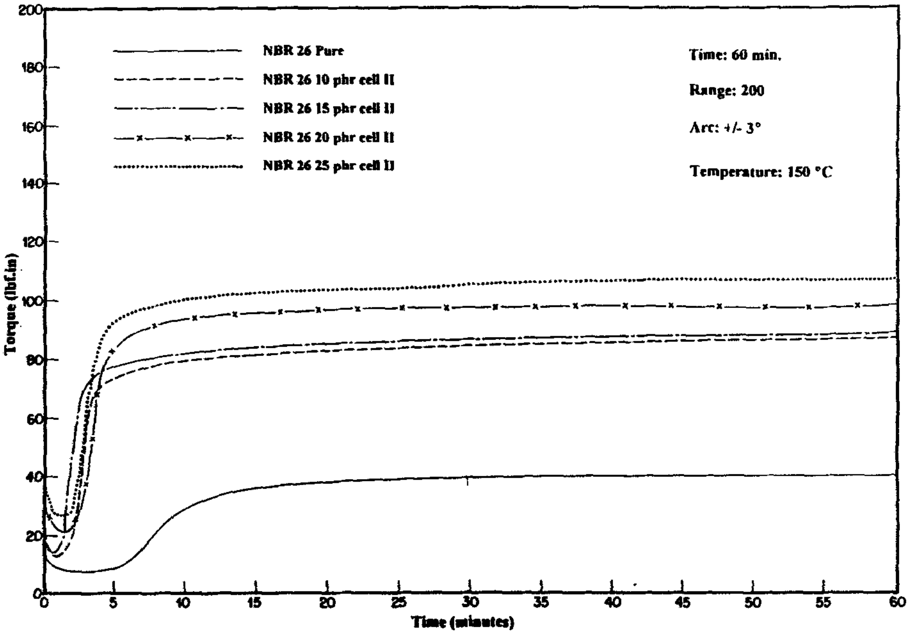

Figure 2- Rheometric curves for NBR 26-cellulose II compositions

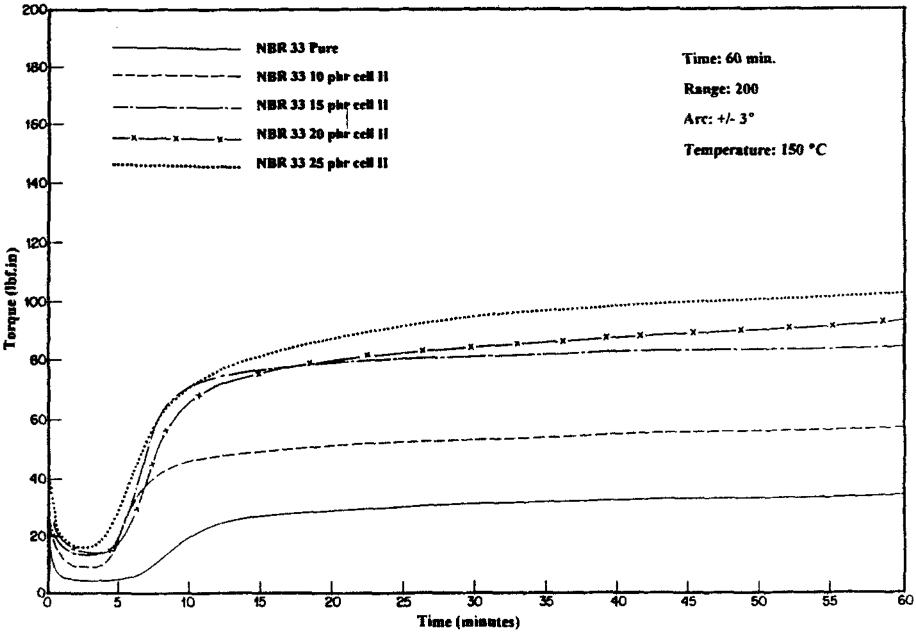

Figure 3- Rheometric curves for NBR 33-cellulose II compositions

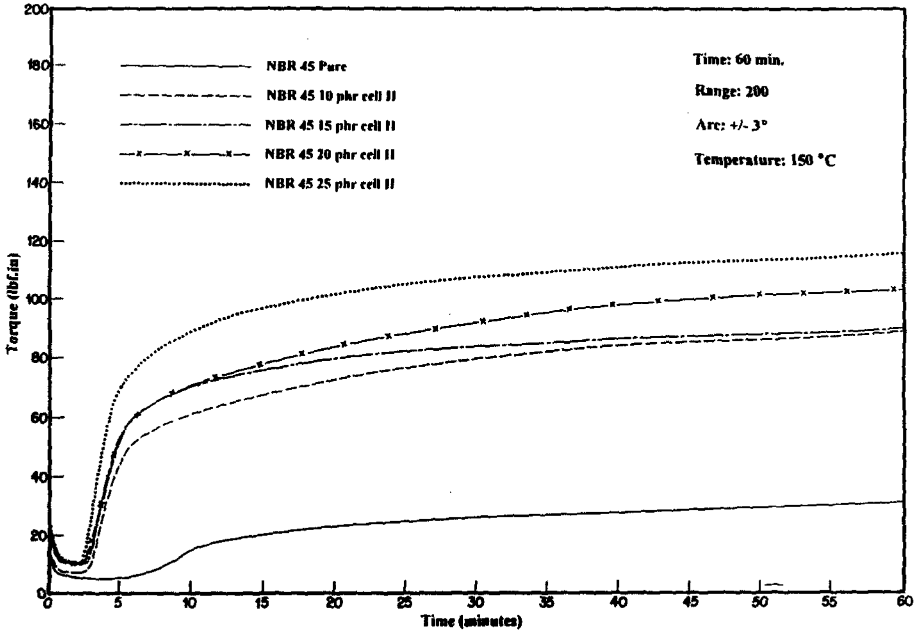

Figure 4- Rheometric curves for NBR 45-cellulose II compositions

It can be suggested that, after the coagulation of cellulose xanthate, the remaining xanthate groups present in the system, would allow a certain acceleration in the cure process. This would lead the optimum cure time (t90) to lower values by increasing the cellulosic quantity.

CONCLUSION

It can be shown through thermodynamic (crosslink density by swelling method) and physical (rheometer) studies, a rubber-filler interaction, as well as the polar character of the investigated elastomers.

It was noteworthy the influence of acrylonitrile and cellulose II quantities on both the crosslink density values and rheometric parameters. With regard to crosslink density, a gradual increase with crescent amounts of filler and acrylonitrile in the composites occured.

The residual sulphur from cellulose xanthate coagulation mixed with the elastomeric latex, combined with the elastomer polarity, could be answerable for the crosslink formation, as well as for the increase of the maximum torque and the reduction of the cure optimum time.

ACKNOWLEDGMENTS

The authors thank Nitriflex SA Ind. e Com., Rhodia Ind. Quím. e Têxteis for providing latex of nitrile rubber and cellulose xanthate respectively. They are also indebted to CAPES, PADCT-FINEP, CNPq and CEPG/UFRJ for financial support.

REFERENCES

1. Boonstra BB (1982) Reinforcement by fillers. In: Blow CM and Hepburn C (ed) Rubber Technology and Manufacture. Newnes-Butterworths, London (cap. 7, pp 269-308).
2. Voet A (1980) Journal Of Polymer Science: Macromolecular Review 15: 327.
3. Le Blas J, Papirer E (1978) Journal Of Applied Polymer Science 22: 525.
4. Dannenberg EM (1975) Rubber Chemistry and Technology 48(3): 410.
5. Nunes RCR, Mano EB (1991) Revista ABPol Maio: 31.
6. Nunes RCR, Mano EB (1992) Polímeros: Ciência e Tecnologia Julho/Setembro: 23.
7. Nunes RCR (1989) D. Sc. Thesis, Instituto de Macromoléculas (UFRJ) Rio de Janeiro (RJ) Brazil.
8. Affonso JE de S (1994) M. Sc. Thesis, Instituto de Macromoléculas (UFRJ) Rio de Janeiro (RJ) Brazil.
9. Persson JE, Raanby B (1990) PCT Patent Appl 90/03411.
10. Coran Y (1986) Vulcanization. In: Mark, Bikales, Overberg, Menger (ed) Encyclopedia Of Polymer Science & Enginnering. Wiley & Sons,New York (vol. 17, pp 666-97).
11. McKenna GB, Flynn KM and Chen Y (1990) Polymer 31: 1937.
12. Neppel A (1985) Rubber Chemistry and Technology 59: 46.
13. Labama SS (1986) Cross-Linking. In: Mark, Bikales, Overberg, Menger (ed) Encyclopedia Of Polymer Science & Engineering. Wiley & Sons, New York (vol 4, pp 350-95).
14. ASTM Method D3187-85 (1986) Philadelphia, section 9, 9.01: 715.
15. ASTM Method D2084-81 (1986) Philadelphia, section 9, 9.01: 533.