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Processing and Properties of Nanocomposites Based on Layered Silicate and Carboxylated Nitrile Rubber

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Nanocomposites based on carboxylated nitrile rubber (XNBR) and organomodified clay were prepared under different mixing conditions. At higher mixing temperatures, a mixed intercalated/exfoliated morphology was obtained as evidenced by X-ray diffraction studies and transmission electron microscopy. A remarkable improvement of physical properties was achieved when the layered silicates were mixed at high temperatures. The presence of carboxylic group in the rubber improves the interaction and exfoliation process which can be shown by IR studies. With the increase of the organoclay loading and processing temperature, a considerable effect on dynamic properties was found during strain sweep analysis which was explained by 'Payne'-like effects. Finally, a mechanism of the layered silicate dispersion in carboxylated nitrile rubber has been proposed.

Keywords: Carboxylated nitrile rubber, montmorillonite, processing temperature, reinforcement

1 Introduction

Polymer-layered silicate composites with nanoscale reinforcements are now becoming a challenging area of polymer reinforcement. It is frequently reported that nano-scale dispersion of filler particles often endows polymers with unprecedented beneficial properties, making it possible to extend their utility to newer or more advanced applications. Strictly speaking, so far as the rubber-layered silicate nanocomposite is concerned, there are rare reports on the use of layered silicates as fillers by the rubber industry. However, the literature is full of reports where incorporation of organosilicates into rubbers results in enhanced mechanical strength (1–6), improved thermal stability (7–8) and flame retardancy (9–10), increased solvent resistance (11–12) and barrier properties (11, 13–15), decreased heat shrinkability (16), and improved tribological properties (17). In any case, low concentration of clay and insignificant property trade-offs are the most important aspects of rubber layered silicate nanocomposites. The main factor of nano reinforcement which governs the influence on the ultimate properties of such a type of composites depends on the degree of dispersion of the inorganic clay into the organic rubber matrix. It is very difficult to disperse inorganic particles from its stacked layer structure into individual mono layers in the rubber matrix with poor surface energy. This factor is particularly noticeable in cases of non-polar rubbers like EPDM, NR, SBR etc. Several efforts have been made to minimize the phase incompatibility between layered silicate and rubber (18–23).

The insertion of carboxylic group in the acrylonitrile butadiene rubber backbone served as an attractive means of chemically modifying rubber for various applications in several technical rubber goods. This rubber already has been an alternative of traditional acrylonitrile butadiene rubber in harsher application conditions. On the other hand, carboxylated nitrile rubber, being a polar rubber is expected to interact with layered silicate more efficiently in comparison to other diene rubbers. In the literature, only a few reports could be found concerning the utilization of layered silicate in XNBR. Very recently, it was reported that in the presence of layered silicate, the tensile properties of the XNBR vulcanizates have been decreased to a considerable extent (24). The explanation given behind this undesired effect is a reduction of the number of ionic crosslinking due to consumption of ionic clusters formed by the metal and carboxylic groups by the layered silicates. Successful preparation of layered silicate nanocomposites by latex coagulation method was also reported (25).

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However, this method and the physical properties are very acceptable for practical applications. Till now, there has been no report about the preparation of layered silicate-XNBR nanocomposites which can be prepared in mass scale by a high shearing mixing method with the evolution of physical properties at a desired level. There is almost no attempt to find out the optimum loading of layered silicate in XNBR matrix to get the full potential of layered silicates in the reinforcement process.

Very recently we reported about the utilization of XNBR in the preparation of high performance elastomer nanocomposites by melt mixing (26, 27). In a second paper we also described the polymer dynamics close to filler interphases of XNBR filled with layered silicate investigated by dielectric and dynamic-mechanical analysis, as well as IR spectroscopy (28).

In our present work, commercially available layered silicate has been incorporated into a XNBR matrix in order to get rubber nanocomposites with improved physical properties. Efforts have been made to optimize the processing conditions for the nanocomposite preparations. Finally, a mechanism of reinforcement by layered silicate in XNBR matrix has been proposed.

2 Experimental

Carboxylated nitrile rubber used in this study was obtained from Lanxess, Germany [Krynac 7.40, ML 1+4(@100°C 38 +/− 4, acrylonitrile content 26.5, carboxylic acid content 7%]. Zinc oxide, stearic acid, diphenyl-guanidine (DPG), n-cyclohexyl-2-benzothiazole-sulfenamide (CBS) and soluble sulfur were used as a vulcanization system. Organomodified montmorillonite was supplied by Süd-Chemie, Germany. This clay contains quaternary ammonium salt as an organic modifier and the basal spacing of this organoclay is 2.98 nm. For variation of the mixing temperature, the temperatures 40°C, 80°C, 120°C and 160°C have been chosen. The amount of organoclay was varied between 2.5 and 10 phr (part per hundred rubber). The compounding of XNBR with organoclay and vulcanization ingredients was done by a laboratory size open two roll mixing mill (Polymix 110L, size : 203 × 102 mm Servitec GmbH, Wustermark, Germany,) and by an internal mixer (Haake PolyLab-System, Rheocord Haake RC300p, Thermo Electron GmbH, Karlsruhe, Germany) in dependence of the mixing temperature. For lower temperatures (40 and 80°C), requisite amounts of organoclay were incorporated in previously masticated rubber on a two-roll mixing mill using a 10 min compounding cycle. Finally, the accelerator, sulfur and ZnO were added to the mix within 5 min. The friction ratio of the mill was 1:1.2 during the mixing tenure. For higher temperature processing, the mixing was done by the internal mixer. Here, at first, the rubber and organoclay were mixed at 120°C and 160°C, respectively and then the rest of the curatives were added at 40°C on the two-roll mill.

The curing study was carried out with a moving die rheometer (Scarabaeus V-50, Scarabaeus GmbH, Langgöns, Germany) at 160°C. The stocks were cured under pressure at 160°C to optimum cure (t_{90}). The same instrument was employed for dynamic property measurements with a variation of double strain amplitude at a low deformation angle. In this experiment, the samples were cured up to the corresponding t_{90} at 160°C. Then, the moving die rheometer (MDR) was cooled and conditioned to 60°C for 10 min with higher pressure. The strain sweep analysis was carried out from 0.14 to 140% of strain at 60°C at 0.1 Hz frequency. The IR(ATR) spectra were taken with a Brucker IFS 66v/s FTIR spectrometer. Philips XRD-6000 wide-angle X-ray instrument (WAXD) with Cu-K_α radiation (30 kV and 40 mA) and a wavelength of 1.542 Å was used for X-ray diffraction studies. The scanning 2θ angle ranged between 2° and 15° with a step scanning rate of 2 deg/min. The d-spacing of the layered particles was then calculated from Bragg's equation $n\lambda = 2d \sin\theta$, where λ in the wavelength of the X-ray, d is the interlayer distance and θ is the angle of incident X-ray radiation. Tensile tests have been performed by Zwick 1456 (model 1456, Z010, Ulm, Germany) with a crosshead speed of 200 mm min^{-1} (ISO 527). For TEM experiments, ultra-thin sections were cut by microtome at about −100°C and the images were taken by Libra 120 transmission electron microscope (Zeiss, Oberkochen, Germany) with an acceleration voltage of 200 kV. The thermo gravimetric study was carried out using a TA TGA, Q 500 instrument (USA) with a heating rate of 10°C/min under nitrogen atmosphere up to around 600°C when the samples were swept by oxygen flow.

3 Results and Discussion

3.1 Rheometric Characteristics

Direct polymer intercalation/exfoliation from the melt using various types of polymer compounding equipments provide a straightforward commercial process, but may not be completely effective. Thus, for compounding of nanocomposites conditions such as the rotor speed, (which governs mixing intensity and heat generation), mixing temperature, and mixing time should still be optimized. Preferred conditions would generally feature a long mixing time at low mixing temperature for avoiding undesirable degradation of the materials (29). However, the present study is focused on the effect of temperature on the intercalation and exfoliation process keeping the other parameters of internal mixer like speed and time fixed.

As can be seen from the rheometric data summarized in Table 1, the maximum rheometric torque is slightly higher for those mixes derived from the internal mixer at 160°C compared to the curing torque produced by the gum. In most of the cases, the maximum rheometric torque increases with increasing filler amount. The compounds

Table 1. Formulations and curing characteristics of organoclay filled XNBR cured at 160°C

*Mix Number**	*Mixing Temperature (°C)*	*Organoclay*	*R_∞ (dNm)*	*t_2 (min)*	*t_{90} (min)*
1	40	0	8.53	1.12	16.47
2	40	2.5	7.84	1.1	16.6
3	40	5	7.82	1.03	16.91
4	40	7.5	7.12	1	16.19
5	40	10	8.17	0.97	16.57
6	80	2.5	7.05	0.87	16.14
7	80	5	7.47	0.87	15.76
8	80	7.5	7.22	0.79	15.58
9	80	10	7.36	0.76	15.86
10	120	2.5	7.23	0.87	15.39
11	120	5	7.44	0.91	16.69
12	120	7.5	7.49	0.84	15.42
13	120	10	7.73	0.79	15.57
14	160	2.5	8.59	0.92	16.84
15	160	5	8.91	0.93	15.91
16	160	7.5	9.39	0.92	16.12
17	160	10	9.31	0.83	15.88

*All the mixes were vulcanized with 3 phr ZnO, 2 phr stearic acid, 1.4 phr sulfur, 1.7 phr CBS and 2 phr DPG.
'phr' stands for parts per hundred rubber.

mixed at 40°, 80° and 120°C show lower torque compared to the gum. Additionally, the effect on the curing time with the incorporation of organoclay is negligible. The preliminary rheometric study shows that the compounds mixed at 160°C exhibit better curing activity compared to the other compounds mixed at lower temperatures.

3.2 Morphological Studies

X-ray diffraction is a powerful tool to possess a preliminary understanding of the intercalation/exfoliation phenomena of a nanocomposite comprised of layered silicates. However, though it is a necessary study, it is still not sufficient enough to establish the nano-scale dispersion. An insufficient amount of clay, preferred orientation of clay, esspecially in the case of rubber processing and molding and also peak broadening always leads to a wrong interpretation of the disappearance of a basal peak like that of the 001 plane of a montmorillonite type clay (30–31). It is evident from Figure 1 that at 2.47 nm, a sharp peak is appearing in the XNBR gum compound. The presence of this sharp peak can also be observed in the 2.5 phr organoclay containing a XNBR sample, but the position is shifted towards lower angles and the corresponding spacing value is 2.95 nm. Moreover, the same peak has disappeared or merged with the main scattering coming from organoclay at relatively higher loading of organoclay and may be due to the *in situ* formation of zinc stearate. At higher loading of organoclay, the excess zinc oxide may be adsorbed on the surface of clay, whereby the *in situ* formation is hindered. For organoclay, the main peak appears at 2.98 nm and there is also another reflection at 1.21 nm. It is clear that the reflection from the 001 plane is shifted towards a lower angle for all cases of the XNBR vulcanizates filled with organoclay and the interlayer spacing increases to about 4 nm. This observation supports the fact that intercalation takes place for all the vulcanizates containing organoclay. The appearance of other peaks can also be seen at higher angles and the intensity of all these peaks rise with the increase of organoclay.

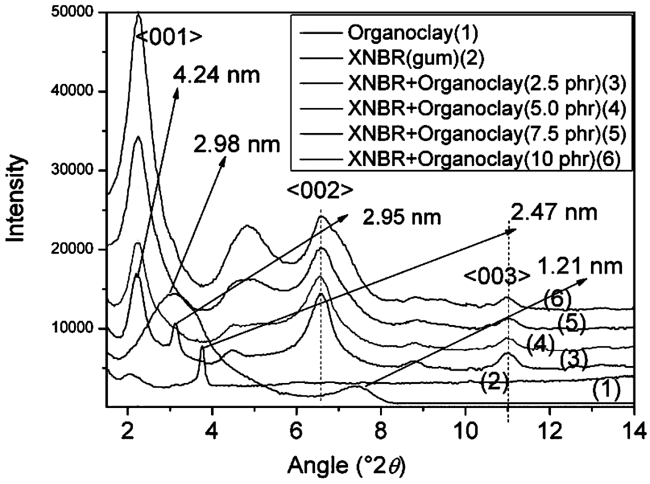

Fig. 1. WAXD patterns of XNBR reinforced with organoclay. Notes: the spectra of the related clays and organoclay were also shown. The position of the (001), (002), and (003) reflexes is indicated by dotted line.

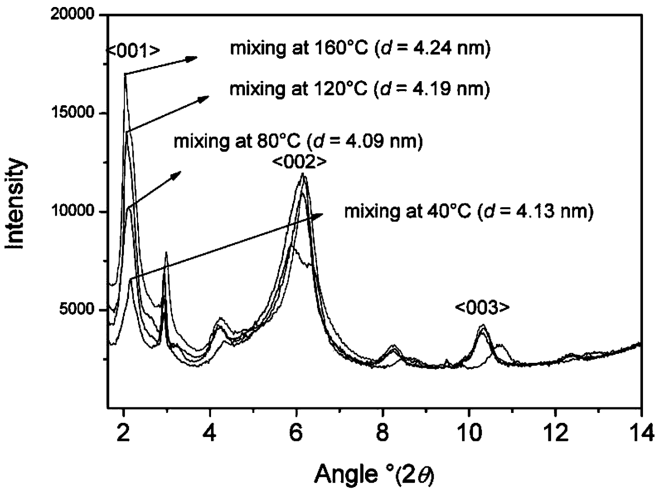

Fig. 2. WAXD patterns of 2.5 phr organoclay filled XNBR processed at different temperature.

This observation signifies the fact that a higher amount of organoclay in the rubber matrix results in an order of the clay particles and the particles are rearranged into a more coherent symmetrical form. So, the XRD study indicates that intercalation is a common process from 2.5 phr to 10 phr organoclay mixed at 160°C.

The effect of mixing temperature on the microstructure is also analyzed by WAXS experiments. The X-ray scattering patterns were taken from 2.5 phr filled XNBR matrix at different mixing temperatures. It is observed from Figure 2 that in all vulcanizates the space gap has been increased to some extent from low temperature mixing to high temperature mixing. It is also noticed from this figure that the peak intensity is becoming more intense in the high temperature mixed compound. Here, higher peak intensity means a higher number of intercalated layered species under the X-ray beam. The maximum number of intercalated layered silicate has appeared in the rubber matrix from the aggregated mass of the organoclay. In the case of low temperature mixing, a few number of intercalated clay layers makes the reflection of X-ray less intense from the corresponding 001 plane. It can be remembered here that the XRD study always has been done on the reflection mode with the samples of 2 mm thickness. It should be very interesting to note the appearance of the extra scattering in between 4 to 5° 2θ angle. From Figure 1 it is realized that the organoclay has a broad peak around 3° 2θ angle. So it may occur that some portion of the organoclay is deintercalated (gallery collapsing) by the removal of the quaternary ammonium ions and ultimately these cations reacts with the carboxylic group to form a carboxyl ammonium complex (32).

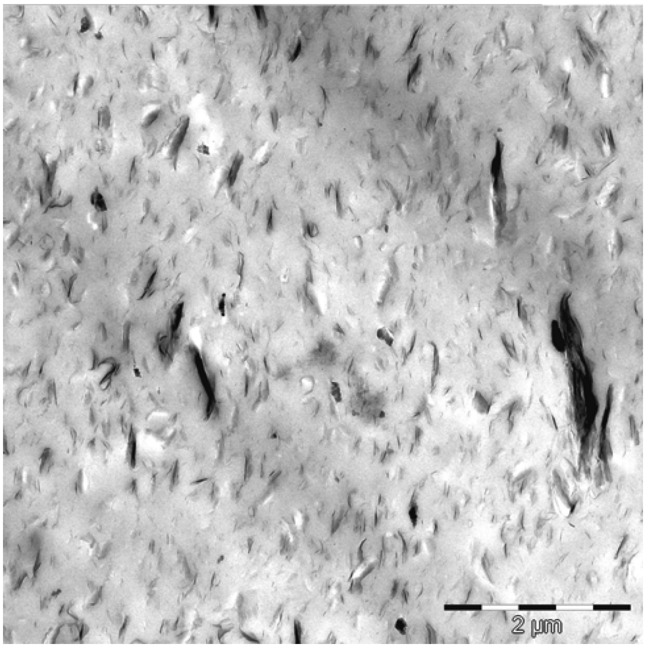

Fig. 3. TEM images of the XNBR nanocomposite containing 5 phr organoclay.

TEM pictures give direct visual evidence about the nanoscale dispersion of the layered silicate in the rubber matrix. Figure 3 shows the XNBR matrix filled with 5 phr organoclay mixed at 160°C. The silicate layers in the rubber matrix are oriented preferably during the processing which is quite common for layered silicate rubber nano-composite (2). A closer look gives the simultaneous existence of intercalated and exfoliated structures. Nevertheless, there are still a few agglomerated staged silicate layers, so total exfoliation/intercalation is not achieved through melt processing. Figure 4 is a magnified selection from Figure 3. Here

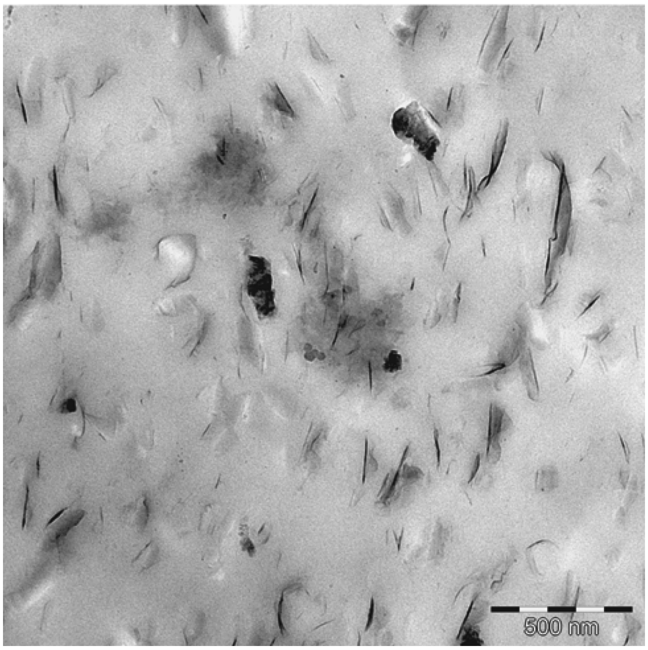

Fig. 4. TEM images of the XNBR nanocomposite containing 5 phr organoclay.

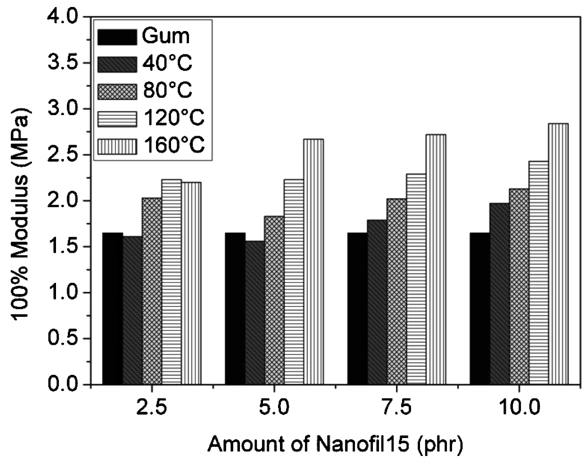

Fig. 5. Variation of 100% modulus values with the organoclay mixed at different temperatures.

most of the visible silicate layer thickness is around few nm and the length is a multiple of hundred nm. Therefore, it may be considered that most of the silicate layers are not mono layers but a couple of layers attached together.

3.3 Physical Properties

Carboxylated nitrile rubber shows excellent physical properties even in the gum form. Nevertheless, it is expected that with the addition of reinforcing a filler, the properties of XNBR will be enhanced. It has been found that even a very small amount of organoclay, like 5 phr, enhances the XNBR physical properties to a remarkable extent. In Figure 5, the stresses at 100% elongation (M100, so called 100% modulus) are plotted against loading of the clay mixed at different temperatures. It is evident from this figure that with the increase of clay loading, the values rise gradually and this effect is much more pronounced with a higher mixing temperature. A sharp increase in the 100% modulus can be found from 2.5 phr to 5 phr loading at 160°C mixing temperature. At 5 phr content of organoclay the 100% modulus was increased by 72% compared to the vulcanizates mixed at 40°C and 160°C. It can be said that at elevated temperatures the extent of the intercalation/exfoliation processes is facilitated. At lower loading of organoclay such as 2.5 phr and 5 phr, the addition of the filler mixed at a low temperature like 40°C does not produce any significant change in the rubber matrix in terms of the M100 elongation compared to the gum value. However, in high temperature mixes, the difference is quite remarkable. Obviously, at low loadings and low temperatures, no proper dispersion of the organoclay can take place which explains the indifferent nature of the physical properties. In Figure 6, the modulus at 300% elongation is plotted against loading of the organoclay, and as observed, a high mixing temperature has a strong contribution on the physical properties. For example, at 10 phr organoclay loading, an increment of 39% in the M300 was found for those vulcanizates mixed at 160°C as compared to 40°C. In addition, it is reflected from Figure 7 that with the same loading of organoclay, the tensile strength is increased quite sharply with increasing temperature. The maximum tensile strength was found for the vulcanizates containing 7.5 phr organoclay mixed at 160°C. Here, the increment of the tensile properties is 120% compared to the gum without filler. This type of strong reinforcement is only possible with such low concentration of inorganic filler if exfoliation/intercalation occurs to a considerable extent. In this context, a mechanical scheme is shown in Figure 8 in order to explain the exfoliation /intercalation processes. It is assumed that at the higher mixing temperature, a reaction between the silanol (–OH) groups on the edge of the clay and carboxylic (–COOH) groups of the XNBR takes place forming an ester type bond. This

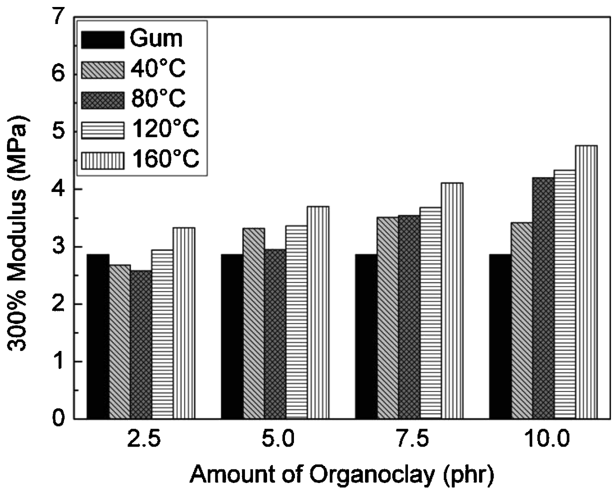

Fig. 6. Variation of 300% modulus values with the organoclay mixed at different temperatures.

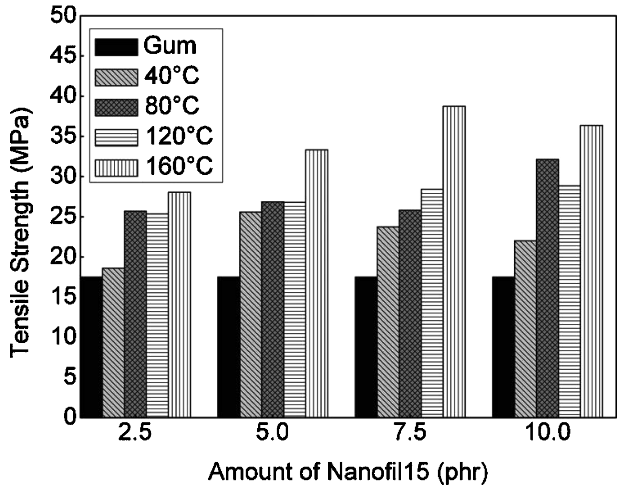

Fig. 7. Variation of tensile strength values with organoclay mixed at different temperatures.

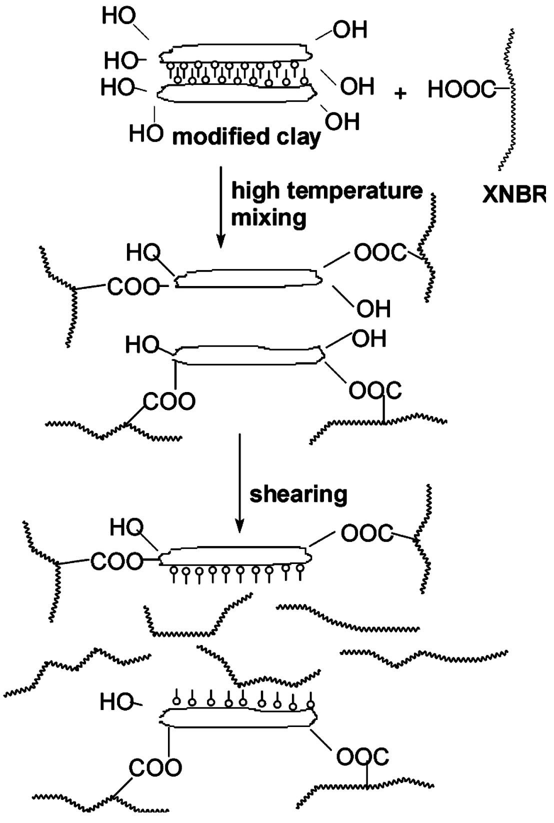

Fig. 8. Schematic mechanism of exfoliation/intercalation.

type of chemical bond between clay and rubber (first step in Figure 8) is formed under the conditions of high shearing force (internal mixer) and at a high temperature such as 160°C. So, it is expected that the strong shearing force can be transferred from the rubber to the layered silicate and delaminates the staged layers by overcoming the force between two adjacent silicate layers and ultimately results in an exfoliated clay structure in the rubber matrix. However, the exfoliation/intercalation processes have no significant effect on the elongation at break values as seen from Figure 9.

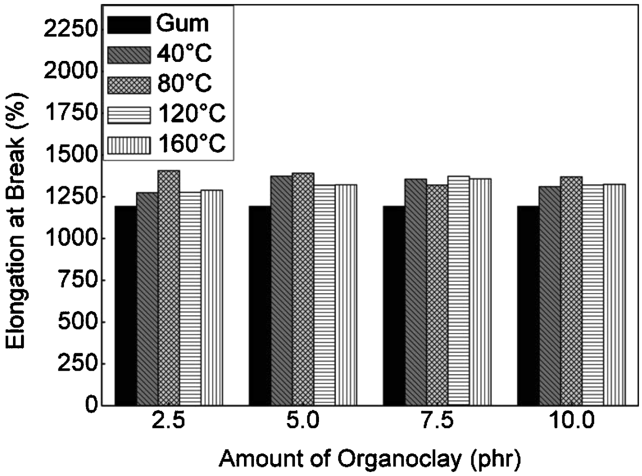

Fig. 9. Plots of elongation at break values with an amount of organoclay mixed at different temperatures.

The tensile experiment can also be depicted as stress vs. strain curves. The stress-strain curves obtained from different mixing temperatures at loading of clay of 5 phr are shown in Figure 10. In the low strain region (0–300% elongation) the curves are steeper with the increase of the mixing temperature at 5 phr filler loading. So, it can reasonably be said that the reinforcing efficiency of organoclay is increased with the increase of mixing temperature, as well as with the shearing forces given on the silicate layers, which also supports the scheme in Figure 8. It is also interesting to discuss the nature of the stress-strain plot at higher elongation. It is surprising to note the three crossovers of the gum over the 40°, 120° and 140°C mixed vulcanizates (indicated by circles). It can be assumed that at low temperature mixing (40°–120°C), there may exist some clusters of organoclay like a local filler-filler network. These local networks do not exist in a continuous fashion over the whole rubber matrix but in discrete zones which affect the homogeneity in the rubber matrix and ultimately deteriorate the reinforcement. At higher elongation, the stress cannot be transferred from one side of the clay cluster to the other side and as a consequence, the initiation of cracks takes place. On the other hand, for the 160°C mixing temperature, such cluster or aggregate formation of the filler which can deteriorate the stress at the same strain is absent. Obviously, this is the possible reason behind the strange behavior of the filled vulcanizates. This behavior also supports a better degree of dispersion (intercalation/exfoliation) of the vulcanizates mixed at 160°C.

3.4 IR Studies

The IR- ATR spectra taken from organoclay, pure XNBR and the vulcanizates filled with 5 phr clay and mixed at

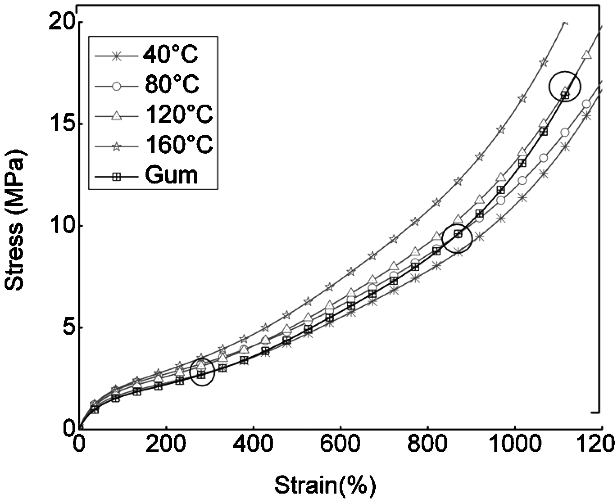

Fig. 10. Stress-strain diagram of the rubber composite mixed at different temperature containing 5 phr organoclay.

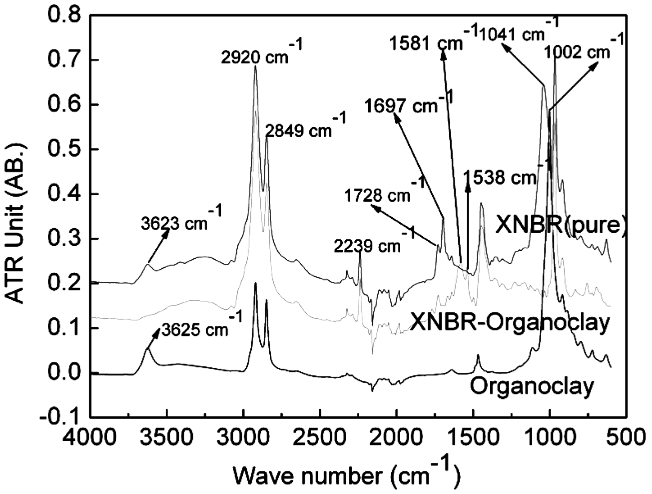

Fig. 11. IR(ATR) spectra of the organoclay, XNBR(gum) and 5 phr organoclay filled XNBR vulcanizates mixed at 160°C.

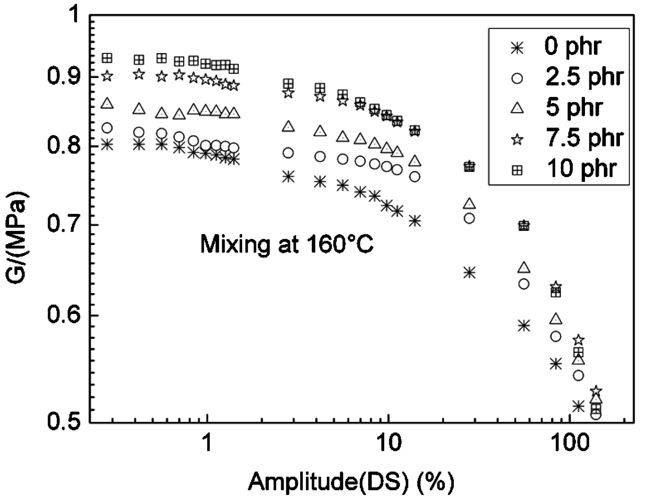

Fig. 12. Strain dependence of G′ at 60°C for XNBR vulcanizates mixed at 160°C.

160°C temperature, are depicted in Figure 11. From the spectra, the principal peaks for the pure organoclay are observed at 2846 cm^{-1} and 2920 cm^{-1} due to the presence of aliphatic —CH2 groups in the hydrophobic tails of the quaternary amine modifier. The broad peak around 3625 cm^{-1} of this material may be attributed to the presence of —OH groups on the surface. The characteristic absorbance for —Si—O—Si— in the clay is seen at 1002 cm^{-1}.

The pure XNBR gives rise to peaks at 2920 cm^{-1} and 2849 cm^{-1} due to the —CH2 groups on the rubber backbone. The characteristic absorbance for —C—N of XNBR can be observed at 2239 cm^{-1}. Peaks in the range of 1500–1700 cm^{-1} result from the >C=O group of the carboxylic part in the rubber. Besides, the absorption at 1040 cm^{-1} arises as a result of the asymmetric stretching of the —C—OH in the carboxylic functionality.

A careful study of the spectrum for the composites shows that the peaks at 1695 cm^{-1} and 1728 cm^{-1} disappear in the cured XNBR matrix, being replaced by two new ones at 1538 cm^{-1} and 1581 cm^{-1}, respectively. These may be assigned to the >C=O stretching in different chemical environments. The former one corresponds to the stretching in tetra- coordinated zinc-carboxylate complex, and the latter to that in a hexa-coordinated one. The peak at 3625 cm^{-1} on the pure organoclay spectrum disappears in the nanocomposite, probably owing to an interaction with the —COOH groups on the XNBR. Furthermore, a shift in characteristic absorbance of —Si—O—Si— is observed from 1002 cm^{-1} to around 996 cm^{-1}, i.e., 6 cm^{-1} to the lower energy side. A similar transition has been observed by Katti et al. (33) in their studies on polyamide-MMT nanocomposites. The linkage of the COOH group on XNBR with the silanol —OH on the clay surface which, in turn, already bonded with the silica tetrahedral of MMT, may have caused this shift of the Si—O stretching band in the composite with respect to the organoclay. All these behaviors give evidence in support of the plausible intercalation- exfoliation mechanism shown in the scheme of Figure 5.

3.5 Strain Sweep Analysis

The dynamic property measurements at low strain amplitude allows us to discuss the filler-filler network, as well as a rubber-filler network of organoclay filled polar elastomer like XNBR. The dependence of G′ on the strain amplitude at very low strain can deliver a good understanding of the filler networking in the rubber matrix. Generally, the values of G′ remain unaltered with the strain for an unfilled rubber system. However, for a filled system, at a very low strain amplitude range, the value of G′ remains constant up to a certain strain and then the value decreases with increasing strain. This nonlinear behavior of a filled rubber system is called the ‘Payne effect’ (34, 35) and can provide information about the dispersion of filler in the rubber matrix. At very low strain, the filler networks are successively broken with the increase of the strain resulting in a gradual decrease in G′ values. In the present investigations, the plots of G′ vs. double strain amplitude of the 160°C mixed vulcanizates are shown Figure 12. It is evident from this figure that up to 10% strain amplitude, the values of G′ are remain constant in all cases and thereafter a significant decrease of the values is observed. This decrease in G′ value is due to slippage of the moving die during the measurements at higher amplitude and not due to the breaking of the filler-filler network since this observation is also provided by the unfilled rubber. There is a considerable difference in the absolute value of G′ at low strain in the different vulcanizates (36). The G′ value increased with the increase of filler loading attributed to the hydrodynamic effect of rigid solid particles. At the high temperature mixing ca. 160°C, the silicate layers are more homogeneously distributed mainly by the exfoliation process which enhances the reinforcing

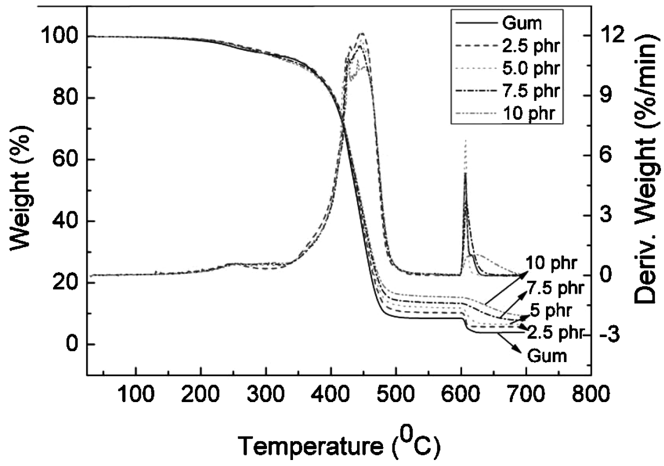

Fig. 13. Thermo gravimetric analyses graphs of clay XNBR nanocomposites.

capability of the filler significantly. With the increase of filler amount, the formation of bound or trapped rubber (dead rubber) enhances. Subsequently, effective volume of the filler is increased substantially, thereby raising the modulus of the rubber matrix.

3.6 Thermal Decomposition Studies

The thermogravimetric analysis was performed on the XNBR nanocomposites and the results are shown in Figure 13. The main chain degradation starts at 340°C almost identically for all the vulcanizates and there is no such significant difference in the thermal stability of the vulcanizates. Additionally, at a lower temperature of 250°C, there is also a small degradation observed in all cases, presumably due to the presence of unreacted organic curatives used for vulcanization. It also observed that with the increase of organoclay content, the residues increase. At 600°C, the flow of nitrogen is replaced by oxygen to burn the rest of the carbonic residue, giving rise to another decomposition pattern. The undecomposed materials at 700°C, under nitrogen flow, are mainly zinc salts and inorganic fillers. The organoclay was also subjected to TGA (Figure 14). It was found that around 160°C there is no thermal decomposition of the organoclay. Hence, processing at this temperature is a safe process with respect to the thermal stability of the organic quaternary amine present in the organoclay.

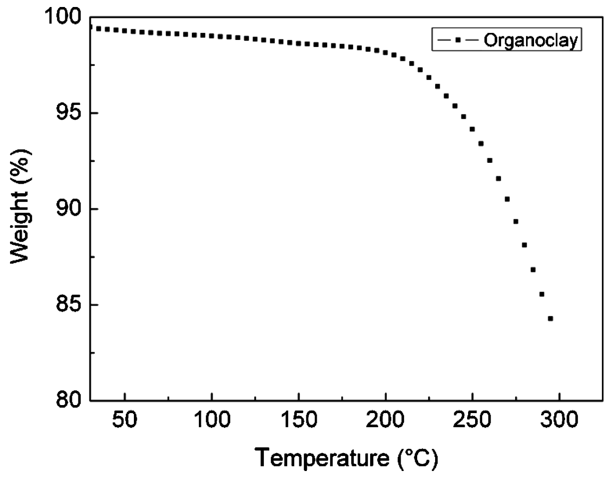

Fig. 14. Thermogravimetric analysis of organoclay.

4 Conclusions

It is revealed that XNBR has a unique role to play in the formation of a synergistic pair with organoclay to offer an excellent reinforced elastomer with good physical and dynamic properties. There is a strong influence of processing temperature on the intercalation /exfoliation process of the rubber-layered silicate composites with nano-order dispersion. Further investigations dealing with rubber-filler network and filler-filler networking at low loadings of organoclay are deemed necessary to have a clear understanding about the concept of elastomer reinforcement by nanoparticles like layered silicates.

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