

Nanoclay as Substitute of Calcium Carbonate in NBR Compounds

Abd. Alipour*

Young Researchers Club, Zarghan Branch, Islamic Azad University, Zarghan, Iran

(Received 15 June 2012; published online 21 August 2012)

The use of organo-modified montmorillonite as substitute of calcium carbonate in NBR compounds were studied. Rubber containing (3,5,7 phr) of nanoclay (Cloisite 30 B) were compared with those of reinforced by 10, 20 and 30 phr calcium carbonate as filler. The modified silicate is analysed by X-ray which suggested intercalation of elastomer chains into silicate layers. Rheological measurement as well as mechanical properties showed both nanoclay and calcium carbonate give rise to a marked increase in elastic modulus and viscosity which could be attributed to the good interaction between polymer/filler. It was noticed that nanoclay can reinforce the NBR much more noticeably than calcium carbonate.

Keywords: Nanoclay, Calcium Carbonate, XRD, Mechanical Properties, SEM Photomicrograph

PACS number: 68.37.Lp

1. INTRODUCTION

In the last two decades, research was focused on the development of other reinforcing agents to replace carbon black in rubber compounds. Sepiolite, kaolin and precipitated silica were commonly used as reinforcing Clays and clay minerals such as montmorillonite, saponite, hectorite, etc, were widely used as filler for rubber and plastic for many years, for saving polymer consumption and reducing the cost. The clay minerals are composed of silicate layers 1 nm thick and 200 – 300 nm in the lateral dimensions. The internal and external cations can be exchanged by other inorganic or by organic ions, for example quaternary alkyl ammonium ions. Organophilic modification makes the silicate compatible with the polymer. These entering guest molecules can either simply increase the distances between the still-parallel layers in an intercalation process or randomly entirely disperse the separate layers in an exfoliation. Organoclays have been mainly tested with engineering plastics, but, up to now there are only a few studies on rubber-clay nanocomposites [1-10]. Okada et al. [1] showed for acrylonitrile-butadiene rubber (NBR), that only 10 phr organoclay were necessary to achieve tensile strength comparable to compounds loaded with 40 phr carbon black. The aim of this study is to evaluate the properties of NBR nanocompounds prepared with an organo-modified montmorillonite in comparison with calcium carbonate compounds.

2. EXPERIMENTAL

2.1 Material

NBR, nanoclay, calcium carbonate and cure ingredients were supplied from Enichem co Italy, Southern clay company (U.S.A), local company (Iran) and Bayer Co, respectively. Samples were prepared by Haak internal mixer at temperature of 110 °C and the rotor speed of 60 rpm for 10 min. Curing agents (stearic acid 1.5 phr, ZnO 5 phr, DEG 3 phr, sulfur 1.5 phr, TMTD 0.2 phr and MBT 1.5 phr) were mixed with compound on two-roll mill (Polymix-200L) at 25 °C and rotor speed of 70 rpm (see Table 1).

Table 1 –Composition of the Samples

Sample Code	NBR	Cloisite 30B	Calcium Carbonate
NBR	100	-	-
NC3	100	3	-
NC5	100	5	-
NC7	100	7	-
NCC10	100	-	10
NCC20	100	-	20
NCC30	100	-	30

2.2 Samples

2.3 Characterization

X-ray diffraction patterns of the samples were recorded on a Philips model X'Pert (50 kV, 40 mA) by using Cu-K α radiation ($\lambda = 1.540598 \text{ \AA}$) with a scanning rate 2°/min at room temperature. The basal spacing of silicates was estimated from the position of the plane peak in the WAXD intensity profile using the Bragg's law, $d = \lambda / (2 \sin \theta_{\max})$. The rheological measurements were performed using a RPA 2000 oscillatory rheometer (Alpha Technology Company) at 80 °C and frequency of 0.01 – 1000 (rad/sec).

3. RESULTS AND DISCUSSION

3.1 X-ray Diffraction

Fig. 1 shows the X-ray diffraction patterns of the clay (a) and the organoclay (b). The interlayer platelet spacing (001 diffraction peak) of nanoclay is of 18.5 Å. In the organoclay a displacement of the peak to lower angles is observed. In this case, the interlayer distance have increased.

Nanocomposites with 3,5,7 phr nanoclay have no evident diffraction peaks in the measured angle scope. According to the literature [7], the absence of the characteristic d(001) diffraction peak of clay is strong evidence for the formation of exfoliated or disordered nanocomposites.

* Abdolmajid.Alipour@gmail.com

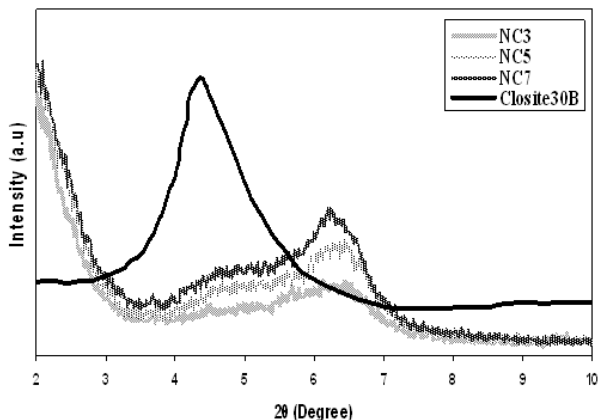


Fig. 1 – XRD Results of the Nanocomposite Samples

It can attributed to large spacing between the layers or because the nanocomposite do not present ordering any more.

3.2 Cure Characteristics

The cure characteristics of the nanocomposite and microcomposite samples expressed in terms of scorch time (t_5), optimum cure time (t_{90}) and torque values ($\Delta M = M_{max} - M_{min}$). The scorch time (t_5) is defined as the time up to the onset of vulcanization or cross-linking in rubber compounds. In Fig. 2 it can be seen that t_5 decreased when nanoclay added to NBR. Similar trends were observed in the t_{90} values of NBR with increasing clay content (see Fig. 3). From these results it can be assumed that the organoclay behaves as an effective vulcanizing agent for NBR, giving rise to a significant increase in the elastomer vulcanization rate.

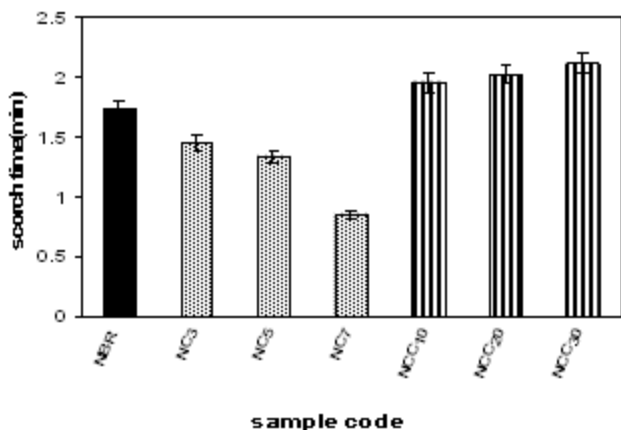


Fig. 2 – Scorch Time of the Samples Prepared

This effect is essentially attributed to the amine groups present in the nanosilicate structure which comes from the organophilization of the clay [7,8]. Similar trends were reported by other researchers [7,8]. However, a different trend is observed for rubber compounds containing Calcium carbonate. This mentioned filler gives a rise to scorch time and optimum cure time.

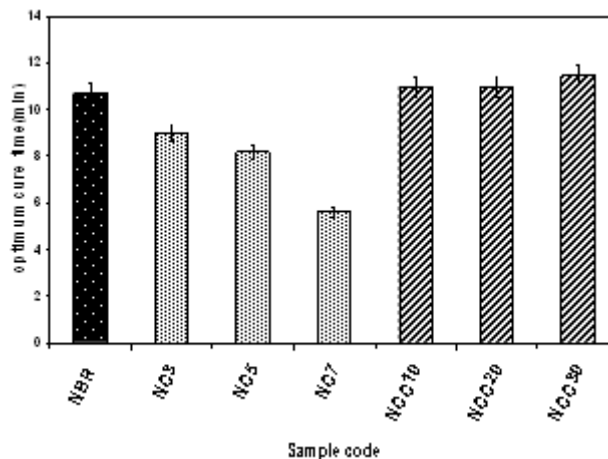


Fig. 3 – Optimum Cure Time of the Samples Prepared

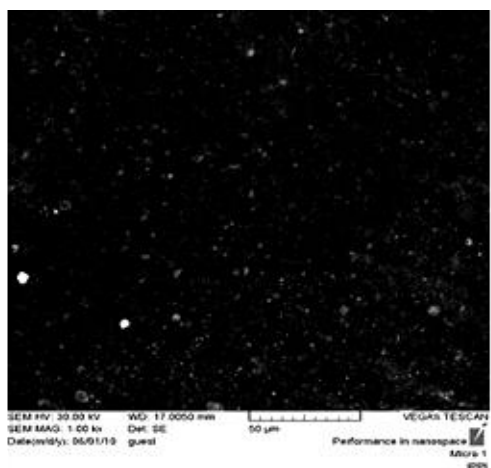
Alongside this, the torque values, ΔM , measured as the difference between the maximum and minimum torque ($\Delta M = M_{max} - M_{min}$) are summarized in Table 2. The increase in maximum and minimum torques as well as their difference is seen with nanoclay and calcium carbonate filled system compared to pristine NBR. Assuming the torque value is related to the cross-links number, it can be deduced that fillers certainly increase the crosslinking density of NBR. However, it is of interest that the organoclay nanocomposite gives rise to a dramatic increase in the torque value compared calcium carbonate filled systems even at high content (30wt %). These results are attributed to the intercalation of the matrix chains between the silicate galleries, so increasing the interlayer distance which facilitates the incorporation and confinement of NBR chains into the silicate galleries. Consequently, a better interaction between nanoclay and elastomer is obtained.

Table 2 – Torque Value of the Prepared Samples

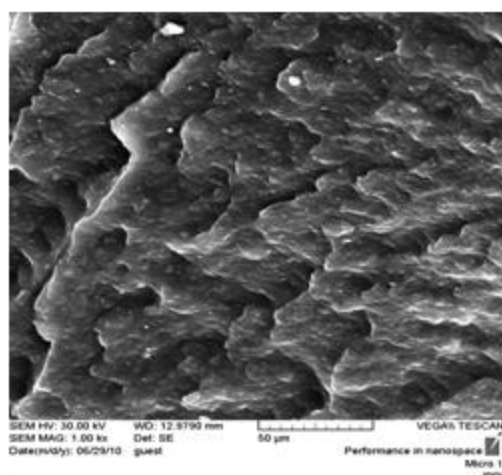
Sample Code	$\Delta M = M_{max} - M_{min}$, (Ibf.in)
NBR	30.91
NC3	49.22
NC3	52.49
NC7	54.15
NCC10	38.15
NCC20	40.29
NCC30	42.35

3.3 Microscopy

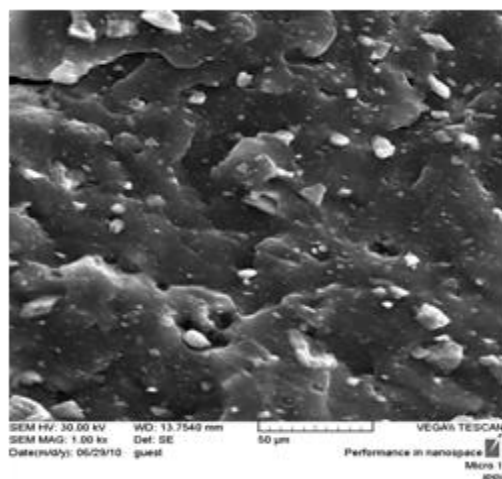
Insights on the morphology of the prepared samples are found in Fig. 4 where SEM micrographs of cryogenically fractured samples, Nn7, and NCC30 is reported. As seen the fractured surface of pristine NBR (Fig. 4(a)) is smooth. The harsh surface of NBR filled compounds exemplifies an effective interaction established between polymer matrix/filler. The dispersion of Calcium carbonate in the rubber matrix was not continuous where the formation of filler agglomeration started due to the interfacial interaction between filler and matrix, which led to void formation.



a



b



c

Fig. 4 – SEM Photomicrographs of a) NBR b) NC7 c) NCC30

3.4 Rheological Measurements

Fig. 5 shows the comparison of complex viscosity and dynamic moduli, G' of sample containing nanoclay and calcium carbonate. As been seen, both fillers have an increasing effect in rheological properties. In fact addition of nanoclay and calcium carbonate, lead to an increase in

storage modulus which can be attributed to the good interaction established in the interface of polymer/filler.

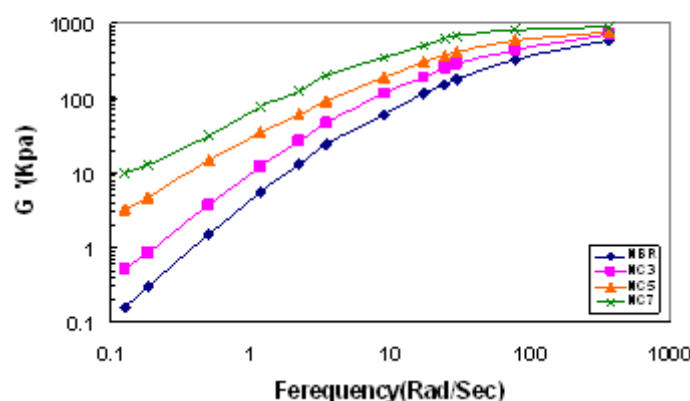
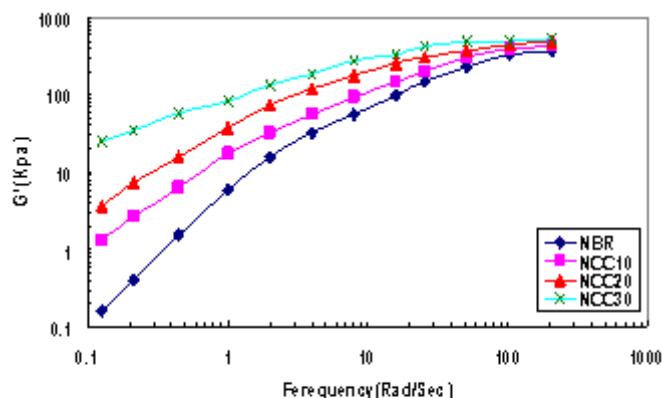


Fig. 5 – Rheological Measurements of the Samples Prepared

It is noticeable that sample containing 7 %wt nanoclay causes a greater effect on the modulus which means more reinforcing than sample with 30 % wt calcium carbonate. On the other hand, G' of samples have an ascending trend by filler loading. In comparison with pristine NBR, the filled samples show higher value of dynamic moduli. It is because of this fact that both fillers form a network structure which increases interaction between polymer/filler and as a consequence, G' increases. It is obvious that nanoclay filled samples show higher dynamic modulus [7,8].

3.5 Mechanical Properties

Table 3 shows the mechanical properties of NBR and their composites filled by nanoclay and Calcium carbonate. Introduction of both nanoclay and calcium carbonate fillers causes that tensile strength of NBR increases. It should be mentioned that it is necessary to add 30 wt % calcium carbonate to obtain nearly similar tensile strength as the composite with 7 wt % organoclay. Since Calcium carbonate filled samples show less value of tensile strength than nanoclay filled ones, it can be deduced that interaction between nanoclay /rubber macromolecules to be stronger than that of calcium carbonate and rubber macromolecules.

Modulus is an indication of the relative stiffness of the material. Fillers are known to increase modulus provided the modulus of the filler is higher than that of the polymer matrix.

Table 3 – Mechanical Properties of the Prepared Samples

Sample Code	Tensile Strength, Mpa	Modulus 300 %, Mpa	Elongation %
NBR	1.67	1.63	306
NC3	4.1	2.58	325
NC3	4.81	3.34	362
NC7	5.6	3.59	345
NCC10	1.79	1.81	299
NCC20	2.01	1.72	275
NCC30	2.36	1.79	264

From Table 3 it can be seen that nanoclay improved the stiffness of the rubber blends, whereas Calcium carbonate showed a small increase in this property. This could be ascribed to the huge surface area of clay dispersed at nanometer level and the largest aspect ratio of silicate layers, which results in the increased silicate layer networking. The improvements of tensile strength, tensile modulus and hardness in case of pol-

mer-clay nanocomposites were given by some researchers [2-10]. Their studies suggested that the increase of strength and modulus is related to the degree of dispersion of clay layers into the polymer matrix.

4. CONCLUSION

NBR compounds containing nanoclay and calcium carbonate were prepared via vulcanization process and characterized by several techniques. In these materials rubber chains could penetrate into silicate layers resulting an increase in d-spacing of layers which was confirmed by XRD results. On the other hand enhanced viscosity and dynamic moduli as well as mechanical properties of samples suggested a good interaction between polymer matrix and filler particles that also confirmed SEM photomicrographs. It also was concluded that nanoclay is a better reinforcing filler than calcium carbonate.

REFERENCES

1. A. Okada, A. Usuki, T. Kurauchi, O. Kamigaito. *Hybrid organic-inorganic composites* (ACS Symp Ser: 1995).
2. A.K. Ghosh, S.C. Debnath, N. Naskar, D.K Basu, *J. Appl. Polym. Sci.* **181**, 800 (2000).
3. M.W. Hess, P.C. Vegvari, R.A. Swor, *Rubber. Chem. Technol.* **58**, 350 (1985).
4. D.V. Sarbach, *Rubber Age*, **89**, 283-290 (1961).
5. M. Arroyo, M.A. López-Manchado, J.L. Valenti'n, J. Carretero. *Comp. Sci. Tech.* **67**, 1330 (2007).
6. S. Varghese, J. Karger-Kocsis, K.G. Gatos. *Polymer.*, **44**, 3977 (2003).
7. A. Alipour, G. Naderi, G.R. Bakhshandeh, H. Vali, Sh. Shokoohi. *Internationa Polymer Processing*, **XXVI**, 48 (2011).
8. A. Alipour, G. Naderi, G.R. Bakhshandeh, Sh. Shokoohi. *Iran Rubber Magazine* **62**, 26-34 (2011).
9. A. Alipour, G. Naderi, M.H.R. Ghreishy, *J. Appl. Polym. Sci.*, DOI: 10.1002/app.37752, (2012).
10. A. Alipour, *Journal of Bioscience, Biochemistry and Bioinformatics* **2**, 79 (2102).