Preparation, Structure, and Properties of Montmorillonite/Cellulose II/Natural Rubber Nanocomposites

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ABSTRACT: In this work, sodium montmorillonite clay was added, as filler, to nanocomposites of natural rubber (NR) and cellulose II (regenerated cellulose) in amounts varying from 0 to 5 phr (per hundred resin). Natural rubber (NR)/cellulose II/montmorillonite nanocomposites were prepared by co-coagulating NR latex, montmorillonite aqueous suspension and cellulose xanthate. The clay was previously exfoliated in water, and the resulting suspension was then added to the mixture of NR latex with cellulose xanthate. Morphological, rheometric, mechanical, and dynamic mechanical properties were evaluated, and an increase in these properties was observed upon the addition of cellulose and clay nanomaterials to the rubber matrix. The results show the advantage in using cellulose as a nanopolymer as well as MMT as nanofiller. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 458–465, 2011

Key words: nanocomposites; mechanical properties; rubber; nanolayers

INTRODUCTION

Sodium montmorillonite clay minerals have been used as reinforcement in rubber compositions in nature and in the organofilled form.[1–3] By exfoliating these layered silicates in water, which is accomplished by mechanical stirring at high speeds, it is possible to have the separated layers of sodium montmorillonite and the formation of an aqueous suspension. This exfoliation process of sodium montmorillonite in water gives rise to a nanoclay which can be observed by wide angle X-ray diffraction.[2] The polymer/clay nanocomposites form a new class of materials that stand out for their superior mechanical properties, such as low permeability to gases, and which are excellent as flame retardant materials. Other benefits provided are greater tensile strength, higher elastic storage coefficient, anti-flame properties, and higher chemical resistance. The gain in strength given by the clay-rubber nanocomposites is attributed to the structure resulting from the rubber and clay, built during processing.[4,5]

The remarkable performance of these materials has directed the researchers interest towards the development of nanocomposites of rubber/clay, and today many papers and patents have been published on the subject.[6–8] The nanocomposites of natural rubber/clay combine the properties of natural rubber with those of the clay, giving rise to a set of properties not found in any of the components individually. The use of clay as reinforcement in rubber compositions can be attained at clay levels lower than 10 phr, a very low value when compared to the higher loads of conventional fillers normally used.[9] The high aspect ratio of the exfoliated montmorillonite layers is responsible for the increase in mechanical properties of the resulting materials.[10]

Among the methods used to prepare elastomeric clay nanocomposites, the co-coagulation technique shows the advantages of eliminating the need for the chemical modification of the clay and the use of high temperatures. These two advantages allow the preparation of exfoliated and intercalated clay dispersions in natural or synthetic polymer latex.[11]

Natural rubber nanocomposites with cellulose II (regenerated cellulose)[12–16] have been developed by our research group. The co-coagulation system allows one highly crystalline polymer (cellulose II) to be incorporated in the form of nanopolymer on an amorphous one (NR), leading to excellent mechanical and low permeability properties.[14] The preparation of NR-cellulose II nanopolymer is based on co-precipitation of elastomeric latex with alkaline solution of cellulose xanthate.[15,16] From previous studies, it was observed that the incorporation of 15 phr of cellulose into NR promotes good mechanical performance.[15,16] So, in this work, the objective was

the study of properties resulting from the incorporation of cellulose II and montmorillonite clay as nanomaterials into natural rubber matrix. Compositions of NR with 15 phr of cellulose and varying levels of montmorillonite were prepared to combine the properties of the rubber, clay, and cellulose.

EXPERIMENTAL

Materials

Natural rubber latex (solid content 61.9%) was kindly supplied by Comércio e Beneficiamento de Látex Talismã Ltda (São Paulo, Brazil); Na-montmorillonite (Na-MMT) (Volclay SPV 200) from Wyoming, EUA was provided by Bentonit União Nordeste S. A.; and cellulose xanthate (cellulose content 9.8%) by Vicunha Têxtil S/A (São Paulo, Brazil). The vulcanizing ingredients and others additives were used as received.

Preparation of NR/cellulose II/clay nanocomposites

Na-MMT was purified according to Ref. 17. The purified product, at concentrations of 0–5 phr, was dispersed in deionized water with vigorous stirring until an aqueous suspension of silicate was obtained. This MMT suspension was then added to a given amount of NR latex under stirring. To this system (NR latex/Na-montmorillonite) cellulose xanthate solution containing 15 phr of cellulose II was added. The resulting system was kept under stirring until complete homogenization. This mixture was coagulated by adding, under stirring, an equimolar acid solution containing sulfuric acid and zinc sulfate. After coagulation, the fine rubber-cellulose II-MMT particles were washed with distilled water to remove the residual acidity. The product was separated from the aqueous suspension by filtration and dried in an air-circulating oven at 40°C.

The rubber compounds were prepared in an open two-roll mill at a speed ratio of 1 : 1.25, according to ASTM D 3182, at room temperature. The ingredients used to compound the rubber are presented in Table I.

Characterization of the obtained nanocomposites

X-ray diffraction

Wide-angle X-ray diffraction (XRD) was used to characterize the clay and to study the nature and extent of clay dispersions in the composites. The X-ray diffraction (XRD) measurement was performed on rubber samples using the Bruker-D4 Endeavor diffractometer equipped with Co Kα radiation ($\lambda_{Co} = 1.79$ Å) at 0.02° 2θ step size. Bragg's Law equation ($n\lambda = 2d \sin \theta$) was used to calculate the crystallographic spacing (d).[18]

TABLE I
Formulation for NR Compounds

Ingredient	Content (phr)
NR	100
ZnO	3.5
Stearic acid	2.5
Sulfur	2.5
CBS[a]	0.8
Aminox[b]	2.0
Cellulose	15
Montmorillonite	1–5

[a] Accelerator (*N*-cyclohexyl-2-benzothiazolesulphenamide).
[b] Anti-oxidant—product of the reaction at low temperature, between diphenylamine and acetone.

Rheometric properties

Rheometric properties were obtained according to ASTM D 2084 on an Oscillating Disk Rheometer, model TI-100, operating at 150°C and 1° arc. The parameters determined from the curves were:

- M_L: minimum torque which can be related to the viscosity of the mixture under the experimental conditions;
- M_H: maximum torque which is related to the content of crosslinks;
- t_{s1}: pre-vulcanization or scorch time, also known as the safety time. Under the used experimental conditions, this parameter was taken as the necessary time for minimum torque to be raised by one unit;
- t_{90}: optimum vulcanization time, necessary to have 90% of the crosslinks formed;
- CRI: cure rate index, equal to $100/(t_{90} - t_{s1})$

Vulcanization was carried out at 150°C in an electrically heated hydraulic press, during cure times established previously in the rheometer.

Dynamic mechanical properties

Dynamic mechanical properties were evaluated by using a dynamic mechanical thermal analyzer model Q-800, TA Instruments, at a fixed frequency of 1 Hz, with 3°C/min heating rate, and liquid nitrogen for sub ambient temperatures. Storage modulus (E') and loss factor (tan δ) were obtained by single-cantilever clamped-bending. The strain amplitude used in all the experiments was 0.05% at temperatures ranging from 100°C to 20°C.

Mechanical properties

Tensile tests were performed on dumb-bell shaped specimens according to DIN 53504 on an EMIC universal testing machine. Tear strength was carried out
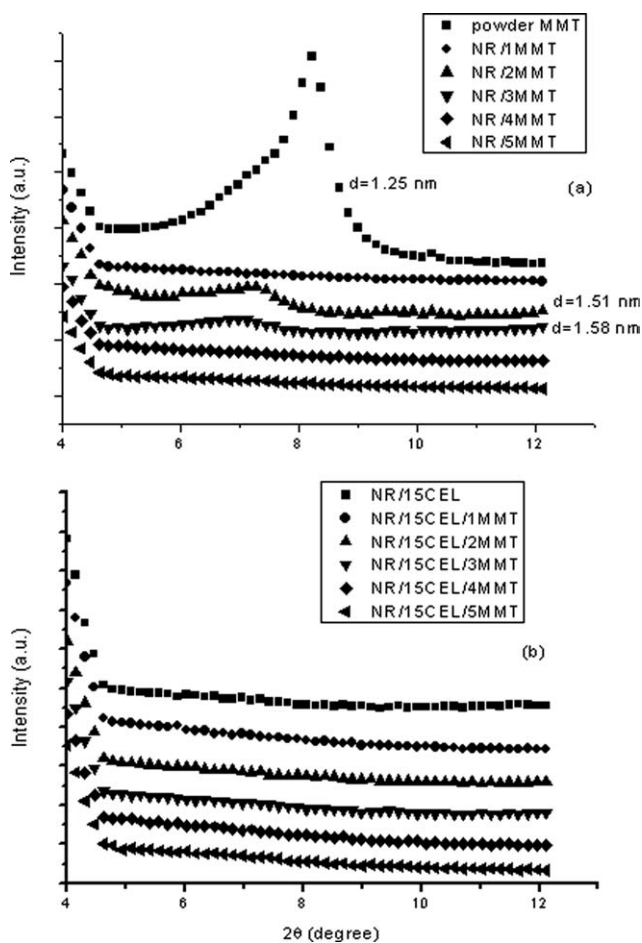
Figure 1 XRD analysis of (a) NR/clay nanocomposites and (b) NR/cellulose/clay nanocomposites.

according to ASTM D 624. Shore A hardness was measured according to ASTM D 2240. The abrasion loss test followed DIN 53516, on a Bareiss Abraser. In the test, a 5N weight was used over 40 m distance.

Scanning electron microscopy

The morphology obtained after the abrasion resistance test was observed by using a scanning electron microscope (JEOL, Model JSM-6460 LV). The surface of the samples was covered with a fine layer of gold, and the micrographs were taken at an acceleration voltage of 20 kV.

RESULTS AND DISCUSSION

Structural characterization of NR-cellulose-montmorillonite nanocomposites

Figure 1 shows the X-ray diffraction (XRD) patterns of (a) NR/MMT and (b) NR/CEL/MMT nanocomposites with montmorillonite contents varying from 0 to 5 phr. The MMT clay shows a diffraction peak at $2\theta = 8.2°$, corresponding to the (001) plane reflections of the silicate layer aggregates.[19] From Figure 1, the MMT peak corresponds to a basal distance of 1.25 nm, and for all NR/MMT nanocomposites the intergallery distances were found to be larger than the initial value for montmorillonite peak, which seems to indicate that rubber molecules are intercalated into the clay interlayer. The upper limit amount for MMT to produce nanomaterials seems to be around 2 phr. The results of Figure 1(b) show that the addition of cellulose to the system leads to a total disappearance of the diffraction peaks not allowing the identification of the limit amount of MMT in the mixture in this case. The intercalation and exfoliation of montmorillonite layers,[3,19,20] observed by means of this technique together with TEM analysis[16] for NR/celluloseII, confirm the formation of nanocomposites.

Table II shows the rheometric properties of NR/MMT and NR/CEL/MMT systems. Before the cure

TABLE II
Rheometric Properties of NR Nanocomposites

Composition	M_L (dN m)	M_H (dN m)	ΔM (dN m)	t_{S1} (min)	t_{90} (min)	CRI (min^{-1})
NR/MMT nanocomposite						
NR	1.2	23.1	21.9	7.80	14.4	15.1
NR/1MMT	3.9	25.5	21.6	10.8	14.4	27.7
NR/2MMT	5.1	25.8	20.7	12.0	18.6	15.1
NR/3MMT	5.1	25.5	20.4	10.2	22.2	8.3
NR/4MMT	5.2	22.6	17.4	11.4	25.2	7.2
NR/5MMT	4.5	22.9	18.4	10.2	28.2	5.6
NR/15CEL/MMT nanocomposite						
NR/15C	2.9	35.9	33.0	5.7	12.0	15.8
NR/15C/1MMT	5.1	36.1	31.0	8.0	15.4	13.5
NR/15C/2MMT	6.4	32.4	26.0	7.9	16.8	11.2
NR/15C/3MMT	6.8	31.7	24.9	7.8	17.4	10.4
NR/15C/4MMT	5.0	30.7	25.7	8.4	19.8	8.8
NR/15C/5MMT	5.5	29.9	24.4	9.6	21.0	8.8

M_L = minimum torque; M_H = maximum torque; $\Delta M = M_H - M_L$; t_{s1} = scorch time; t_{90} = time at 90% of cure (optimum cure time).
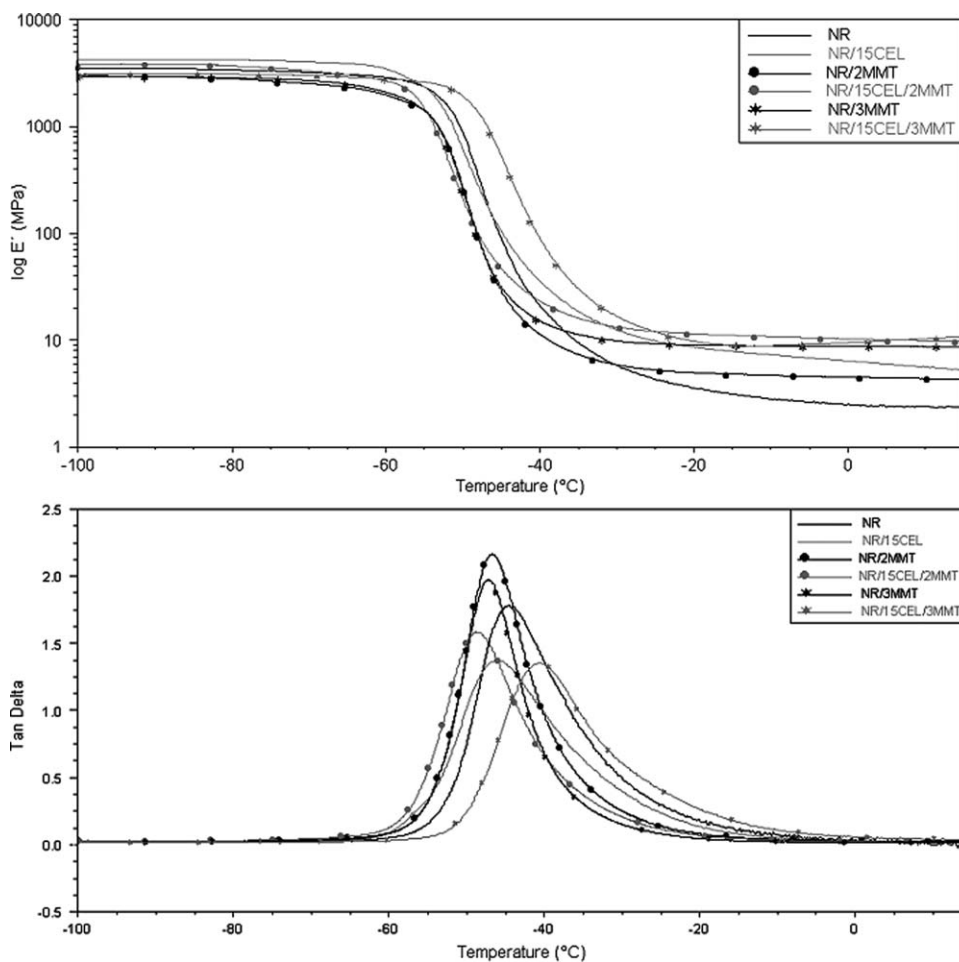
Figure 2 (a) The storage modulus (E') as a function of temperature and (b) Mechanical loss factor (tan δ) against temperature for NR nanocomposites.

process, the values of minimum torque (or viscosity) underwent a small increase upon addition of MMT up to 3 phr. After cure, a positive effect on maximum torque (or stiffness) can be observed as MMT was added up to 2 phr. These observations corroborate X-ray diffractogram results showed in Figure 1(a). Pojanavaraphan and Magaraphan[10] report that when the values of maximum torque for clay-filled rubber compounds are higher than those for the gum, this effect can be attributed to the reinforcing effect of the clay and to a good interaction between the clay and rubber.

NR/CEL/MMT nanocomposites exhibit higher maximum rheometric torque than NR/MMT system and pure gum due to presence of cellulose II. It can also be noticed that the NR/CEL/MMT compositions offer more resistance to the rotor oscillation even in the uncured stage which can be seen from the viscosity, given by the values of minimum torque. There were an increase in minimum torque for NR/15CEL/MMT compositions at MMT amounts up to 3 phr and a small decrease in both maximum torque and ΔM as MMT varied from 1 to 5 phr.

Clay content also influenced the optimum cure time (t_{90}), causing an increase in t_{90} and consequently a decrease in CRI. This delay in the vulcanization reaction suggests that an interaction between the components of the cure system and the clay surface is occurring.[21] It was also observed that NR/CEL/MMT compositions were cured faster as the overall cure times were reduced, compared with the compositions with no cellulose. The addition of cellulose II to the system promoted an improvement of some rheometric properties, when compared to the compositions containing only clay.

As far as the viscoelastic behavior of polymeric materials are concerned, dynamic mechanical analysis (DMA) has emerged as one of the most powerful tools available.

The dynamic storage modulus, E', and the loss factor, tan δ, as a function of temperature for representative composites are shown in Figure 2(a,b), respectively. Some results of dynamic mechanical properties are presented in Table III. As seen in Figure 2(a), the modulus of the composite NR/15CEL/3MMT is the highest in the glass region, considering

TABLE III
Dynamic Mechanical Properties of the NR Nanocomposites

Composition	Dynamic mechanical properties	
	Storage modulus (E') at 15°C (MPa)	T_g (tan δ) (°C)
NR	2.50	−44.54
NR/1MMT	1.21	−46.71
NR/2MMT	4.29	−46.75
NR/3MMT	8.67	−47.22
NR/4MMT	6.64	−47.63
NR/5MMT	4.16	−46.30
NR/15CEL	5.43	−45.87
NR/15CEL/1MMT	8.92	−47.68
NR/15CEL/2MMT	9.68	−48.75
NR/15CEL/3MMT	10.80	−40.90
NR/15CEL/4MMT	8.32	−49.39
NR/15CEL/5MMT	8.66	−50.70

all the materials, and this probably reflects the strong confinement of the rubber molecules inside the dispersed nano-montmorillonite layers and cellulose II.[19] Below the glass transition temperature (T_g = −47°C), NR/CEL/MMT storage moduli increase when compared to clay filled compounds. From the analysis of the storage modulus at 15°C in the rubber phase, seen in Table III, it can be observed that the cellulose compositions show a better performance probably due to the characteristics of the cellulose macromolecular structure as well as to its distribution and dispersion at nanometric level. Composition NR/15CEL/3MMT is the composition that exhibited the highest value of storage modulus in the rubber phase.

The composition NR/15CEL shows a slow decay of tan δ versus temperature curve. The heights of tan δ peaks are significantly reduced in cellulose/montmorillonite compositions suggesting a strong adhesion between NR and both fillers.[22] From the curves in Figure 2(b), which present the effect of

MMT and CEL addition, it can be seen that practically no change in T_g was observed. The increased addition of MMT up to 3 phr imparted modification in the storage modulus in the rubber phase thus corroborating the values of 300% modulus and hardness. The addition of cellulose II to the NR/Clay system promoted increase in storage moduli in the rubber phase which were found to be higher than the values achieved by the NR/clay system with up to 3 phr of MMT. This effect can be associated to the nanocrystalline character of cellulose II.

Mechanical properties of rubber compositions are dependent on the type of reinforcing filler used, that is, structure and characteristics of such fillers, including particle size, surface area, and degree of dispersion in the elastomeric matrix. Some mechanical properties commonly used for classification of a load either as reinforcing or not are tensile and tear strengths, and hardness.[23]

The mechanical properties of these NR nanocomposites with various clay contents are shown in Tables IV and V and in Figure 3. Table IV shows that in the absence of cellulose, modulus at 300%, stress at break, and the energy at break increase gradually with tensile deformation, up to 2 phr montmorillonite load. However, further clay increments resulted in strain decay. According to Vu and coworkers, the rubber chains are placed on the surface of the exfoliated/intercalated MMT lamellae. As the exfoliated/intercalated clay has a high surface area, the increase in the content of this filler allows a greater amount of rubber chains to be adsorbed in-between the lamellae which results in a reduced deformation capability.[24] This result is corroborated by X-ray diffraction showed in Figure 1.

The presence of 15 phr of the nanopolymer cellulose II in the NR/MMT system causes an increase in the tensile properties, compared with the compositions with no cellulose. This behavior can be credited

TABLE IV
Mechanical Properties of the NR Nanocomposites

Composition	Property				
	300% modulus (MPa)	Stress at break (MPa)	Energy at break (J)	Elongation at break (%)	Mechanical characteristics
NR	1.6 ± 0.2	14.9 ± 1.8	3.3	609.7 ± 67.2	Higher flexibility
NR/1MMT	1.3 ± 0.1	18.4 ± 1.6	5.5	798.9 ± 45.0	
NR/2MMT	1.8 ± 0.0	19.5 ± 2.2	5.6	776.2 ± 13.3	
NR/3MMT	1.5 ± 0.1	15.3 ± 1.5	4.9	793.7 ± 46.2	
NR/4MMT	1.6 ± 1.5	12.1 ± 1.3	4.4	759.8 ± 20.5	
NR/5MMT	1.6 ± 0.1	12.6 ± 2.5	4.5	758.2 ± 45.1	
NR/15CEL	4.1 ± 0.1	20.4 ± 1.2	8.0	688.4 ± 24.2	Higher rigidity
NR/15CEL/1MMT	5.5 ± 1.4	21.4 ± 2.9	7.8	498.6 ± 41.7	
NR/15CEL/2MMT	6.3 ± 0.3	24.1 ± 2.1	10.9	631.9 ± 15.0	
NR/15CEL/3MMT	3.1 ± 0.2	18.8 ± 2.7	8.7	792.9 ± 34.2	
NR/15CEL/4MMT	4.1 ± 0.2	17.8 ± 2.1	8.0	694.9 ± 58.8	
NR/15CEL/5MMT	3.6 ± 0.3	17.3 ± 4.9	7.9	693.4 ± 55.2	

TABLE V
Tear Strength and Hardness (Shore A) of Natural Rubber/CelluloseII/Montmorillonite Nanocomposites

Composition	Tear strength (kN/m)	Hardness (Shore A)
NR	38.45 ± 4.02	28
NR/1MMT	49.97 ± 3.15	32
NR/2MMT	48.36 ± 3.56	34
NR/3MMT	44.19 ± 3.48	35
NR/4MMT	30.30 ± 2.24	30
NR/5MMT	27.21 ± 2.07	29
NR/15CEL	100.50 ± 6.03	57
NR/15CEL/1MMT	51.70 ± 2.35	56
NR/15CEL/2MMT	51.90 ± 2.84	52
NR/15CEL/3MMT	54.90 ± 4.96	45
NR/15CEL/4MMT	51.27 ± 2.58	48
NR/15CEL/5MMT	45.89 ± 0.32	50

to the extremely crystalline character of cellulose and also to its dispersion and distribution in the rubber matrix.[25] The compounds with cellulose show bigger energy at break than the compounds without cellulose. The best performance was given by NR/15CEL/2MMT. Thus, MMT addition leads to materials with similar resistance at break and stiffness. As for cellulose addition, nanocomposites with similar resistance at break and different stiffness are obtained.

It can be observed from Table V that NR/1MMT showed the highest tear strength. In the presence of 15 phr of cellulose the best result was given by NR/15CEL/3MMT compound. The increase in tensile and tear strengths of the nanocomposites filled with up to 3 phr of the montmorillonite and the subsequent reduction in these properties can be attributed to the exfoliation/intercalation of clay, as shown in Figure 1.

The presence of cellulose in the NR/MMT systems promotes higher values of hardness, as compared with pure gum, caused by the addition of the crystalline nanopolymer. The effect of MMT addition up to 3 phr is to promote small increases in Shore A hardness. However, as more montmorillonite is added to the system, the hardness starts to decrease. This effect is in agreement with modulus at 300%, maximum torque and energy at break obtained from stress versus strain curves.

The increase of clay content in the NR matrix causes influences in the mechanical properties of the composites. The largely increased reinforcement and the tear resistance of the nanocomposites should be ascribed to the dispersed structure of clay at the nano level, the high aspect ratio, and the planar orientation of the silicate layers.[26] The nanometric dispersion of cellulose[16] and silicate layers impart an efficient reinforcement and lead to improved mechanical properties. The silicate layers may have

favored the formation of immobilized or partially immobilized polymer phases, which also increased the mechanical properties.[27] According to Pojanavaraphan,[10] sodium montmorillonite can be considered as a reinforcing agent since it improves stress at break, hardness, and tear strength when introduced in a rubber matrix.

Martins and coworkers[28] evaluated the reinforcement promoted by the addition of the nanopolymer cellulose II in natural rubber compounds by ^{13}C-NMR spectroscopy in the solid state. The technique was used to study the interaction between NR and cellulose II and these results were correlated with the mechanical properties results. It was observed that the addition of cellulose II in the NR matrix did not change the natural rubber chemical displacements. These results showed that a physical interaction between NR and cellulose II occurred. The compound with 15 phr of cellulose II exhibited increased molecular stiffness and the highest stress at break when compared with neat natural rubber. The authors assigned these results to a good dispersion of the cellulose into the rubber matrix which is an evidence of the strong physical interaction between rubber and filler.

The results of abrasion loss are presented in Figure 3. In general, the abrasion resistance of polymer nanocomposites will be affected by the amount of filler added, filler–matrix interaction, and type of matrix.[29] It can be observed that no significant change in the abrasion loss was observed when the amount of montmorillonite increased. On the other hand, the addition of the crystalline cellulose nanopolymer made the compositions more resistant to abrasion loss.

Figure 4 shows the images obtained from Scanning Electron Microscopy (SEM) of the natural rubber nanocomposites after the abrasion resistance test. On Figure 4(a), NR shows the aspect of the abrasion surface with accentuated nerves and nearly rounded surface cavities between them, which are typical aspects of NR. Upon the addition of MMT to the NR
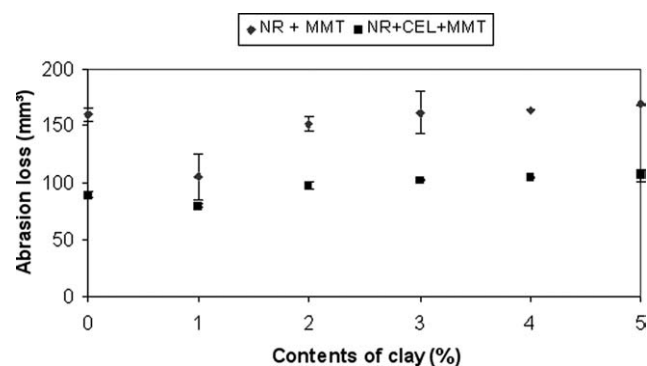
Figure 3 Abrasion loss of NR nanocomposites with cellulose and montmorillonite.
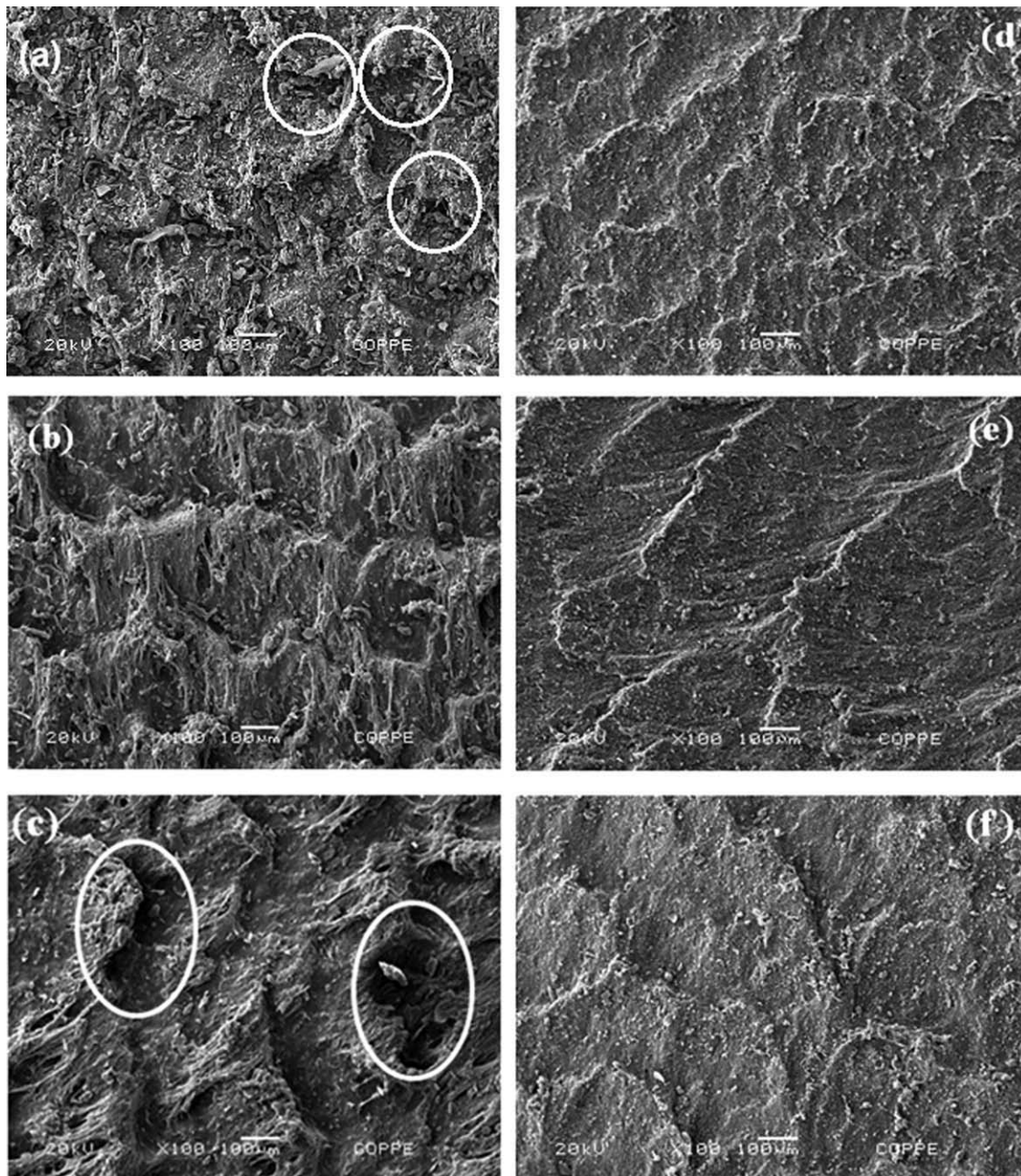
Figure 4 SEM micrographs of natural rubber nanocomposites after the abrasion resistance test of (a) NR, (b) NR/2 phr MMT, (c) NR/5 phr MMT, (d) NR/15CELII, (e) NR/15CELII/1MMT, and (f) NR/15CELII/2MMT.

elastomeric matrix, an increased generation and proximity of the nerves can be observed in Figure 4(b,c), leaving the surface between the nerves a bit smoother, the generation of cavities tends to be more accentuated. The increase in MMT content intensifies this behavior in the nerves and cavities.

The addition of cellulose changes the abrasion mechanism so that on Figure 4(d) modifications in the aspect of surfaces can be observed. Nerves are more aligned and much less rounded and the reduction of cavities is significant. Through addition and increased MMT content in the NR/CELII system, it

can be observed that the effect of nerves and cavities were much reduced, as shown on Figure 4(e,f).

CONCLUSIONS

Based on the technique of co-coagulating natural rubber latex, cellulose xanthate, and clay aqueous suspension, it was possible to obtain nanocomposites. The preparation process is simple, effective, and widely applicable to rubbers in the latex form. XRD patterns indicated that an intercalated structure

occurred when the clay was added at loads up to 3 phr. Being a nanopolymer, the cellulose addition caused a significant increase in storage modulus, thus reflecting in a strong confinement of dispersed nanoclay layer and cellulose on the rubber molecules. The tan δ peaks were significantly reduced thus suggesting a strong adhesion between NR, montmorillonite, and cellulose, which resulted in improved mechanical properties.

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