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Investigation of NBR-cellulose II nanocomposites by rheometric and equilibrium swelling properties

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Summary

Nanocomposites of butadiene-acrylonitrile copolymer (NBR) and cellulose II were obtained from mixtures of nitrile rubber latex and cellulose xanthate by using a co-coagulation system. The influences of low and medium acrylonitrile content in NBR and the cellulose II content, varying from 0 to 30 phr, were investigated by means of rheometric and equilibrium swelling experiments. The cure parameters obtained from the Oscillating Disk Rheometer data were utilized to characterize the structure of cellulose II present in the rubber vulcanizates through Wolff's equation. The swelling experiments were analyzed by using Flory-Rehner theory and Kraus and Cunneen-Russel equations to evaluate the NBR-Cel II interaction. From the results it was possible to conclude that cellulose II promotes a positive influence on cure parameters and crosslinking formation. It was also observed that the high butadiene content in NBR facilitated the interaction rubber-cellulosic component. The dispersion and distribution of cellulose in NBR matrix gave rise to nanomaterials, as observed by transmission electron microscopy.

Introduction

The effective additional crosslinks that reduce swelling in the filled vulcanizate presumably arise from a combination of several mechanisms. Possibilities that have been advanced include adhesion of the matrix through physical adsorption on the filler surface, chemical bonding of elastomer to the filler surface and formation of excessive polymer crosslinks at or near the surface of the filler by nonspecified catalytic effects. Swelling studies related to polymer-particle interaction have been limited previously to equilibrium swelling data. For this, three factors are balanced: on the one hand the solvating tendency of the swelling fluid tending to expand the elastomer network, the entropy effect causing the network to tend to contract and on the other hand extraction soluble materials by the swelling fluid [1-3].

Fillers are known to influence the crosslinking reaction during vulcanization. A convenient and simple technique to study effects on cure rate and crosslinking is by using Oscillating Disk Rheometer data [4,5].

The swelling measurements of vulcanized rubbers in contact with organic solvents are used to determine the crosslinking density, which can be related to changes in physical properties. The degree of swelling depends upon the compatibility of the rubber and the solvent on a molecular scale. It also depends on the amount and type of filler present in the rubber [1,6-9].

There is a very pronounced decrease in matrix swelling when reinforcing fillers are added. The degree of swelling is quantitatively expressed by the Flory-Rehner theory through Equation (1) which is frequently used to calculate ν, the crosslink density, from swelling measurements [10]:

$$\nu = -\frac{[\ln(1-V_r)+V_r+\chi V_r^2]}{V_o(V_r^{1/3}-1/2V_r)} \qquad \mathbf{(1)}$$

In this equation, V_0 is the molar volume of the solvent, V_r is the volume fraction of rubber in the swollen gel and χ is the interaction parameter. From the equilibrium swelling of the filled vulcanizate it is possible to evaluate the polymer-filler interaction by using equations 2 and/or 3:

$$\text{Kraus equation: } V_{r0}/V_{rf} = 1-m\phi/(1-\phi) \qquad \mathbf{(2)}$$

$$\text{Cunneen-Russel equation: } V_{r0}/V_{rf} = ae^{-z} + b \qquad \mathbf{(3)}$$

where V_{r0} represents the volume fraction of rubber in the unfilled vulcanizate; V_{rf} 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; m is a parameter calculated from the slope of the curve and is related to filler-polymer interaction and filler structure in the vulcanizate, where higher values of m suggest stronger interaction between filler and the rubber matrix; z is the weight fraction of filler in the vulcanizate, and a and b are characteristic constants for the system [11-12].

The incorporation of cellulose II into elastomers, based on two different processes [13-14], has been a matter of interest of our research group [15-18]. Each process leads to composites with distinct properties but all the composites were found to be light coloured and in the nanoscale, no matter the process used. As a consequence of cellulose xanthate decomposition in acidic medium during its incorporation in the elastomeric latex, the formation of cellulose II is obtained [19-20].

In this work, cellulose xanthate was incorporated into two nitrile latexes, with 27 and 33% nitrile contents (NBR-27 and NBR-33) [14]. The nanocomposites were prepared by co-coagulating mixtures of nitrile latex and cellulose xanthate in acid medium in such a way as to have the cellulose II content varying from 0 to 30 phr [14,16-18]. Rheometric and equilibrium swelling properties of nitrile rubber nanocomposites were studied to evaluate the influence of cellulose II in the elastomeric matrix. Transmission Electron Microscopy (TEM) was used to show the dispersion and distribution of cellulose II within the rubbery matrix as nanoparticles.

Experimental

The butadiene-acrylonitrile copolymer (NBR) latexes were supplied by Nitriflex S.A. Indústria e Comércio, Rio de Janeiro, Brazil, with acrylonitrile contents of 33% (NBR-33) and 27% (NBR-27) and Mooney viscosities of 56 and 63, respectively. The cellulose xanthate was supplied by Vicunha Têxtil S.A., Americana, São Paulo, Brazil, with the following characteristics: 8 % cellulose, 2.13% total sulfur, 1.19% xanthic sulfur, 6.43% salt index and 4.94% NaOH.

In previous work [18] it was demonstrated that nanocomposites are formed during co-coagulation of rubber latex with cellulose xanthate mixture. In this work, each latex of NBR was mixed with cellulose xanthate and coprecipitated by a gradual addition of the mixture on to a $H_2SO_4/ZnSO_4$ 1:1 molar solution, with constant stirring. The cellulose II content in these compositions varied from 0 to 30phr. By using this system compounds of light colour were obtained.

Incorporation of additives was carried out on a Berstorff two-roll (10 cm x 22.5 cm) mill at 50^{o}C. The formulation used followed ASTM D 3187 (in phr): 100 rubber; 3.0 zinc oxide; 1.5 sulphur; 1.0 stearic acid; 0.7 N-t-butyl-2-benzothiazol sulfenamide (TBBS) and 0-30 cellulose II.

Cure parameters were determined at 150^{o}C and 1^{o} arc, using an Oscillating Disk Rheometer (Model TI 100) according to ASTM D 2084. The vulcanization was carried out at 150^{o}C, during cure times established previously in the rheometer, in an electrically heated hydraulic press. From the resulting torque-time curve, one can obtain:

- Minimum torque, M_{min}, representing the effective viscosity of the unvulcanized mix;
- Maximum torque, M_{max}, representing a measure of shear modulus or stiffness of the fully cured vulcanizate;
- Scorch time, ts_1, representing a measure of processing safety, being the time for a fixed small rise above the minimum torque to occur;
- Cure time, t_{90}, being the time to developed 90% of the highest torque;

Equilibrium swelling was carried out at room temperature in acetone, with molar volume V_o = 73.4 mol/cm^3 and the interaction parameter NBR-acetone χ = 0.345 (the value is the same for the two types of nitrile rubbers, in that the solubility parameters for NBR-33 and NBR-27 are similar, δ = 9.36 (cal/cm)^2 [21-24].

The degree of swelling is usually expressed in terms of the fraction:

$$V_r = \frac{Volume\ of\ rubber}{Volume\ of\ the\ swollen\ rubber - solvent\ gel}$$

In a filled vulcanizate the important unit is:

$$V_r = \frac{Volume\ of\ rubber\ in\ vulcanizate\ (total\ volume - filler\ volume)}{Volume\ of\ swollen\ rubber\ gel\ (total\ swollen\ volume - filler\ volume)}$$

and it is of interest to determine the ratio $R = V_{r0}/V_{rf}$ (V_{r0} is V_r of the unfilled vulcanizate), as a function of the increasing filler loading [25].

If the filler swelled just as much as the surrounding rubber-matrix, then that ratio would stay equal to unity as the percentage of filler in the compound increases. However, most fillers do not swell and if the matrix is restricted by the filler through attachments on the filler surface the ratio V_{r0}/V_{rf} will decrease as the filler loading increases. Remarkably, this ratio increases with increasing filler fraction if the filler is of the non-adhering type as was pointed out by Kraus [11,25].

The phase morphology was examined by Transmission Electron Microscopy (TEM) using a Hitachi H-800MT with GATAN (200kV).

Results and Discussion

Figures 1 and 2 show typical rheograms for NBR-Cellulose II compositions with different loadings of cellulose II. It can be seen that the curves for the NBR-Cel II system level off after reaching the maximum vulcanization. Table 1 presents the rheometer parameters, according to ASTM D 2084, for the compositions under investigation. The values of the minimum torque (M_{min}) increases with the increasing addition of cellulose II, which indicates the increase in viscosity of these compositions.

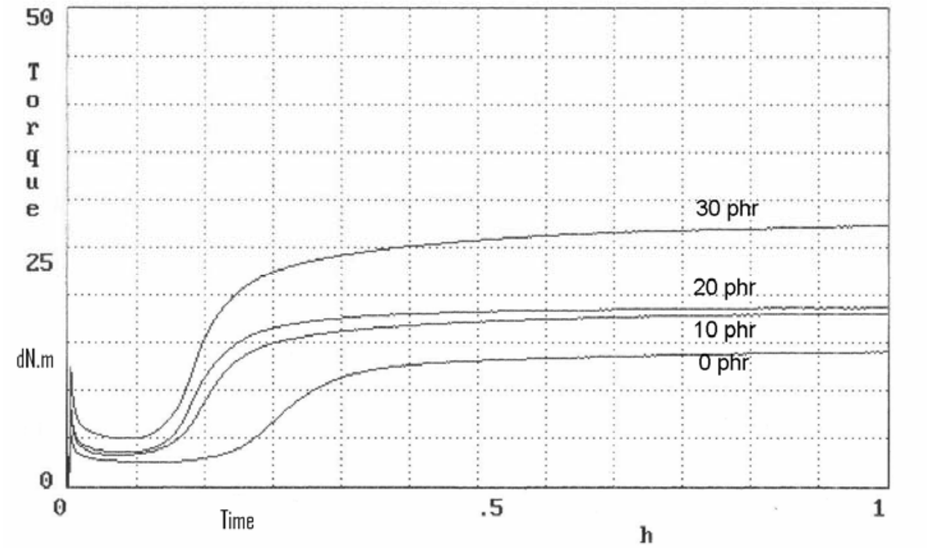

Figure 1 – Rheograms of NBR-cellulose II compositions (NBR-33)

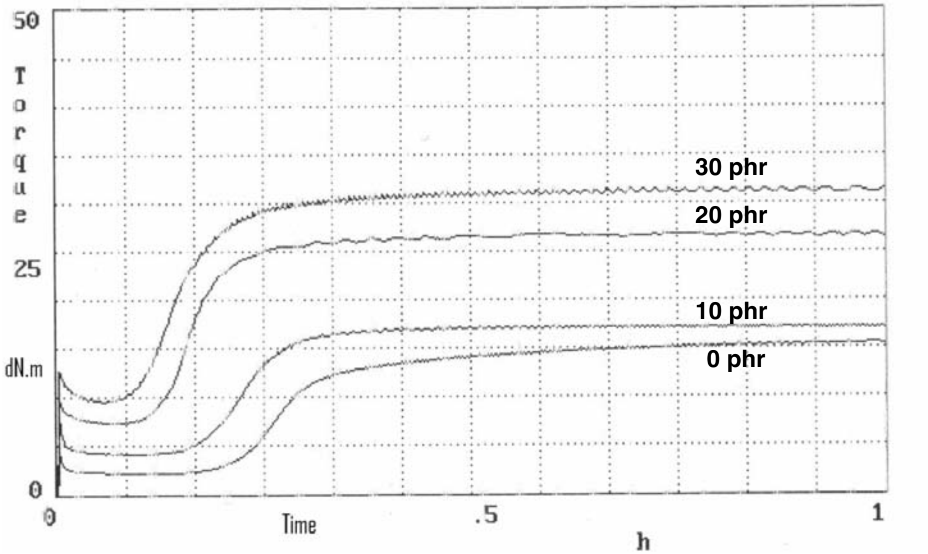

Figure 2 – Rheograms of NBR-cellulose II compositions (NBR-27)

The maximum torques (M_{max}) are also increased by the filler content as an indicative of developping stiffness caused by cellulose. The difference ($\Delta M = M_{max} - M_{min}$) can suggest an effective interaction filler-polymeric matrix, influencing crosslinking. Analyzing these rheometric data, two types of behavior are found: one related to the reactivity towards crosslinking leading to lower values of optimum cure time, upon addition of cellulose II, as compared to pure gum for both elastomers, and the other behaviour, concerned with molecular rigidity, as confirmed through minimum and maximum torque data, which are superior in the case of NBR-27, the rubber with the highest polybutadiene content.

Table 1 – Rheometric parameters of NBR/CEL II nanocomposites

NBR/cel II (phr)	M_{min} (dN.m)	M_{max} (dN.m)	$\Delta M = M_{max} - M_{min}$ (dN.m)	ts_1 (min)	t_{90} (min)
NBR 33					
100/0	2.4 ± 0.5	14.1 ± 0.8	11.7	11.4 ± 1.3	28.2 ± 1.7
100/10	3.2 ± 0.1	18.1 ± 0.1	14.9	7.2 ± 0.4	23.4 ± 1.7
100/20	3.5 ± 0.5	18.7 ± 0.2	15.2	7.2 ± 0.2	17.4 ± 0.4
100/30	4.9 ± 0.1	27.3 ± 0.6	22.4	6.6 ± 0	24.6 ± 1.1
NBR 27					
100/0	2.1 ± 0.3	15.5 ± 0.8	13.4	12.6 ± 0.1	31.8 ± 2.1
100/10	4.1 ± 0.4	17.2 ± 1.3	13.1	10.2 ± 1.3	18.0 ± 1.3
100/20	7.3 ± 0.9	26.9 ± 1.6	19.6	6.6 ± 1.5	15.0 ± 0.9
100/30	9.5 ± 1.5	31.5 ± 0.6	22.0	5.4 ± 0.4	16.2 ± 1.3

Another way of using the results from the oscillating rheometer is based on the investigations by Wolff [26-28]. The ratio between the increase in torque of the filled compound and that of the gum compound is directly proportional to the filler loading:

$$\frac{[\Delta M]^f}{[\Delta M]^g} - 1 = \alpha_F \frac{m_f}{m_p} \qquad (4)$$

where: $[\Delta M]^f = M^f{}_{max} - M^f{}_{min}$, is the maximum change in torque during vulcanization for the filled rubber and $[\Delta M]^g = M^g{}_{max} - M^g{}_{min}$ is the maximum change in torque for the gum. The ratio of the weight of filler to the polymer is expressed as m_f / m_p. By plotting these values against filler loading, a straight line is obtained. The slope was defined by Wolff as α_F, which in his investigation was shown to characterize the in-rubber structure of the carbon black (Figure 3) [26-28].

From Equation 4 and rheomeric data, Wolff characterized the structures of the filler present in rubber vulcanizates, particularly in the case of carbon black. For certain types of carbon black with constant surface area and particle size, α_F tends to increase as the different filler structures (low to high structure) show increasing tendency to agglomerate. So the parameter α_F represents the filler final structure, that is, how the filler is found in the vulcanizate after processing and vulcanization [26-28].

The application of the Wolff relationship allows to foresee if the crosslink density is affected or not by the presence of filler, by means of the linear analysis model. If a linear relationship is accepted for each composition, this implies to consider that α_F independs of the filler content and that the structures in the rubber matrix remain constant throughout the range investigated. If a non linear relation is obtained, the filler may be affecting the vulcanization [28]. So, in the Figure 3 and Table 2 the compositions with NBR-27 and NBR-33 present considerable deviation from linearity. This can indicate a direct influence of cellulose II on the vulcanization. The compositions studied in this work exhibit two very close values of α_F (Table 2): the lowest for the compositions with NBR-27, as an indication that in this elastomer, cellulose particles seem to be less packed (low structure) than in NBR-33 matrix. As expected the results of α_F are very close because the same filler was used. It can be concluded that the better dispersion of cellulosic component in NBR is a function of the higher content of polybutadiene in NBR (NBR-27).

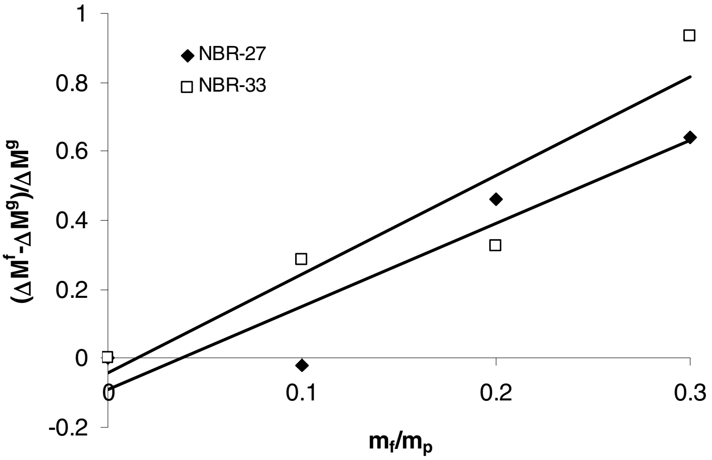

Figure 3 – Relative increase in the torque as a function of the filler loading plotted in the Wolff form

Table 2 – Parameters of Wolff's Equation

NBR-Cel II	α_F	Correlation coefficients R^2
NBR-33	2.85	0.8725
NBR-27	2.41	0.8707

Fillers, in general, reduce swelling and this effect is more pronounced with reinforcing filler than with inert one. The V_r (volume fraction of rubber in the swollen gel) depends on the density of the crosslinks so that, larger values means higher network complexity, resulting in lower degree of swelling. Observing the results shown in the Table 3, V_r increases with the increasing addition of cellulose II, specially for the compositions with NBR-27 thus corroborating maximum torque data and indicating a more pronounced influence of the filler on the crosslinks formation in this elastomer. The values of V_r were used to calculate the crosslink density according to Equation (1). The results of crosslink density based on equilibrium swelling, seen in Table 3, showed that the rubber with the highest content in butadiene (NBR-27) underwent a higher degree of crosslinking thus favouring the filler-rubber interaction. The presence of cellulose II induced a significant increase in the crosslink density and suggests a rubber-filler interaction.

Table 3 – Crosslink density and swelling parameters by Kraus and Cunnen-Russel equations of NBR/CEL II nanocomposites

NBR/ Cel II	ν ($x10^3$) (mol/cm^3)	Vr	Vr_0/Vr_f	$\phi/(1-\phi)$	m	e^{-z}	a	b
NBR 33					1.418		1.152	0.129
100/0	49	0.263 ± 0.001	1	0		1		
100/10	56	0.278 ± 0.001	0.946	0.055		0.918		
100/20	63	0.293 ± 0.001	0.898	0.111		0.853		
100/30	98	0.349 ± 0.001	0.754	0.166		0.803		
NBR 27					1.680		1.425	0.420
100/0	70	0.305 ± 0.002	1	0		1		
100/10	89	0.335 ± 0.005	0.911	0.056		0.918		
100/20	143	0.402 ± 0.004	0.759	0.111		0.853		
100/30	153	0.412 ± 0.005	0.741	0.166		0.803		

Kraus [11] showed that swelling of a large number of vulcanizates containing highly reinforcing fillers follows a mathematical model as described in Equation (2), that permits to evaluate the restriction to swelling of a matrix, imposed by filler. Figure 4 presents Kraus plots for different NBR-Cel II compositions. It is shown that elastomer-cellulose II compositions obey Equation 2. 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. In the present work, m is higher for the NBR-27 compositions, which means that the filler has a better interaction with this matrix. This result may be related to the flexibility of NBR-27, which is higher when compared with NBR-33.

Interaction is detected for every filled composition, in the filler range studied, as the ratio Vr_o/Vr_f is less than 1.

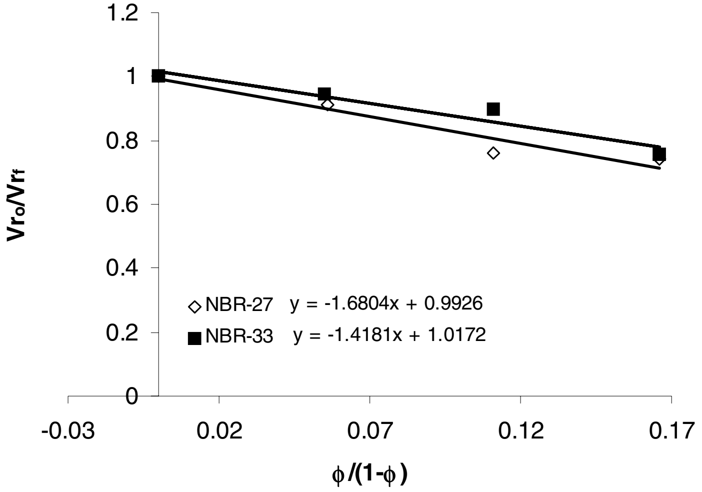

Figure 4 – Relationship between concentration of cellulose II and equilibrium volume swelling in acetone of NBR network plotted in the Kraus form

Figure 5 shows the Cunnen-Russel plots for the 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 of b indicate strong polymer-filler

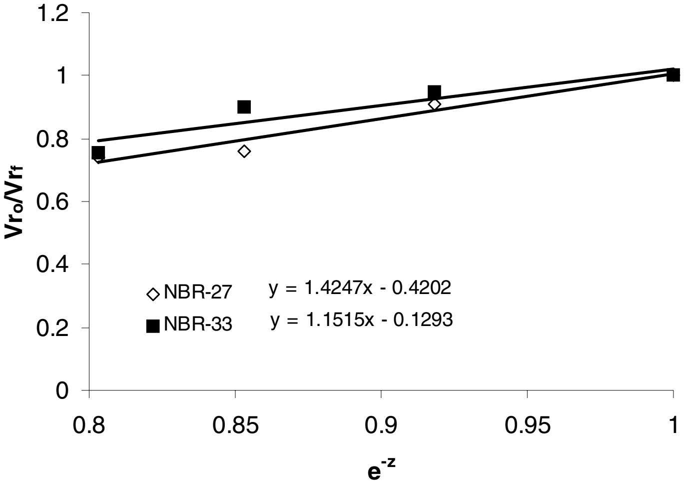

Figure 5 – Relationship between concentration of cellulose II and equilibrium volume swelling in acetone of NBR network plotted in the Cunneen and Russel form

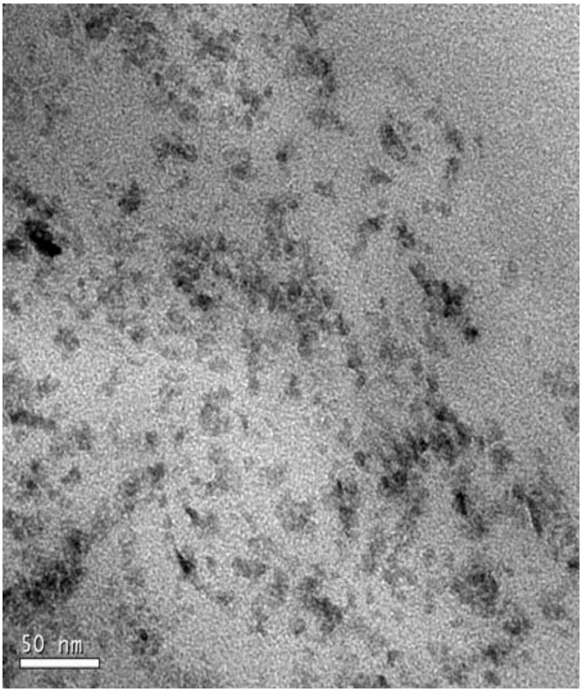

Figure 6 – Transmission electron microscopy of NBR/Cel II nanocomposite containing 20 phr of cellulose II (NBR-33)

attachment. The results in Table 3 show again that nitrile rubber has a good interaction with the cellulosic component.

The nanocomposite character of these NBR-Cel II systems was confirmed by transmission electron microscopy and is presented in Figure 6 that shows the good dispersion of cellulose.

Conclusions

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

- Cellulose II promotes a positive influence on cure parameters.
- Through the application of the Wolff´s equation it was possible to foresee an effect of cellulose II dispersion in rubber matrix.
- The presence of cellulose II induced a significant increase in the crosslink density and suggests a rubber-cellulose II interaction.
- Through the equilibrium swelling test in the filled vulcanizates it was possible to evaluate the rubber-cellulosic component interaction; this interaction was found to be facilitated by the higher butadiene content in NBR (NBR-27).
- The co-coagulation process is responsible for the obtention of nanocomposites, as comproved by Transmission Electron Microscopy.

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