



CURING AND PHYSICAL PROPERTIES OF NATURAL RUBBER/CASSAVA STARCH BLENDS

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1 General Introduction

During the last years, the effects of different types of fillers on Natural Rubber compounds have been studied, in search of improvements on its physical and mechanical properties. Amongst these fillers are carbon black, silica, calcium carbonate, etc. Recently, the application of fillers of organic nature has attracted interest due to their low cost, renewable and environment friendly nature. Several cellulosic materials such as starch, ground wood waste, nut shells, bamboo, white rice husk, and cereal straw have been used as fillers for plastics and elastomers [1]. Starch is one of the substances more widely distributed in nature. It is a biopolymer consisting of amylos and amylopectin, present in most plants and in considerable amounts. There are some investigations concerning the reinforcement of elastomers with cassava starch [2], but only a few report the effect of this material on the physical properties of the elastomers. Thus, it is the aim of this contribution to assess the potential utilization of cassava starch, obtained from typical trees of Venezuela, in Natural Rubber compounds, studying the effect of starch content and the use of maleated natural rubber on the rheological and mechanical behavior of NR composites.

2 Experimental

2.1 Materials and Specimens

Composites prepared were based on Natural Rubber (NR) SMR-20 and different proportions of Cassava starch (CS). The filler was obtained from the eastern zone of Venezuela. The filler was grounded and sieved until and average particle size of 120 μm . Also, the same NR was functionalized with 10 phr of maleic anhydride (MNR) as a coupling agent

between NR and CS. Table 1 shows the formulations prepared.

Table 1. Formulations

Materials	F1	F2	F3	F4	F5	F6	F7
NR	100	100	100	100	100	80	80
MNR	-	-	-	-	-	20	20
CS	-	10	20	40	60	-	20

Curing additives for all formulations based on 100 parts of rubber were: 1 phr of antioxidant, 5 phr of Zinc oxide (ZnO), 2.5 phr of sulphur (S), 1 phr of (MBTS) and 2 phr stearic acid.

Compounds were prepared using a Banbury® internal mixer, with a fill factor of 0.75, at a rotor speed of 60 rpm. Firstly, rubber was masticated, and then the antioxidant and the ZnO were added. Half of the filler was afterwards incorporated and mixing continued for 120 s; the remaining half and stearic acid were added at that time and after 180 s of mixing. Curatives (S and MBTS) were added in a second step using the same equipment. The compound obtained was then passed through a milling roll for banding.

2.2 Testing

Cure characteristics were studied using a Rotorless rheometer model EKT-2.000SP at 160 °C (433 K) and 0.5° oscillation according to ASTM D5289 procedure. All rubber compounds were compression molded into sheets in a Carver hydraulic press at 160 °C according to their t_{90} and to their thickness. All specimens were then cut from the vulcanized sheets.

Crosslinking density was determined according to equilibrium swelling measurements in toluene, for 72 h (259.2×10^3 s) at room temperature. Tensile and tear properties of vulcanized blends were determined using a Lloyd Instruments machine model EZ20 according to ASTM D412 and ASTM D624 procedures, respectively.

3 Results

3.1 Rheometric Properties

Table 1 shows that the time needed to reach 90% of maximum torque (t_{90}) and the scorch time (t_s) of those formulations filled with CS are slightly lower to those of NR, even though it seems to be independent of CS content. Also, the maximum elastic torque (S'_{max}) increased slightly with CS content. In general, the presence of fillers imparts restriction to the deformation, and consequently, the composite becomes harder and stiffer. On the other hand, when substituting part of NR by its maleated homologous (F6 and F7) t_s and t_{90} increase considerable; the retardation on the curing of mercapto-acelerated compounds is due to the reaction between MBTS and free maleic anhydride and/or succinic acid (from a ring opening reaction of the grafted maleic anhydride) [2]. The crosslinking degree (ν) values denote that the presence of CS makes more difficult the vulcanization process of the NR compounds.

Table 1. Curing Parameters and crosslinking density

Formulation	S'_{max} (dN.m)	t_s (min)	t_{90} (min)	ν (10^4) mol/kg
F1	7.3	1.5	3.2	2.5
F2	7.1	1.3	2.9	1.9
F3	7.9	1.3	3.0	1.8
F4	8.0	1.4	3.0	1.4
F5	8.4	1.3	3.0	1.3
F6	5.2	2.8	6.0	1.8
F7	8.1	2.2	5.6	1.4

3.1 Mechanical Properties

Table 2 shows that the overall tensile properties of the NR composites with 20 phr of CS are not considerably modified, since all values (σ_{300} , ϵ_r) are

similar to those of pure NR. When CS content is increased (F4 and F5) σ_r and ϵ_r decrease due to the formation of filler aggregates between the flexible chain segments, which act as obstacles to their sliding. If tear properties (TR) are analyzed, the awaited effect is to obtain a rise on this property with filler content, since filler offers opposition to tear patterns, making the crack propagation more difficult. However, this behavior is not observed. The MNR did not act in this case as a coupling agent since the incorporation of 20 phr (F6 and F7) affected negatively the properties of pure NR and NR filled with 20 phr CS. This effect was probably due to the lower crosslinking degree obtained for these two composites.

Table 2. Mechanical Properties

Formulation	σ_{300} (MPa)	σ_r (MPa)	ϵ_r (%)	TR (kN.m)
F1	1.8	22.4	1063	51.3
F2	1.5	18.6	1184	44.8
F3	2.1	21.3	1003	43.3
F4	1.8	14.2	967	36.2
F5	1.4	9.7	920	29.3
F6	1.3	15.6	1134	36
F7	1.3	13.9	1105	34

4 Conclusions

When Cassava Starch, considered as a biopolymer, is incorporated in a proportion of 20 phr to NR compounds, it does not alter the mechanical properties of this elastomer, contributing to the cheapness of the formulation. The blends with MNR with and without CS retard the curing process and do not improve the overall properties of NR.

References

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