Polymer Bulletin 36, 759-766 (1996)

Polymer Bulletin

Mechanical properties of NR/BR/cellulose II composites

Arisia Vieira, Regina C. R. Nunes*, Leila L. Y. Visconti

Instituto de Macromoléculas Professora Eloisa Mano, Universidade Federal do Rio de Janeiro, P.O. Box 68525, 21945-970 Rio de Janeiro, RJ, Brasil (Fax: 55-021-2 70-13 17)

Received: 5 February 1996/Accepted: 6 March 1996

Summary

Blends of natural rubber (NR) and butadiene rubber (BR) with cellulose filler have been investigated. The coprecipitation of the rubber latex-cellulose xanthate mixtures by acidulation lead to elastomer-cellulose II composites in granular form. In these blends, the NR/BR ratio has been varied from 75/25 to 25/75, and the cellulose content has been increased from 0 to 25 phr. Mechanical tests have been applied to the composite samples, and the results showed that cellulose II may be considered as a reinforcing agent. Those results gave also an insight into the role of NR and BR on the properties of the composite samples.

Introduction

Blending of two or more rubbers is carried out for three main goals: improvement in technical properties, better processing and lower compound cost. Many products in the rubber industry are based on blends. Tyres are typical examples of products in large-scale volume production where NR/BR blends are extensively used (1-3).

Reinforcement of elastomers by fillers has been defined as their ability to increase stiffness of unvulcanized compounds as well as to improve various vulcanizate properties such as tensile strength and tear and abrasion resistances. The majority of rubber articles contains fillers, amongst which carbon black and silica are the most common reinforcing fillers (4).

Short fibers have also been used in rubbers to form short-fiber-reinforced elastomer composites.The reinforcement of elastomers with fibers combines the elastic behaviour of the rubbers with the strength and stiffness of the reinforcing fiber. Composites of this type are useful as engineering materials (5,6).

Crystallites act as reinforcing filler particles and as "physical"crosslinks which permit an unvulcanized semi-crystalline rubber to support stress indefinitely.The crystallization of natural rubber can be induced by stressing, producing a state in which the stress-induced degree of crystallinity raises the strength of this rubber (7).

It was verified that a method to incorporate short fibers of cellulose in elastomer compounds has been efficient in producing composites with good performance (8-12).

In the present work mechanical properties of natural rubber/butadiene rubber/cellulose II (NR/BR/CEL II) composites are investigated.

* Corresponding author

Experimental

Materials

The elastomers used in this work were: natural rubber latex (NR) supplied by Lemgruber S.A., RJ, Brasil and butadiene rubber latex (BR) manufactured by Nitriflex S.A. Indústria e Comércio, RJ, Brasil . All the ingredients in the formulations were used as received: viscose (cellulose xanthate) (Rhodia Indústrias Químicas e Têxteis, SP, Brasil), zinc oxide (Uniroyal do Brasil S.A. Indústrias Químicas, SP, Brasil), stearic acid (Companhia Estearina Paranaense, PR, Brasil), phenyl-ß-naphthylamine (PBN) (Indústrias Monsanto S.A., SP, Brasil), sulfur (Vetec Química Fina Ltda, RJ, Brasil) and N-cyclohexyl-2-benzothiazolesulfenamide (CBS) (Bayer do Brasil S.A., RJ, Brasil).

Blending Procedure

Different ratios of the elastomers NR and BR in latex form were mixed (NR/BR - 75/25, 50/50, 25/75).To these blends cellulose xanthate was added under constant stirring. The coprecipitation of the mixtures NR/BR - cellulose xanthate was carried out by gradual addition of a 1:1 molar aqueous solution of sulfuric acid and zinc sulfate also with stirring and pH control at room temperature. The cellulose II content in the blends was varied up to 25 phr. The obtained granules were washed several times with distilled water and oven dried at about 50°C, during approximately 48 hours.

The vulcanizing ingredients (5 phr zinc oxide, 2 phr stearic acid, 1 phr phenyl-ß-naphthylamine, 3 phr sulfur, 0,7 phr N-cyclohexyl-2-benzothiazolesulfenamide) were incorporated into NR/BR/CEL II compositions on a 10 x 22,5 cm Berstorff laboratory mill, at 50°C, following ASTM D 3182. This formulation was based on ASTM D 3184, ASTM D 3189 and literature data (2,3).

Measurements

Cure behaviour was determined at 150°C using a Monsanto Oscillating Disk Rheometer at 3° arc, according to ASTM D 2084. The stocks were cured under pressure, at 150°C, to optimum cure and the vulcanizates were kept for 24 h, at ambient temperature, before measurements of mechanical properties. The investigated properties were: tensile strength, modulus (ASTM D 412); hardness (ASTM D 2240); tear strength (ASTM D 624); abrasion resistance (ASTM D 2228); resilience (ASTM D 2632) and compression set (ASTM D 395).

Results and Discussion

Mechanical properties of elastomer blends depend on their morphology, chemical nature, crystallinity, processing, testing procedures, elastomer ratio and cure system. In this work the mechanical behaviour of NR/BR/CEL II systems was evaluated in function of cellulose filler, NR and BR contents. All results were also compared with pure gum and are shown in Figures 1-10. In these blends, NR/BR ratio has been varied from 75/25 to 25/75 and cellulose content has been increased from 0 to 25 phr.

Stress-strain data are shown in Figures 1-3. Tensile strength at break for the composites is better visualized in Figure 4. It is observed that when BR is present in smaller quantities the systems always exhibit higher tensile strength at break. This is probably due to the auto-reinforcing characteristics of NR under tension. At the limit of filler studied in this work, the results of tensile strength at break increase with increasing amount of cellulose II. Hence, it can be said that the gradual adittion of cellulose in

NR/BR blends improves the mechanical performance of these systems, indicating the action of this filler as a reinforcing agent for the kind of incorporation process used.

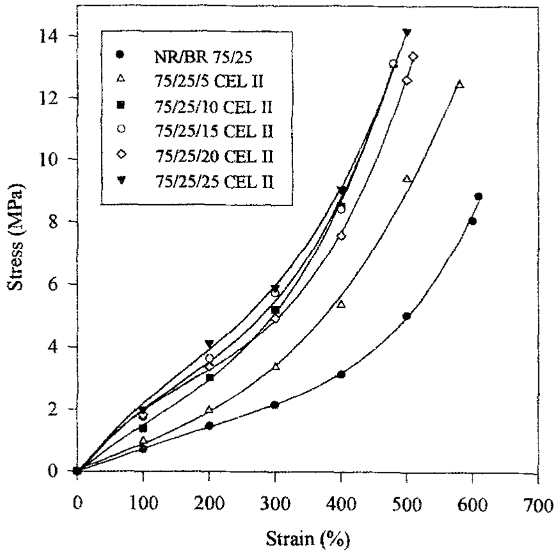

Fig. 1.- Stress-strain curves of NR/BR/CEL II (75/25) compositions

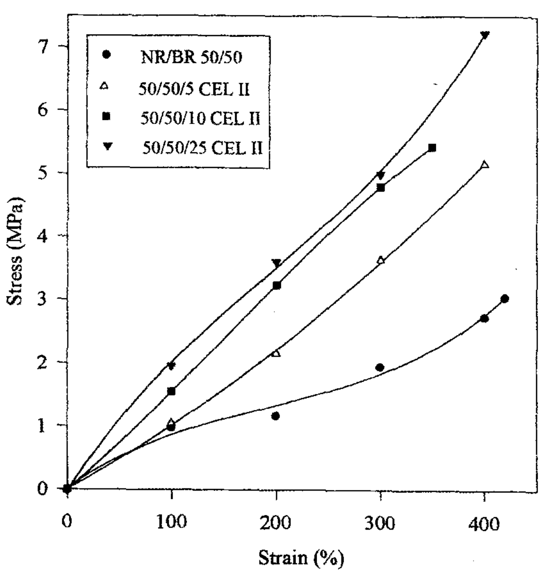

Fig. 2.- Stress-strain curves of NR/BR/CEL II (50/50) compositions

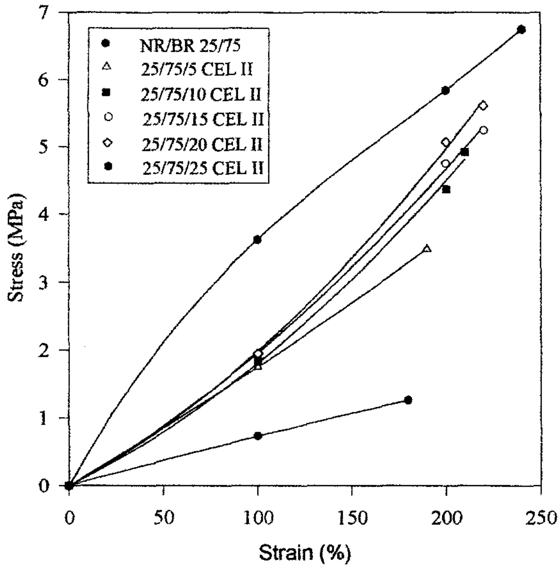

Fig. 3.- Stress-strain curves of NR/BR/CEL II (25/75) compositions

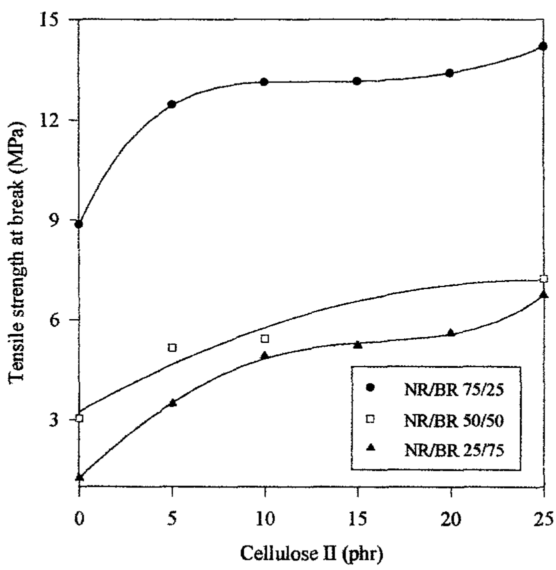

Fig. 4.- Tensile strength at break of NR/BR/CEL II compositions

Modulus (Figure 5) and hardness (Figure 6) are also enhanced with the adittion of cellulose II and the predominance of BR in the composites. These behaviours show the contribution of the filler stiffness and the higher molecular rigidity of BR compared to NR.

Tear strength (Figure 7) is higher for all compositions filled with cellulose II as confronted to pure gum, showing the reinforcing feature of this type of filler. In the composites NR/BR/CEL II (75/25) and (50/50) the development of this property is more pronounced up to 10 phr of filler, after which the values become close to each other.

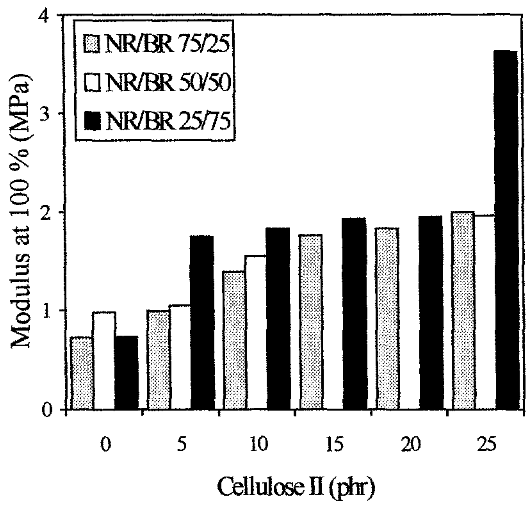

Fig. 5.- Modulus at 100% of NR/BR/CEL II compositions

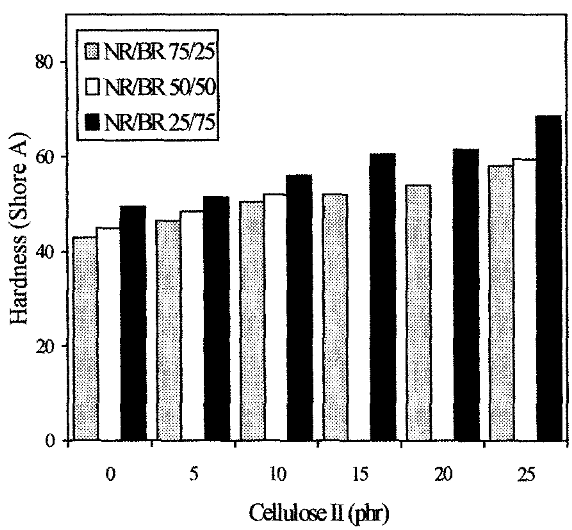

Fig. 6.- Hardness of NR/BR/CEL II compositions

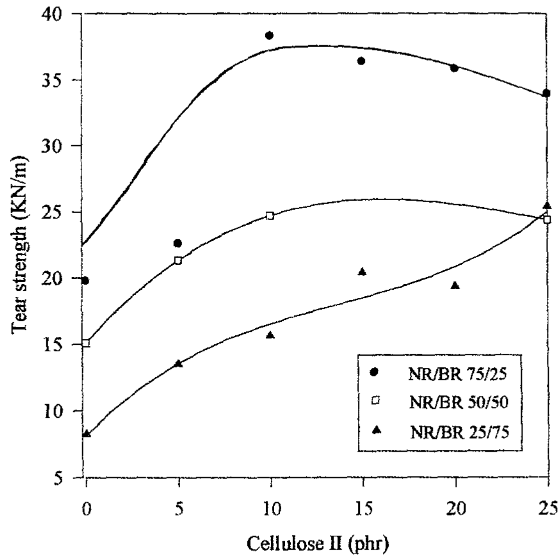

Fig. 7.- Tear strength of NR/BR/CEL II compositions

As for the abrasion resistance (Figure 8) an improvement of this property is also observed, as cellulose II is added, corroborating the reinforcing effect of the filler in these elastomer systems. The best results are obtained when cellulose II content is 15 phr.

Concerning the NR/BR/CEL II mixtures under study, the composites with higher NR contents display better tensile strength, tear strength and abrasion resistance properties which are affected by filler quantity.

Improvement in tensile strength, tear strength and abrasion resistance characterize, in this case, a positive influence of filler in the composites and the examination of the data confirms the reinforcing action of cellulose II in NR/BR compounds.

The optimum cellulose II content depends on each of the analysed property and varies from 15 to 25 phr. In accordance to the literature data this behaviour is presumed to be due to the different ratios with which mechanical properties are developed in rubber vulcanizates (13).

Resilience is a measure of the instantaneous recovery of a material at low strain. Resilience data for the studied compositions are plotted in Figure 9. All compositions present decreasing values of resilience with increasing cellulose II content . This result is expected considering the small elastic recovery capability of fillers as compared to elastomers.

The high resilience of BR leads to an improvement in this property by increasing its content in the composition. An interesting observation is the decrease in resilience when comparing compositions NR/BR (50/50) and (25/75) in relation to the increase of BR. The blends NR/BR (25/75) for which BR contents are the highest, do not present the best results, as would be expected. This suggests a state of subvulcanization in these blends.

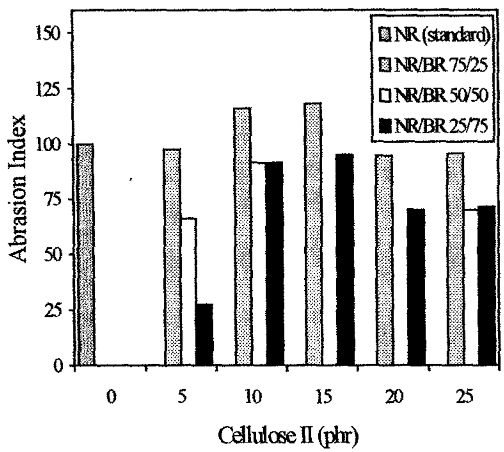

Fig. 8.- Abrasion resistance of NR/BR/CEL II compositions

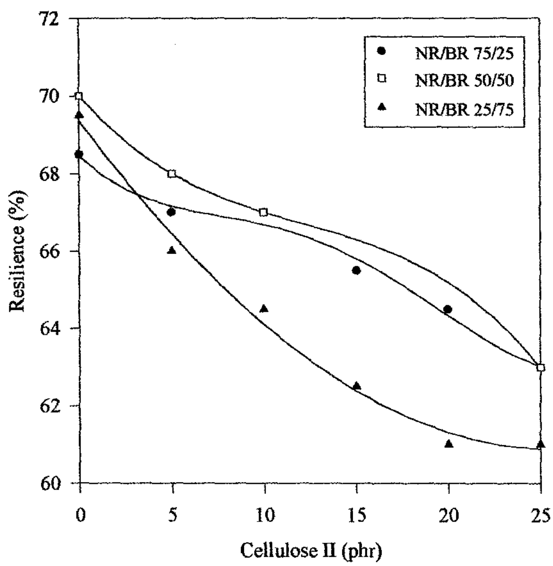

Fig. 9. - Resilience of NR/BR/CEL II compositions

The ability of rubber compounds to retain elastic properties after prolonged action of compressive stresses is given by compression set measurements. In this work, the obtained compression set data are plotted in Figure 10. This property shows crescent values with increased cellulose II content. This demonstrates a reduction in the elastic properties of the compositions in the presence of a more rigid structure. By analysing compression set data as a function of BR content, the same behaviour previously found for the resilience values is verified. NR/BR (25/75) compositions do not exhibit better results, i. e., smaller values as compared with the other compositions. These results corroborate the resilience observations.

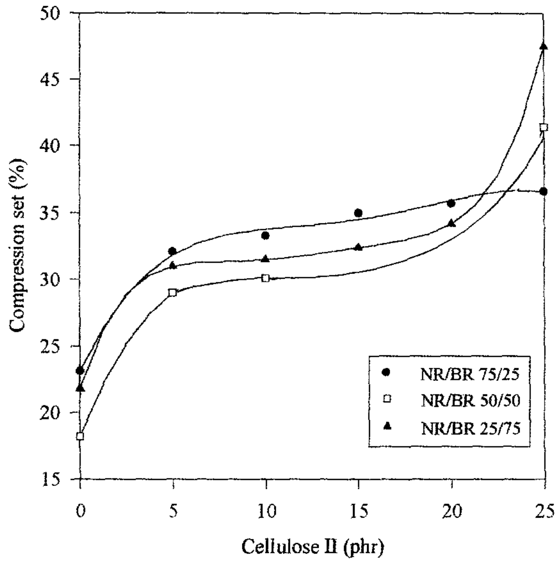

Fig. 10.- Compression set of NR/BR/CEL II compositions

Conclusions

- The results of tensile strength, tear strength and abrasion resistance show that cellulose II can be considered as a reinforcing filler for NR/BR blends.
- Stress-strain data display an auto-reinforcement of NR in NR/BR/CEL II composites, since the predominance of NR in the mixtures gives rise to a better mechanical performance.
- Modulus and hardness, which are related to material resistance at small strains, increase with increasing of cellulose II content and BR ratio for all composites.
- Resilience and compression set are functions of the material elasticity.The obtained values for these two properties are the highest for those compositions where BR predominates and cellulose II is in smaller ratio.

Acknowledgements: The authors thank the CAPES and CEPG/UFRJ for financial support.

References

1. Zanzig D J, Magnus F L, Halasa A F, Testa M E (1993) Rubber Chem Technol 66:538
2. Joseph R, George K E, Francis D J Thomas K T(1987) Int J Polym Mater 12:53
3. Joseph R, George K E, Francis D J (1988) Int J Polym Mater 12:111
4. Nakajima N, Chu M H (1990) Rubber Chem Technol 63:110
5. O'Connor E (1977) Rubber Chem Technol 50:945
6. Zuev Y S (1992) Int Polym Sci Technol 19:8
7. Eirich F R (1978) Science and Technology of Rubber, Academic Press, New York
8. Mano E B, Nunes R C R (1977) Revista Brasileira de Tecnologia 8:35
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. Vieira A (1994) M. Sc. Thesis, Instituto de Macromoléculas , UFRJ, Brazil
12. Affonso J E S, Nunes R C R (1995) Polym Bull 34:669
13. Cheremisinoff N P (1987) Polymer Mixing and Extrusion Technology, Marcel Dekker, New York