

CHARACTERIZATION OF NATURAL RUBBER/CASSAVA STARCH/MALEATED NATURAL RUBBER FORMULATIONS

Miren N. Ichazo ^{1*}, Carmen Albano ^{2,3*}, Marianella Hernández ¹, Jeanette González ¹, Jenny Peña ²

1: Universidad Simón Bolívar, Departamento de Mecánica, Caracas, Venezuela.

2: Universidad Central de Venezuela, Facultad de Ingeniería, Caracas, Venezuela.

3: Instituto Venezolano de Investigaciones Científicas, Centro de Química, Caracas, Venezuela.

* E-mail: michazo@usb.ve; carmen.albano@ucv.ve

Recibido: 10-Jul-2009; Revisado: 37-Jul-2010; Aceptado: 22-Sep-2010

Publicado On-Line el 15-Nov-2010

Disponible en: www.rlmm.org

Resumen

El objetivo del presente trabajo fue estudiar el comportamiento reológico y tensil de los compuestos de caucho Natural (NR) con almidón de yuca natural (CS) y plastificado (PCS) para evaluar la posible utilización de estos materiales como carga reforzante. También, se sintetizó el caucho natural maleado (MNR) y se estudió su influencia como un agente acoplante para las formulaciones en estudio. Los resultados obtenidos indican que la adición de CS al NR incrementa el torque máximo y produce una ligera disminución de los tiempos scorch y de curado. La adición de MNR al NR con y si CS retarda el proceso de curado. También, se demostró que una proporción de 20 ppc de CS no altera las propiedades tensiles del NR vulcanizado, lo que implica que es posible lograr una formulación menos costosa. Las propiedades de los compuestos con PCS se mantuvieron similares a las de los compuestos de NR/CS. Con respecto al uso de MNR como agente acoplante, se demostró que no produce efectos positivos en el comportamiento global del NR. De los estudios termodegradativos del NR, se infiere que el comportamiento térmico del NR no se ve afectado por la adición de CS, mientras que el PCS acelera el proceso degradativo del compuesto.

Palabras Claves: Caucho natural, Caracterización, Almidón de yuca, Caucho natural maleado, Vulcanización.

Abstract

The objective of this research study was to study the rheological and tensile behavior of natural rubber (NR) compounds with cassava starch (CS) and plasticized cassava starch (PCS), with the aim of using cassava as potential filler for NR vulcanizates. The authors also evaluated the synthesis and use of maleated Natural Rubber (MNR) as a coupling agent. The results obtained indicate that the presence of CS originates changes such as an increase in the maximum torque and a slight reduction in scorch and curing time. The addition of MNR to the blends of NR with and without CS also retarded the curing process. With regard to the mechanical properties, 20 phr of CS did not alter the tensile properties of the NR vulcanizates, so a cheaper formulation with equivalent properties can be obtained. The properties of the compounds with PCS were similar to those of the NR/CS compounds. Concerning the use of MNR as a coupling agent, it did not improve the overall properties of NR. Finally, the thermal degradation behavior of NR was not affected by the addition of CS, while the use of PCS accelerated the degradative process of NR.

Keywords: Natural rubber, Characterization, Cassava starch, Maleated natural rubber, Vulcanization.

1. INTRODUCTION

Over the past few years, the effects of different types of fillers on Natural Rubber compounds have been studied, in search of improvements on their physical and mechanical properties. Recently, the use of fillers of organic nature has been object of interest due to their low cost, light weight, environmentally friendly nature, and because they enhance the mechanical properties of the filled materials [1,2].

Several cellulose materials such as ground wood waste, nut shells, bamboo, white rice husk, and cereal straw have been used as fillers for plastics [3,4] and elastomers [5–9].

Starch is one of the substances most widely found in nature. It is a biopolymer consisting of amylose and amylopectin. In addition, due to its hygroscopic nature (high hydroxyl group content), starch must be treated in such a way that it becomes more compatible with non-polar polymers such as polyolefins and rubbers of general use.

One of the modifications that may be made to starch is the addition of hydroxylic compounds such as glycerol [10], formamide [11], or mixtures of urea and formamide [12]; all of them form hydrogen bonds with the starch and replace the strong interactions between the hydroxyl groups of the starch molecule, so it becomes less brittle and more thermoplastic, in such a way that the interactions that this material may have with a non polar polymer may be enhanced.

Another way to improve the polymer–filler interaction is by using compatibilizing agents, such as polymers modified by chemical reactions. Functionalized polymers are obtained by the grafting of carboxylic acids and anhydrides, via free radical. Such groups react with the active site existing on the other component, thus creating a functional polymer [13,14]. The functionalization in the molten state of different types of elastomers, in order to use them as compatibilizers in blends with other polymers (thermoplastics, elastomers) or with organic and inorganic fillers, has been studied [15,16].

Some research studies on the influence of starch on the rheological and curing properties of NR, NR/MNR (natural rubber functionalized with maleic anhydride) blends [17], NR/Epoxidized natural rubber blends [18,19] and Natural Rubber–g–Poly(methyl methacrylate) [20,21] have been reported. Nonetheless, only few research works [22] have studied the effects of Cassava Starch and the use of maleated Natural Rubber (MNR) on the physical properties of Natural Rubber (NR).

Thus, this research is aimed at assessing the potential use of cassava starch (CS) in Natural Rubber compounds in its natural state and after been plasticized (PCS), by studying the rheological and tensile behavior and thermal ageing of vulcanized NR compounds. The authors also studied the synthesis and use of maleated Natural Rubber (MNR) as a coupling agent.

2. EXPERIMENTAL

Compounds prepared were based on Natural Rubber (NR) supplied by Distribuidora Poliquímica and 10, 20, 40 and 60 phr of cassava starch (CS). The latter came from plantations in Miranda state, Venezuela.

Glycerol (Aldrich) was used to treat the Cassava Starch. The Maleic Anhydride (MAH) used to prepare the graft copolymer was also obtained from Aldrich Chemical Company. Toluene and ethanol

used for washing and recovering the graft copolymer were supplied by J. T. Baker. Xylene (Fisher Scientific) was employed as a solvent for titration. A solution of sodium hydroxide in methanol was prepared as the titration solution. Phenolphthalein (Fisher Scientific) was used as a titration indicator.

The thermoplastic starch (PCS) was prepared in an internal mixer Haake Rheomix, varying the water and glycerol content. The optimum composition chosen was 33% water, 19% glycerol and 48% cassava starch [23]; if the water content increased, the starch obtained was very viscous and very difficult to work with, while if the water percentage was lowered, a hardening of the starch occurred. The increase in glycerol content gave rise to a gel-type starch, which was very difficult to process.

In order to select the mixing conditions of the starch, glycerol and water blend, the temperature and the rotor speed were varied, with the optimum values being 70°C and 50 rpm. Mixing time was reduced to the minimum (5 min) where the blend could be homogeneous and have a plasticized consistency, that is to say, with the possibility of milling it for mixing it afterwards with the polymer.

Before the plasticization, the starch, glycerol and water blend was let stand at room temperature for one hour, so starch particles could swell in the water. The thermoplasticized starch (CSP) obtained was dried for 24 hours in a convection oven at 90°C. Then, it was passed through a mortar and milled until the minimum particle size was obtained.

NR was modified through a functionalization process for the purpose of using it as a coupling agent. Natural Rubber functionalized with maleic anhydride (MNR) was prepared in a Haake Rheomix with a capacity of 50 g. The functionalization took place without the presence of a chemical initiator; the shear action of the rotors was sufficient for generating the free radicals.

Before functionalizing the NR, it was dried in a vacuum oven at 40°C for 24 h. Then it was introduced in the internal mixer and mixed for 2 min at 135°C and at a rotor speed of 60 rpm. A determined quantity of maleic anhydride (3, 5, 7, 9 and 11 wt%) was then incorporated, mixing it at the same temperature and rotor speed for 10 min. The non reactive maleic anhydride was removed from the mixture by reflux in toluene at 100°C for 6 h. The solution was precipitated with an excess of

acetone, and then filtered and dried in a vacuum oven for 24 h at 40°C [24].

The quantity of MA grafted onto the NR was determined by titration of the acidic groups derived from the anhydride functions. The dried and purified functionalized NR (0.3 g) was again dissolved in 30 ml of xylene at 120 °C. Distilled water was added to hydrolyze the anhydride functional groups into carboxylic acid functional groups. Then the solution was refluxed for 2 h to complete the hydrolysis. The carboxylic acid concentration was determined by titration of a sodium hydroxide solution in methanol 0.01 M. The indicator used was a solution of 1% phenolphthalein in methanol. The carboxylic concentration was converted to the grafted MA content as follows [25,26]:

$$\% \text{ grafted MA} = \frac{V_t C_t E_W}{E_W} 100 \quad (1)$$

Where: V_t is volume of NaOH solution in MeOH (L); C_t is concentration of NaOH in MeOH (mol/L); E_W is specific weight of maleic anhydride (98g/mol) and W is sample weight (g).

Pressed molded films of each MNR were analyzed in a Nicolet Magna 750 FT-IR spectrophotometer, within the range of 4000 cm^{-1} to 400 cm^{-1} .

Additives for all formulations based on 100 parts of rubber were: 1 phr of antioxidant, 5 phr of zinc oxide (ZnO) and 2 phr of stearic acid used as activation complex, 1 phr of dibenzothiazole disulphide (MBTS) used as the accelerator and 2.5 phr of sulfur (S) used as the vulcanizing agent.

All compounds shown in Table 1 were prepared using a Banbury® internal mixer, at a rotor speed of 60 rpm. NR and MNR were mixed in ratios of 90/10 and 80/20, respectively. For each proportion of MNR, one formulation without cassava starch and one with 20 phr of cassava starch were prepared.

Curing characteristics were studied using a Rotorless rheometer model EKT-2.000SP at 160°C and 0.5° oscillation according to the ASTM D5289 procedure. Tensile and tear properties of the vulcanized blends were determined using a Lloyd Instruments machine model EZ20 according to the ASTM D412 and ASTM D624 procedures. Test for hardness was carried out using a Shore type A Durometer in accordance with ASTM D2240.

Crosslinking density was determined by equilibrium swelling measurements in toluene, of small pieces of vulcanizates during 72 h at room temperature.

Table 1. Formulations.

Materials	NR (phr)	MNR (phr)	CS or PCS (phr)
NR	100	-	-
NR/CS10; NR/PCS10	100	-	10
NR/CS20; NR/PCS20	100	-	20
NR/CS40; NR/PCS40	100	-	40
NR/CS60; NR/PCS60	100	-	60
NR/MNR(90/10)	90	10	-
NR/MNR(80/20)	80	20	-
NR/MNR(90/10)/CS20	90	10	20
NR/MNR(80/20)/CS20	80	20	20

The swollen samples were weighed, the solvent was removed in air for three days, and then the dried pieces were weighed again. The volume fraction of the rubber in the swollen vulcanizates (V_r) was then calculated using the following equation [27]:

$$V_r = \frac{(m_1 / \rho_r) - V_f}{(m_1 / \rho_r) - V_f + (m_2 - m_3) / \rho_s} \quad (2)$$

Where: m_1 is the initial weight of the specimen; m_2 is the weight of the swollen specimen; m_3 is the weight of the specimen after solvent evaporation; V_f is the volume of the filler, ρ_r is the density of rubber; and ρ_s is the density of the solvent (866.9 kg/m^3 for toluene) [28]. V_r was then replaced in the Flory–Rehner equation:

$$M_c = \frac{\rho_r V_0 (V_r^{1/3} - V_r / 2)}{\ln(1 - V_r) + V_r + \mu V_r^2} \quad (3)$$

Where M_c is the molecular weight of polymer chains between two crosslinks, μ is the polymer–solvent interaction parameter ($\mu = 0.42$ for NR–toluene) [27], and V_0 is the molar volume of solvent ($V_0 = 106.2 \times 10^{-3} \text{ m}^3/\text{mol}$ for toluene) [27]. Crosslinking density (ν) can be calculated as $1/2M_c$.

The thermal ageing resistance test of NR vulcanizates was performed in order to determine the influence of elevated temperatures and time on the mechanical properties and on the crosslinking density of vulcanized rubber with and without cassava starch, compared to the unaged specimens, based on ASTM D 573–88 and ASTM D 2000. The dumbbell specimens were placed in a hot-air oven at a temperature of 70°C for 70 h.

Morphological studies of cryogenically fractured samples of NR with CS and PCS were carried out using a scanning electron microscope (SEM), Hitachi S-2400. Samples were fractured in liquid nitrogen and the surface covered with a thin layer of platinum–palladium.

The temperature for the initiation of the degradation process (T_{id}) and the activation energy (E_a) were determined from the thermograms obtained in a thermogravimetric analyzer (TGA) Mettler Toledo Star System. In particular, the activation energy is a parameter related to the thermal stability of the material, thus it can be used as an indicative of the beginning of the degradative process. The conditions at which the thermograms were obtained were: heating rate of 10°C/min in nitrogen atmosphere and within temperature range from 20 to 650°C. The average weight of the samples was 10 mg. The values of T_{id} were determined by the derivative of the weight loss curve as a function of temperature.

3. RESULTS AND DISCUSSION

Concerning the morphology of the treated starch, Figure 1 shows that there occurs a major formation of agglomerates due to swelling [29], if compared to the size of the original structure of the natural cassava starch (Figure 2).

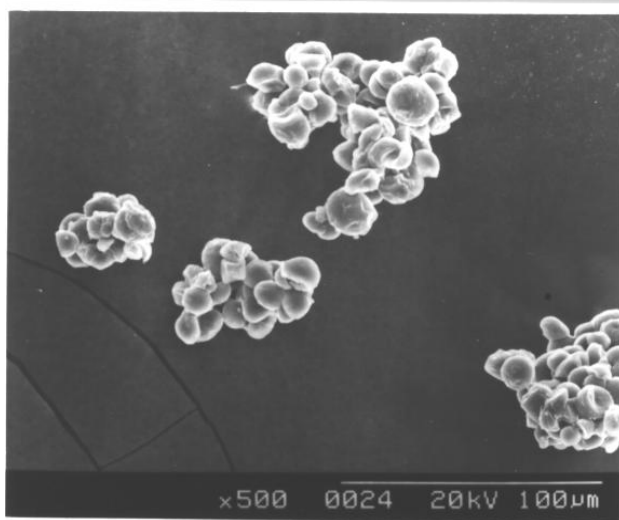


Figure 1. Microphotograph of plasticized cassava starch.

From the FT-IR spectra of the maleated natural rubber (MNR) presented in Figure 3, we can notice the presence of peaks corresponding to the absorbances at 1667 and 836 cm^{-1} resulting from the stretching of the C=C bond of the NR, and at 1720 cm^{-1} characteristic of the carbonyl groups due to the

carboxylic acid formed by the reaction of the anhydride functional group with moisture (the anhydride peaks at 1850 and 1780 cm^{-1} have disappeared, indicating that a ring-opening reaction of the anhydride group has taken place) [30]. The possible mechanisms of functionalization of NR with AM and of hydrolysis of the MNR are shown in Figures 4 and 5 [21].

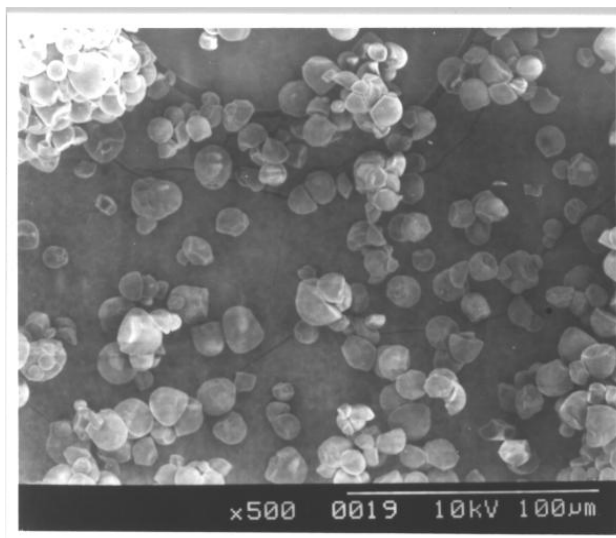


Figure 2. Microphotograph of natural cassava starch grounded.

Also, with respect to the functionalization of NR, Figure 6 shows an increase in the grafting degree with the monomer content, until a maximum is reached at 7 wt% of maleic anhydride. This behavior is due to possible reactions of homopolymerization of the MAH when the amount of MAH increases [31]. In spite of this result, the NR functionalized with 7 wt% was employed for the compatibilization of the compounds studied in this work.

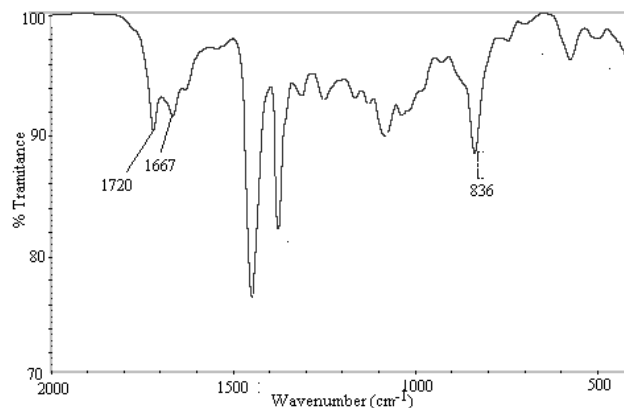


Figure 3. Spectrophotometry of MNR with MAH (7wt%).

An example of the curing behavior of NR and NR blended with 20 phr of CS is presented in Figure 7. Both curing curves have a maximum torque and a slight reversion at the final stage of the test. The reversion process is typical for a NR vulcanized with a conventional system, where the amount of sulfur is larger than the amount of accelerants, and basically consists of the progressive decrease of the crosslink structures due to the temperature and shear effect. The level of reversion is slightly lower for the compound with CS.

Table 2 shows that the minimum and maximum elastic torque ($S'_{\min}$ and $S'_{\max}$) of NR formulations increased slightly with the CS content. In general, the presence of fillers restricts deformation, and

consequently, the compound becomes harder and stiffer thereby increasing the torque of the vulcanizates. However, at a similar filler loading, PCS-filled vulcanizates consistently exhibit lower $S'_{\max}$ than CS-filled vulcanizates, being this effect more pronounced for higher contents of PCS (40 and 60 phr). On the other hand, the minimum torque for the NR/PCS compounds does not exhibit changes while the PCS content increases; in this case, there seems to be a competition between two processes: the rise in the viscosity of the elastomers due to the presence of a rigid filler and the decrease in viscosity as a result of the plasticization effect of the glycerol.

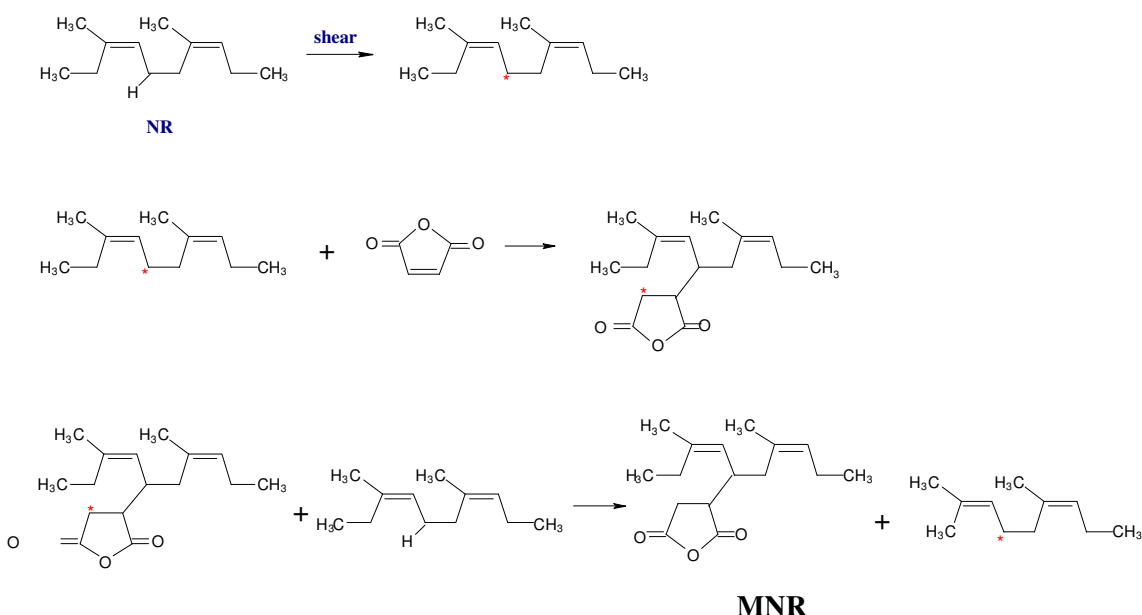


Figure 4. Possible mechanisms of functionalization of NR with AM²¹.

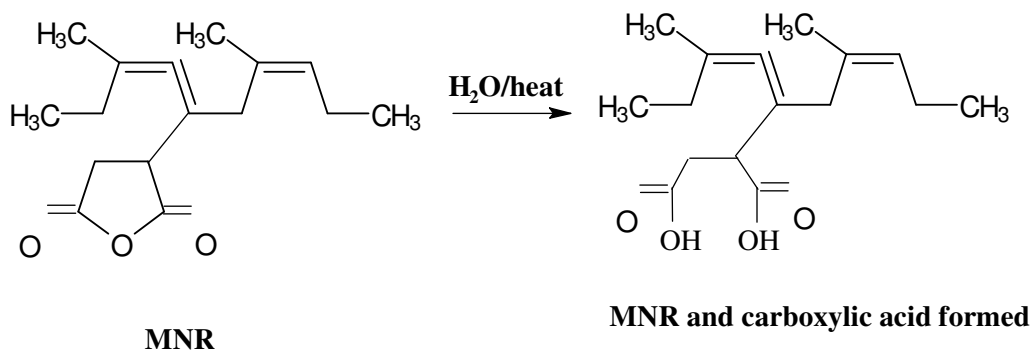


Figure 5. Hydrolysis of the MNR²¹.

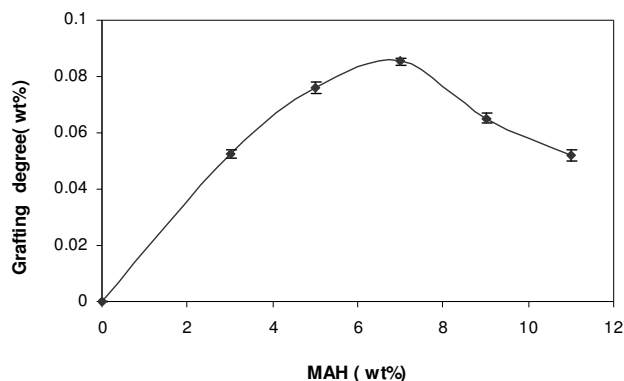


Figure 6. Functionalization degree vs. maleic anhydride (MAH) content.

The data presented in Table 2 also indicates that the time needed to reach 90% of the maximum torque (t_{90}) and the scorch time (t_{s2}) of those formulations filled with CS are slightly lower than those of NR. The decrease in t_{s2} values can be related to the basic character of cassava starch, which is responsible for the shorter times that the filled composites need for beginning the cure reaction. Similar results were obtained by Martins *et al.* [32] in their work on the addition of cellulose II to polychloroprene, where they reported a decrease in the scorch time due to the basic nature of the cellulose. It is known that the presence of small amounts of organic bases accelerates the vulcanization process of natural rubber with sulphur [33].

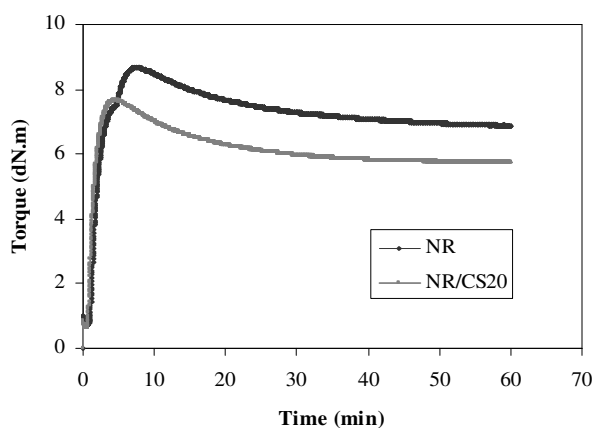


Figure 7. Curing curves of NR and NR/CS20.

In the formulations with PCS, the decrease in the scorch time and in t_{90} with respect to pure NR is higher than in the formulations with CS. This tendency is even more evident in the curing rate index (CRI) values (Table 2). The CRI is a parameter proportional to the average slope of the curing rate in the step region ($100/(t_{90}-t_{s2})$). The

positive effect of the treated filler on the curing rate is probably attributed to the increase in the amount of OH groups caused by the use of glycerol in the plasticization process of the cassava starch that enhances the curing rate even more [33].

On the other hand, when replacing part of the NR by its maleated homologous (MNR), t_{s2} and t_{90} increased considerably for both the formulations with CS as well as without CS (Figure 8); the delay of the curing of mercapto-accelerated compounds is due to the reaction between the MBTS and the free maleic anhydride and/or succinic acid (from a ring-opening reaction of the grafted maleic anhydride) [12]. The occurrence of this type of reactions decreases the amount of accelerant that will effectively actuate in the vulcanization reaction of the rubber. Therefore, when increasing the proportion of MNR in the blend, the increase in both times (t_{s2} and t_{90}) is even more evident. In addition, Table 3 presents the values of the minimum and maximum torque of the MNR and of the NR/MNR blends. As it can be seen, the maximum torque of the MNR is markedly lower than the value corresponding to NR (Table 2). This result is probably a consequence of the degradative action suffered during the synthesis, which lowers the molecular weight of this rubber.

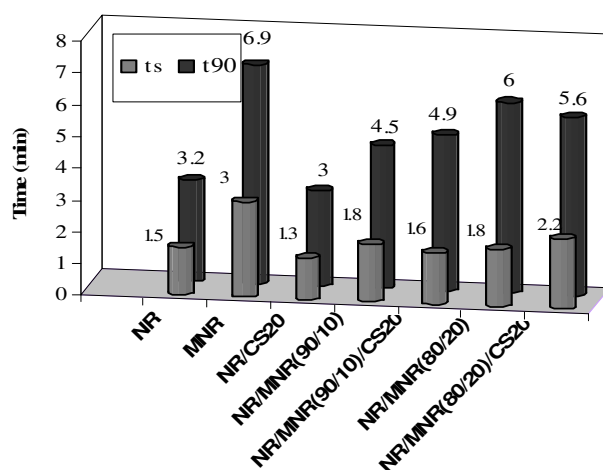


Figure 8. Scorch time and cure time of NR, MNR and NR/MNR blends with and without CS.

Besides, the NR/MNR blends in ratios of 90/10 and 80/20 show torque values lower than those obtained for the pure polymers, but very close to those of MNR. The effect of the filler on these parameters is similar to the behavior already discussed for the NR-CS formulations.

Regarding the mechanical performance of the blends hereby studied, Table 4 shows the tensile strength of the NR compounds. It is worth mentioning that the values of the tensile stress at 100% (σ_{100}) and at 300% (σ_{300}) of elongation of the NR/CS compounds increase up to 20 phr and then decrease with further filler loading. The incorporation of the filler into the rubbery matrix improves the stiffness of the vulcanizates [32].

Also, the tensile strength (σ_r) and the elongation at break (ϵ_r) of the NR compounds with up to 20 phr of CS are not considerably modified, since the values are similar to those of pure NR. However, when the CS content is further increased (40 and 60 phr), the tensile properties decrease due to the formation of filler aggregates that act as an isolated body that

cannot be dispersed in the NR matrix, and consequently, increase the hardness of the compound, actuating as stress concentration points and decreasing modulus.

For the NR/PCS blends, σ_{300} and σ_r decrease with the PCS content; these values are generally lower than the ones obtained with the unmodified CS. This behavior can be attributed to the fact that the PCS has a less reinforcing effect, possibly due to the water content and to the glycerol content used in the gelling process that can exert a plasticizing effect (also observed on the lower values of σ_{100}), as well as to the greater size of agglomerates when the starch is plasticized as previously mentioned. Nonetheless, the elongation percentage does not vary when the PCS is added.

Table 2. Curing Parameters of NR, NR/CS and NR/PCS.

Formulation	S'_{min} (dN.m)	S'_{max} (dN.m)	t_{s2} (min)	t_{90} (min)	CRI (min^{-1})	$S'_{max}-S'_{min}$ (dN.m)
NR	0.66	7.30	1.45	3.2	57.8	6.64
NR/CS10	0.68	7.08	1.3	2.9	61.3	6.40
NR/CS20	0.69	7.93	1.28	3.0	64.5	7.24
NR/CS40	0.79	8.04	1.35	3.0	62.5	7.25
NR/CS60	0.83	8.40	1.32	3.0	58.8	7.57
NR/PCS10	0.70	6.39	1.27	2.9	69.9	5.69
NR/PCS20	0.71	5.89	1.35	3.0	88.2	5.20
NR/PCS40	0.69	4.62	1.48	3.0	73.9	3.93
NR/PCS60	0.65	4.69	1.48	3.0	68.0	4.04

Table 3. Curing Parameters of MNR, NR/MNR and NR/MNR blends with and without CS.

Formulation	S'_{min} (dN.m)	S'_{max} (dN.m)	CRI (min^{-1})	$S'_{max}-S'_{min}$ (dN.m)
MNR	0.47	5.5	26	5.03
NR/MNR(90/10)	0.61	5.0	41	4.39
NR/MNR(80/20)	0.75	5.1	36.4	4.35
NR/MNR(90/10)/CS20	0.83	7.3	34.5	6.47
NR/MNR(80/20)/CS20	0.93	8.2	34.1	7.27

Tear strength of the NR (Table 4) decreases proportionally with the CS and with the PCS content. Greater rubber–filler interactions imply greater energy to produce a failure in the rubber, thus we can presume that in the NR/CS and NR/PCS compounds there is a predominance of filler–filler interactions and so tear strength decreases [34].

With respect to the hardness of the NR compounds, the data shown in Table 4 reflects that this property increases with the addition of CS; the viscosity of the rubber increases and so the elasticity of the chains is reduced, resulting in a more rigid rubber, a fact that is in accordance with the increase in the values of the maximum torque (Table 2) and in the tensile stress at 300% of elongation (Table 4). On

the other hand, the NR hardness when CS modified with glycerol is added (PCS), does not present significant variations. This tendency could be the result of a compromise between the plasticizing effect that produces the treatment of the starch and the increase in stiffness due to the presence of the filler.

As a preliminary conclusion, we can say that the addition of 20 phr of CS to NR brings about an increase in the curing rate (CRI), while the minimum torque does not vary significantly; in

other words, these two facts guarantee that the processing conditions of the NR will not be affected by the presence of the CS.

On the other hand, the treatment with glycerol does not apparently contribute to the improvement of the rubber–filler interactions and of the mechanical properties. This is the reason why 20 phr of untreated cassava starch were chosen as the optimum percentage for studying the effect of MNR in NR/CS blends.

Table 4. Physical properties of NR/CS and NR/PCS.

<i>Formulation</i>	σ_{100} (MPa)	σ_{300} (MPa)	σ_r (MPa)	ε_r (%)	<i>Tear strength</i> (kN.m)	<i>Hardness</i> (Shore A)
NR	0.90±0.07	1.8±0.1	22.4±1.8	1063±58	51.3±2.8	41
NR/CS10	0.94±0.05	1.8±0.1	18.6±1.6	1184±61	44.8±3	42
NR/CS20	1.20±0.05	2.1±0.1	21.3±1.9	1003±23	43.3±2.9	44
NR/CS40	1.17±0.1	1.8±0.1	14.2±1.1	967±23	36.2±2.9	47
NR/CS60	0.97±0.03	1.5±0.05	9.7±0.7	920±21	29.3±1.8	49
NR/PCS10	0.74±0.03	1.4±0.05	20.4±1.3	1302±16	45.6±3	40
NR/PCS20	0.96±0.05	1.6±0.1	16.5±1.2	1021±16	40.9±2.1	41
NR/PCS40	1.00±0.05	1.5±0.05	14.2±1.0	1002±26	35.7±3	41
NR/PCS60	1.06±0.05	1.4±0.1	12.2±1.1	1007±30	27.2±1.3	42

According to Table 5 the MNR did not act as a coupling agent, since the incorporation of 10 and 20 phr of MNR negatively affected the properties of pure NR and of NR filled with 20 phr of CS, by decreasing their tensile strength.

We also analyzed the influence of CS on the crosslinking degree (ν). The values obtained (Figure 9) denote that the presence of CS renders the vulcanization process of the NR compounds more difficult, even though a higher curing rate is achieved. We assume that this could be due to the

poor rubber–filler interactions, and consequently, it may possibly be the reason why the mechanical properties (tensile strength and elongation at break) decrease with respect to the unfilled NR. The crosslinking degree of the NR/PCS compounds did not show significant differences with respect to the NR/CS blends. In addition, the crosslinking degree decreases slightly with the use of MNR, and it seems independent of the quantity of MNR used. The incorporation of 20 phr of CS to these blends seems to make this behavior even more marked.

Table 5. Physical properties of NR/MNR formulations.

<i>Formulation</i>	σ_{100} (MPa)	σ_{300} (MPa)	σ_r (MPa)	ε_r (%)	<i>Tear strength</i> (kN.m)	<i>Hardness</i> (Shore A)
NR/MNR(90/10)	0.69±0.04	1.3±0.08	14.2±1.2	1098±55	41±3	37
NR/MNR(80/20)	0.67±0.02	1.3±0.04	15.6±1.3	1134±45	36.4±1.7	37
NR/MNR(90/10)/CS20	0.74±0.03	1.4±0.05	14.3±1.1	1078±52	34.5±2.8	40
NR/MNR(80/20)/CS20	0.69±0.03	1.3±0.05	13.9±0.5	1105±41	34.1±3	40

Figure 10 corresponds to the microphotographs of the NR/CS blends with different proportions of CS

(20 and 40 phr). The presence of two phases and the lack of a complete adhesion between the starch

particles and the NR can be clearly observed. The lack of adhesion was expected since no compatibility is achieved due to the polar nature of the starch and the non-polar characteristics of the NR. On the other hand, as the amount of CS increases, dispersion of the particles becomes more difficult and more agglomerates are formed, generating bigger particles with a more irregular shape. This fact could explain the decrease in the tensile properties for the greater filler proportions used. Concerning the plasticized cassava starch particles (Figure 11), they present shapes different to the natural starch due to the “gelatinous” consistency provided by the glycerol, as mentioned before.

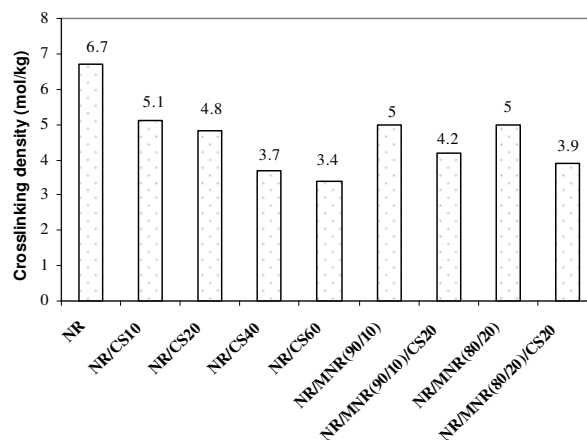


Figure 9. Crosslinking density of some of the formulations studied.

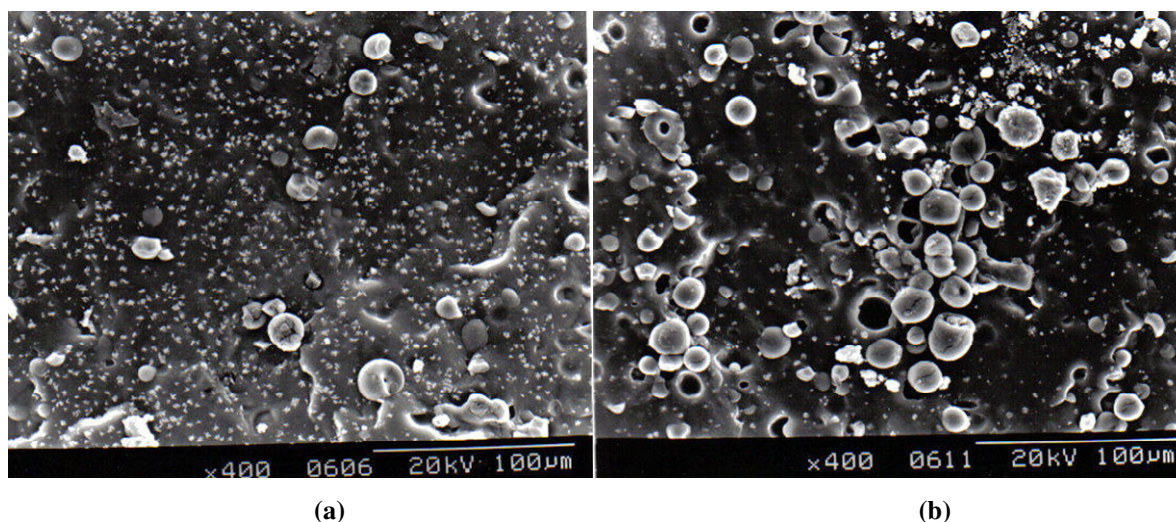


Figure 10. Microphotographs of NR/CS formulations with (a) 20 phr of CS and (b) 40 phr of CS.

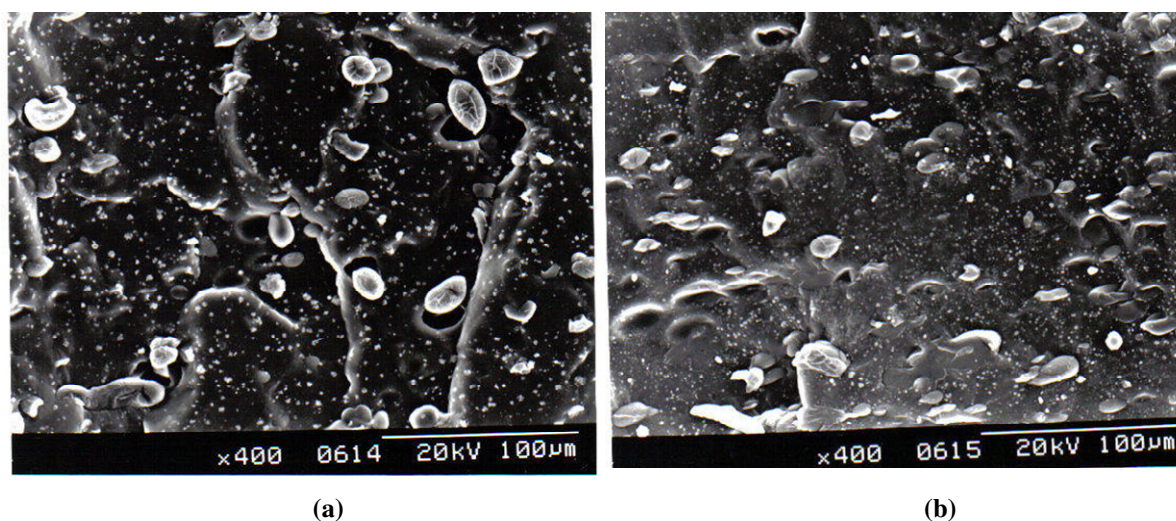
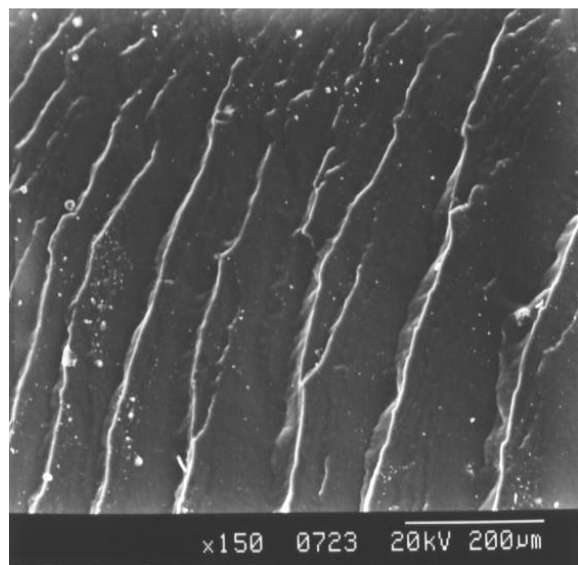


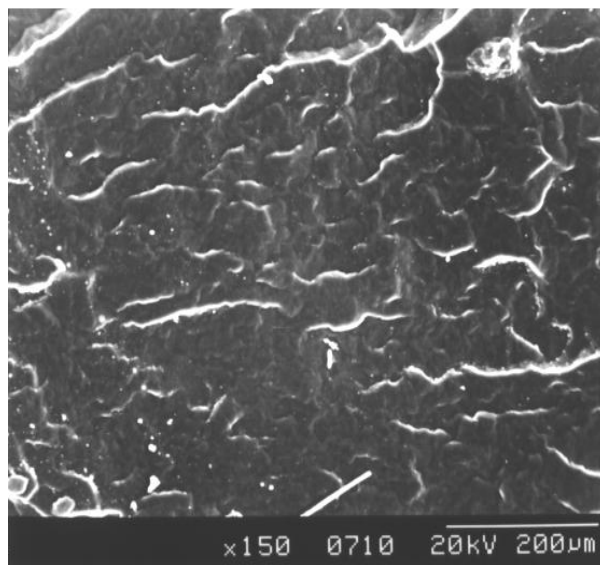
Figure 11. Microphotographs of NR formulations with (a) 20 phr of PCS and (b) 40 phr of PCS.

It can also be observed that the fracture surface of the NR changes with the MNR content (Figure 12). On the other hand, when 20 phr of filler are added for both blend ratios, greater adhesion with the elastomeric matrix can be observed. Figure 13b

shows that there are fewer cavities when compared with Figure 13a; therefore, it could be said that the interfacial adhesion could improve with a greater amount of MNR even though the mechanical properties do not increase.

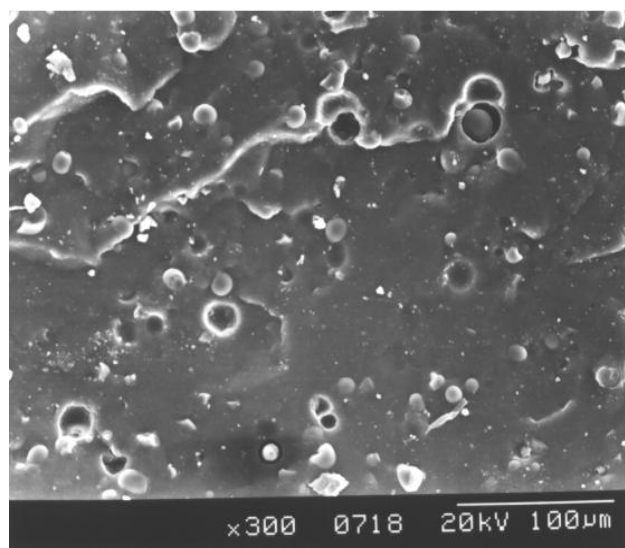


(a)

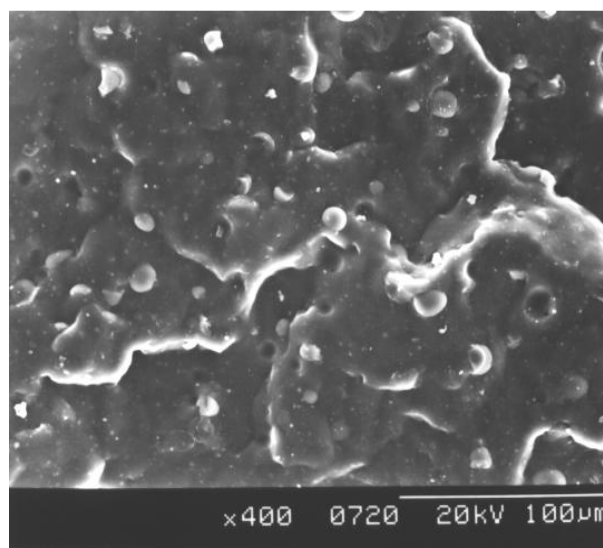


(b)

Figure 12. Microphotographs of the NR/MNR formulations: a) without MNR and b) with 10% MNR.



(a)



(b)

Figure 13. Microphotographs of the NR/MNR formulations with 20wt% CS: a) with 10% MNR and b) with 20% MNR.

The ASTM 2000 standard classifies the vulcanized elastomers according to the analysis of an accelerated ageing test. The purpose of this classification system is to orient the manufacturer as to how to select, in a practical and economic sense,

an elastomeric material. The results must be reported as the percentage variations (except hardness) that the mechanical properties suffer.

Table 6 shows the ageing effect on the mechanical

properties of the NR vulcanizates expressed according to the aforementioned standard. It can be seen that the tensile strength and the elongation at break decrease while the tear strength increases due to the action of temperature and oxygen. NR (poly(cis-1,4-isoprene)) has double bonds which render it particularly sensitive to oxidation in the presence of molecular oxygen [35]. The oxidation of the NR in solid state is complex and involves two competitive processes: scission and crosslinking which can occur simultaneously. Both processes can change the physical properties of the material.

Chain scission produces a drop in the molecular weight of the NR and molecular entanglements, thus resulting in a loss of stiffness and elasticity, whereas the increase in crosslinking reactions will result in increased stiffness and elasticity.

Table 7 presents the percentage variations of the crosslinking density due to ageing of some of the formulations studied; it can be seen that the change is positive for all of them, thus indicating an increase in the property. This effect is generally due to a deficient vulcanization of the NR during the molding process, and so the action of temperature in the ageing process produces the so-called post curing effect. The increase in the crosslinking density necessarily produces a greater stiffness in the rubber, reflected as a positive change in the tensile stress at 100% and at 300% of elongation and in hardness ($\Delta\sigma_{100}$, $\Delta\sigma_{300}$ and ΔH respectively).

The same behavior was observed by Pimolsiriphol [36] in a study on thermal ageing of NR vulcanizates. Ngolemasango *et al.* [37], in their study on the effect of ageing kinetics on the tensile properties of NR, concluded that the scission reactions have higher activation energy (for the modulus) than the crosslinking reactions. Therefore, at lower ageing temperatures between 70 and 100°C, crosslinking reactions prevail, and so an increase in the modulus at 100% occurs.

The decrease observed in tensile strength and elongation at break (negative values of $\Delta\sigma_r$ and $\Delta\epsilon_r$) can be explained according to the two mechanisms previously mentioned, since the scission reactions would cause a decrease in strength because the tensile stress would be carried on fewer chains. However, crosslinking should not necessarily have a negative effect on the mechanical properties associated to the rupture energy such as tear strength, tensile strength and elongation at break. These properties present a parabolic variation with the crosslinking density, that is to say, an increase until a maximum is reached and then, the property starts to decrease [38,39]. So, when NR faces an ageing process in the presence of oxygen, positive or negative variations on the above mentioned properties can be produced, depending on where the maximum value for each property is located with respect to the crosslinking density.

Table 6. Variation on the mechanical properties of aged NR and its formulations at 70 °C for 70 h.

Formulation	$\Delta\sigma_{100}(\%)$	$\Delta\sigma_{300}(\%)$	$\Delta\sigma_r(\%)$	$\Delta\epsilon_r(\%)$	ΔTS	ΔH (shore A)
NR	+6	+35	-12	-19	+10	+8
NR/CS10	+19	+2	-10	-8	+8	+9
NR/CS20	-7	+2	-28	-17	+15	+10
NR/CS40	+3	+7	-15	-14	-2	+8
NR/CS60	+29	+30	-13	-16	+6	+10
NR/PCS10	+43	+49	-22	-34	+5	+12
NR/PCS20	+23	+31	-10	-16	+24	+11
NR/PCS40	+45	+41	-7	-18	+14	+20
NR/PCS60	+40	+41	-11	-18	+25	+23
NR/MNR(90/10)	+15	+21	+39	+2	+18	+3
NR/MNR(80/20)	+19	+23	+30	0	+32	+2
NR/MNR(90/10)/CS20	+23	+29	+17	-5	+15	+4
NR/MNR(80/20)/CS20	+32	+36	+24	-8	+20	+3

In addition, Table 6 shows the variations in the tensile strength of the formulations with MNR; in this case, they are all positive, thus indicating an increase in this property. The crosslinking density of these compounds also increased when aged. Nonetheless, the optimum degree of curing was not surpassed due to the lower activity that these formulations presented faced with curing, as previously discussed (considerable rise in t_{90}).

Based on these results it can be determined that the NR/CS, NR/MNR and NR/MNR/CS compounds are in accordance with the requirements specified by the ASTM D2000 standard for a material classified as “2” AA grade when exposed to ageing. These changes correspond to maximum variations of $\pm 30\%$ in σ_{100} , σ_{300} and σ_r , $\pm 50\%$ in ϵ_r and ± 15 points in hardness.

Table 7. Variation on the crosslinking density of aged NR and some of its formulations at 70 °C for 70 h.

Formulation	$\Delta\delta(\%)$
NR	+24
NR/CS20	+29
NR/CS60	+16
NR/PCS20	+28
NR/PCS60	+13
NR/MNR(90/10)	+32
NR/MNR(80/20)	+30
NR/MNR(90/10)/CS20	+31
NR/MNR(80/20)/CS20	+30

The activation energy was determined by the E_2 function method [40], based on these results it can be observed that the activation energy (E_a) of the vulcanized NR (Table 8) is 67 kJ/mol. The addition of CS does not practically affect this property. This

result is contrary to the one observed in a study on PP/CS blends, where the addition of CS delayed the decomposition process of the PP [41]. It is important to specify that the degradative process of starch is highly complex, where the starch structure is destroyed and the amylase and amylopectine chains degrade.

With respect to the blends of NR with plasticized starch, one can see that E_a decreases, remaining constant with the PCS content. This means that the PCS accelerates the degradative process of the NR. With respect to the initial decomposition temperature (T_{id}), Table 8 shows that this value remains constant with the CS and PCS content. In addition, there is a rise in the residue with the starch content; González *et al.* [41] attribute this behavior in PP/CS blends to a crosslinked structure that is present in the starch granules, since it is impossible to eliminate all the water present due to the starch highly hygroscopic nature. For the NR/PSC compounds, the residue is even higher when compared to the non modified starch; this behavior is attributed to the swelling of the starch when it is heated with water and glycerol, giving rise to a paste, which would be the final residue. According to Sanguanpong *et al.* [42], this residue can be approximately 50% or more depending on the plasticization time, a fact that agrees with the results obtained in this study from the thermograms.

Table 9 presents the thermogravimetric analysis of the NR/MNR formulations. It is noticeable that the addition of MNR to NR brings about a decrease in the activation energy. This is probably due to the lower molecular weight of the MNR (lower value of S'_{min}) which is the result of the shearing action induced during the functionalization of the NR with DEM in the internal mixer.

Table 8. Activation Energy values and Initial Decomposition Temperature of NR/CS and NR/PCS formulations.

Filler (phr)	CS			PCS		
	E_a (kJ/mol)	T_{id} (° C)	Weight loss (%)	E_a (kJ/mol)	T_{id} (° C)	Weight loss (%)
0	67	342	6.5	67	342	6.5
10	70	339	11.1	46	340	10.8
20	69	341	16.6	47	338	20.3
40	68	338	22.2	48	340	30.7
60	66	339	25.7	45	337	31.5

Table 9. Activation Energy values and Initial Decomposition Temperature of NR/MNR formulations with and without CS.

<i>Formulation</i>	<i>E_a</i> (kJ/mol)	<i>T_{id}</i> (° C)	<i>Weight loss</i> (%)
NR/MNR(90/10)	45	344	6.4
NR/MNR(80/20)	45	340	7.3
NR/MNR(90/10)/CS20	44	336	16.1
NR/MNR(80/20)/CS20	44	338	16.1

4. CONCLUSIONS

Natural rubber–maleic anhydride graft copolymer (MNR) was successfully prepared in an internal mixer by the shear action of the rotors and without the need of initiators.

The addition of cassava starch as a filler in a NR compound resulted in an increase in the maximum torque and a slight decrease in the scorching and curing time. Besides, the addition of MNR to the blends of NR with and without CS retarded the curing process.

When cassava starch, considered a biopolymer, was incorporated in a proportion of 20 phr to NR compounds, it did not alter the tensile properties of this elastomer, thereby rendering the formulation cheaper. The treatment of the starch with glycerol did not apparently contribute to improving the rubber–filler interactions, since the mechanical properties obtained when treated CS was added to the NR where in general lower than those of the vulcanizates filled with the natural starch.

The blends with MNR with and without CS did not improve the overall properties of NR.

The NR/CS, NR/MNR and NR/MNR/CS compounds were in accordance with the requirements specified by the ASTM D2000 standard for a material classified as AA. That was not the case of the compounds with PCS.

The thermal degradation behavior of NR was not affected by the addition of cassava starch, while the use of plasticized cassava starch accelerated the degradative process of the NR.

5. ACKNOWLEDGEMENTS

The authors wish to thank the DID–USB, the technical staff from Laboratorio E–USB, Universidad Central de Venezuela, IVIC and FONACIT for the financial support through the grant G–2001000817.

6. REFERENCES

- [1] Ichazo MN, Albano C, González J, Perera R, Candal MV. *Composite Structures*. 2001; **54**: 207–214.
- [2] Ichazo MN, Albano C, González J. *Polym. Int.* 2000; **49**: 1409–1416.
- [3] Albano C, Reyes J, Ichazo M, González J, Chipara M. *Polym. Deg. Stab.* 2001; **73**: 225–236.
- [4] Wang Y, Liu W, Sun Z. *J. Appl. Polym. Sci.* 2004; **92**: 344–350.
- [5] Ismail H, Ishiaku US, Aribab AR, Mohd Ishak ZA. *Int. J. Polymeric Mat.* 1997; **36**: 39–51.
- [6] Zurima M, Ismail H, Bakar AA. *J. Appl. Polym. Sci.* 2004; **92**: 3320–3332.
- [7] Vladkova TG, Dineff PD, Gospodinova DN. *J. Appl. Polym. Sci.* 2004; **92**: 95–101.
- [8] Vladkova TG, Dineff PD, Gospodinova DN. *J. Appl. Polym. Sci.* 2004; **91**: 883–889.
- [9] Hernández M, Ichazo M, González J, Albano C. *ANTEC Proc.* 2004; **3**: 238–242.
- [10] Zuchowska D, Hlavata D, Steller R, Adamiak W, Meissner W. *Polym. Deg. Stab.* 1998; **64**: 339–346.
- [11] Xiaofei M, Jiugao Y. *J. Appl. Polym. Sci.* 2004; **93**: 1769–1773.
- [12] Xiaofei M, Jiugao Y, Feng J. *Polym. Int.* 2004; **53**: 1780–1785.
- [13] Simons A, Baker WE. *Polym. Eng. Sci.* 1998; **29**: 1117–1123.
- [14] Botros SH, Moustafa AF. *J. Elast. Plast.* 2002; **34**: 15–32.
- [15] Ichazo M, Hernández M, Albano C, Auimatre A, Gonzalez J. *ANTEC Proc.* 2005; **3**: 2456–2460.
- [16] Wilhelm HM, Felisberti MI. *J. Appl. Polym. Sci.* 2002; **83**: 2953–2963.

- [17] Nakason C, Kaesman A, Homsin S, Kiatkamjornwong S. *J. Polym. Sci.* 2001; **81**: 2803–2813.
- [18] Nakason C, Kaesman A, Wongkul T, Kiatkamjornwong S. *Plast. Rubber Comp.* 2001; **30**: 154–161.
- [19] Nakason C, Kaesman A, Sainamsi W, Kiatkamjornwong S. *J. Appl. Polym. Sci.* 2003; **91**: 1752–1762.
- [20] Nakason C, Kaesman A, Rungvichaniwat A, Kiatkamjornwong S. *J. Appl. Polym. Sci.* 2003; **89**: 1453–1463.
- [21] Nakason C, Saiwaree S, Tatun S, Kaesaman A. *Polym. Test.* 2006; **25**: 656–667.
- [22] Kiatkamjornwong P, Surunchanajirasakul P, Tasakorn P. *Plast. Rubber Comp.* 2001; **30**: 318–327.
- [23] Rodríguez FJ, Ramsay BA, Fabis BD. *Polymer* 2003; **44**: 1517–1526.
- [24] Nakason C, Saiwaree S, Tatun S, Kaesaman A. *Polym. Test.* 2006; **25**: 656–667.
- [25] Li HM, Chen HB, Shen ZG, Lin S. *Polymer* 2002; **43**: 5455–5461.
- [26] Nakason C, Kaesaman A, Supasanthitikul P. *Polym. Test.* 2004; **23**: 35–41.
- [27] Castro DF, Suarez JCM, Nunes RCR, Visconte LLY. *J. Appl. Polym. Sci.* 2004; **94**: 1575–1585.
- [28] Brandrup J, Immergut EH, Grulke EA, *Polymer Handbook*, 1999; 4th edn., Wiley-Interscience, Vol 1: p. III-61.
- [29] Gupta AP, Sharma M, Kumar V. *Polym. Plast. Technol. Eng.* 2008; **47**: 953–959.
- [30] Saleao J, Phinyucheep P. *J. Appl. Polym. Sci.* 2002; **95**: 28–38.
- [31] Ganzeveld KJ, Janssen PB. *Polym. Eng. Sci.* 1992; **32**: 467–474.
- [32] Martins AF; De Meneses SM, Visconte LL, Nunes RC. *J. Appl. Polym. Sci.* 2004, **92**: 2425–2430.
- [33] Morton M, *Physical Testing of Vulcanizates, Rubber Technol.*, 2da Ed. Van Nostrand Reinhold Com. 1995, p. 74–75.
- [34] Wang MJ, Zhang P, Mahmud K. *Rubber Chem. Technol.* 2001; **74**: 124–137.
- [35] Brydson JA, (ed), *Rubber Chemistry*, 1978; Applied Science Publishers. Chap.4: 70-98.
- [36] Pimolsiriphon V, Saeoui P, Sirisinha C. *Polym. Plast. Technol. Eng.* 2007; **46**: 113–121.
- [37] Ngolemasango EF, Bennett M, Clarke J. *J. Appl. Polym. Sci.* 2006; **102**: 3732–3740.
- [38] Mark JE, Erman B, Eerich FR. *Sci. Technol. Rubber*, 1994; Academic Press.
- [39] González L, Rodríguez A, Marcos A, Chamorro C. *Rubber Chem. Technol.* 1996; 69(2): 203–214.
- [40] Chen H, Lai K, Lin Y. *J. Chem Eng. Japan* 2004; **37**: 1172–1178.
- [41] González J, Albano C, Hernández M, Ichazo MN. *Revista de la Facultad de Ingeniería, UCV.* 2009; **24**: 31–44.
- [42] Sanguanpong S, Chotineeranat S, Piyachamkwan K, Oates CG, Chinachoti P, Sriroth K. *J. Sci. Food Agric.* 2003; **83**: 760–768.