Mechanical properties development of high-ACN nitrile-butadiene rubber/organoclay nanocomposites

S. M. R. Paran, G. Naderi* and M. H. R. Ghoreishy

The nanocomposites of nitrile-butadiene rubber (NBR) with high acrylonitrile content and Cloisite 30B were prepared in the presence of the resorcinol and hexamethylenetetramine (RH) complex as a compatibiliser. The structure of the NBR nanocomposites was characterised by cure characteristics, XRD, TEM and mechanical properties. The mechanical properties of the nanocomposites containing RH were far superior to those of NBR nanocomposites alone. Some hyperelastic models were approved on comparative study of tensile properties and the effect of RH compatibiliser on the material parameters of the models was investigated. The Mori–Tanaka and Halpin–Tsai models were used to estimate the modulus of prepared nanocomposites and compared with experimental results. The effect of RH on the intercalation/exfoliation of silicate layers was investigated from combination of effective particle method and Mori–Tanaka theory. This technique showed that the average number of silicate layers in each effective particle can decrease with RH compatibiliser.

Keywords: High-ACN nitrile-butadiene rubber, Organoclay, Intercalation, Compatibiliser, Hyperelastic

Introduction

Nanocomposites are a new class of composites, which are particle-filled polymers for which at least one dimension of the dispersed particles is in the nanometre range. A one-dimension nanocomposite is characterised by only one dimension in the nanometre range. In this case, the filler is present in the form of one-dimensional sheets, hundreds to thousands of nanometres long. They do not occur as isolated individual units but aggregate to form a crystalline structure.1–5 This family of composites can be grouped under the name of polymer-layered nanocomposites. These materials are almost exclusively obtained by the intercalation of the polymer inside the galleries of layered host crystals.6,7

Polymer–clay nanocomposites can generally attain a higher degree of strength, thermal stability and barrier property, with significantly lower silicate content, than conventional polymer composites. In most cases, polymer/clay hybrid nanocomposites are prepared via either an intercalating polymerisation process or a melt intercalating process.8–11 In the melt-intercalation process, layered silicate is mixed with polymer matrix in a molten state. In this condition, the layer’s surface is sufficiently compatible with the chosen polymer so that it can infiltrate the interlayer space and form either intercalated or exfoliated nanocomposites. This technology requires no solvent so it can be easily utilised for industrial applications.

The core feature of preparing organoclay nanocomposites is to achieve a very high degree of dispersion of organoclay aggregates that yields to very large surface areas. This indeed significantly improves the overall properties of the pristine polymer matrix in competition with ordinary microcomposites.

Immense works have been done in clay nanocomposites for many thermoplastics and thermosetting polymers. However, the studies on rubber-based nanocomposites constitute in lesser dimension.12–16 The most important factor, which indicates the improvement of properties in rubber, is the intercalation/exfoliation of nanoclay. The simple mixing of rubber and nanoclay will not exfoliate the filler in the rubbery matrix.17 Kwak and co-workers18 found that NBR nanocomposite with nanoclay having polar organic modifier has the highest elasticity in NBR nanocomposites, indicating the formation of the largest gallery height. Naderi and co-workers19 investigated the effect of organoclay concentration on the curing and mechanical properties of NR/EPDM blends and found that the polymer chains could intercalate the silicate layers and improve tensile strength of rubber matrix up to 40%. Gatos and Karger-Kocsis20 studied the role of the aspect ratio of the layered silicate platelets on the oxygen permeation properties of HNBR nanocomposites and investigated that the dispersion state and higher aspect ratio of organophilic layered silicates reduced dramatically the oxygen permeability of the rubber matrix. Zhang and co-workers21 investigated the effect of
elastomer matrix, mixing and vulcanisation processes on the formation of nanocomposites and reported that the SBR/organoclay nanocomposites exhibited a well-ordered intercalated structure and mixing process played the predominant role in the formation of nanocomposite, whereas the EPDM/organoclay nanocomposites exhibited a disordered intercalated structure and mainly formed in the vulcanisation process.

On the basis of literature surveys, the most used method for rubber/organoclay nanocomposites manufacturing is on the open two-roll mill. This manufacturing method is reliable from industrial visions but could not guaranty the extreme intercalation of silicate layers. Therefore, the mechanical enhancement of such rubber nanocomposites fairly reaches to optimum quantity with respect to organoclay.

In this study, the authors attempt to develop the rubber–clay nanocomposites, by introducing some reactive compatibilisers in rubber mixing and vulcanisation processes. Nitrile-butadiene rubber (NBR) was used in the experiments as a rubbery matrix. The compatibiliser that used is the resorcinol and hexamethylenetetramine (RH) complex, which can be decomposed into resorcinol and formaldehyde at the temperature above 110°C and can increase the interactions of NBR and Cloisite 30B in the processes of mixing and vulcanisation. The main aim of this research is the using of a compatibiliser such as RH complex to enhance the exfoliation of Cloisite and formaldehyde at the temperature above 110°C and the experiments as a rubbery matrix. The compatibiliser theroretical concept

Hyperelastic materials show large strains and deformation under applied forces and have an elastic potential $W$ (or strain energy density function) that is a scalar function of one of the strain or deformation tensors. This function can be derived with respect to a strain component that determines the corresponding stress component:

$$\sigma_{ij} = \frac{\partial W}{\partial \epsilon_{ij}}$$

where more details about hyperelastic materials can be found in supplementary information.

For building a hyperelastic model, two principal approaches can be used. The former is the Rivlin series reduction or the Ogden expansion. The Rivlin series is given for incompressible materials by the following expression

$$W_{Ri} = \sum_{\rho_p=0}^{\infty} C_{\rho_p}(I_1 - 3)^\rho(I_2 - 3)^\rho$$

and that of Ogden by

$$W_{Og} = \sum_{\rho_p=1}^{\infty} \frac{h_p}{\rho_p} \left( \lambda_1^{\rho_p} + \lambda_2^{\rho_p} + \lambda_3^{\rho_p} - 3 \right)$$

where $I_1$ and $I_2$ are the two first invariants of the Cauchy–Green strain tensor, $\lambda_i$ the principal stretches, $C_{\rho_p}$, $\rho_p$ and $h_p$ are material characteristics, with condition apply: $C_{00} = 0$.

The latter approach is on the basis of modelling the experimental results that $\partial W/\partial I_1$ is independent of $I_1$ and $I_2$ for smaller values of $I_1$ and depends on $I_1$ for large values and $\partial W/\partial I_2$ is independent of $I_1$ but a decreasing function of $I_2$.

The application, corresponding variables and the available data to determine material parameters of the model identifies what kind of hyperelastic models should be used. In this study, the second order of Ogden and Mooney–Rivlin models has been investigated to depict nonlinear stress–strain behaviour of NBR nanocomposites. The results of second order of Ogden model were more stable at all uniaxial or biaxial stresses and strains with respect to higher orders. It should be noted that the full incompressibility assumption is applied for the models, meaning that all the equations only contain the deviatoric part and the volumetric part is neglected.

The prediction of the stiffness for studied nanocomposites was done using Halpin–Tsai equation and Mori–Tanaka theory was derived from Eshelby’s inclusion model and is given in equations (4) and (6), respectively

$$E_C = \frac{1 + 2(L/I)f_p \eta}{1 - f_p \eta}$$

$$\eta = \frac{(E_t/E_m) - 1}{(E_t/E_m) + 2(L/I)}$$

$$E_C = \frac{1}{1 + f_p(A_1 + 2\epsilon_m A_2)/A}$$

where $f_p$ is the nanoclay volume fraction, $(L/I)$ is particle aspect ratio, $\epsilon_m$ represents Poisson’s ratio of the matrix and $A$, $A_1$ and $A_2$ are functions of Eshelby’s tensor for a disk-shaped spheroidal inclusions as described in supplementary information.

Materials

NBR (JSR N215SL) containing 48% acrylonitrile was supplied from Japan Synthetic Rubber Co. Ltd (density, 1.01 g cm$^{-3}$ and Mooney viscosity of 45 (ML (1+4), 100°C). Cloisite 30B, a natural montmorillonite modified with a methyltallow-bis(2-hydroxyethyl) quaternary ammonium salt with cation exchange capacity of 95 mequiv./100 g clay (Southern Clay, Inc., Gonzales, TX, USA), was used as a nanofiller in the preparation of the nanocomposites. Resorcinol (molar mass, 110.1 g mol$^{-1}$, melting point, 110°C and density, 1.28 g cm$^{-3}$) and hexamethylenetetramine (molar mass, 140.186 g mol$^{-1}$ and density, 1.33 g cm$^{-3}$) were supplied from Merck company and other compounding ingredients such as sulphur, zinc oxide, stearic acid, carbon black (N550 and N330) and mercaptobenzothiazolesulphide (MBTS) were purchased from stores and all these materials were used without further purification.

Preparation

Cloisite 30B/RH/NBR masterbatches were prepared using a laboratory size internal mixer (Brabender Plasti-Corder,
Ultracut ultramicrotome (Reichert OMU3) at 90 nm) were carried out for TEM observations, by an ultra-thin cross-sections of the prepared samples (70 nm) using a universal tensile testing machine, Instron 6025. Tensile strength was done according to ASTM D412. The cure characteristics of the compounds were prepared by mixing the above master-batches with NBR containing appropriate amounts of carbon black and curing agents, according to Table 1, in an open two-roll mill for 5 min at 50°C, running at rotor speed ratio of 1:1.2. The final rubber compounds were vulcanised in a compression moulding machine at 160°C for about 15 min according to the optimum cure time obtained from Monsanto Rheometer.

### Characterisation

The cure characteristics of the compounds were studied using a Monsanto Rheometer R-100 testing instrument operating at 160°C with 3° arc at a period of 20 min as per ASTM D2084. The clay gallery height was monitored using an X-ray diffractometer (Philips PANalytical X’Pert PRO) with Cu Kα radiation at a generator voltage of 40 kV, current of 40 mA and wavelength of 0.154 nm at room temperature. The 2θ values in XRD patterns can be converted to layer spacing values d according to the Bragg’s law, 

\[
d = \frac{2 \lambda \sin \theta}{\lambda}\]

where \(\lambda\) is the wavelength of the radiation (\(\lambda = 0.154178\) nm) and \(n\) is an integer. The range of 2θ scanning of X-ray intensity employed was 1–10° with a scanning rate of 1° min⁻¹. Transmission electron microscopy (TEM) analysis was performed with a Philips apparatus using an acceleration voltage of 80 kV. The ultra-thin cross-sections of the prepared samples (70–90 nm) were carried out for TEM observations, by an Ultracut ultramicrotome (Reichert OMU3) at −100°C using a diamond knife.

Dumbbell-shaped specimens for tensile tests were cut from the moulded slabs. Cylindrical-shaped specimens for resilience tests were directly compression moulded. Tensile strength was done according to ASTM D412 using a universal tensile testing machine, Instron 6025 at room temperature with an extension speed of 500 mm min⁻¹. Resilience test was done according to ASTM D2632. The Shore A hardness of the samples was measured, as per ASTM D2240 testing method. For hardness measurements, the sheets having an effective thickness of 6 mm were used.

Swelling test was conducted by immersing the samples in toluene for 48 h and swelling ratios were calculated according to ASTM D471.

### Results and discussion

The cure characteristics and thus process ability of the prepared nanocomposites are as shown in Fig. 1 and the parameters were as shown in Table 2. The results of minimum torque values related to the softening or viscosity decrease of the rubber matrix show a slight decrease with respect to the RH compatibiliser loadings. The decrease can be attributed to the less viscosity of the RH compatibiliser, compared to the NBR matrix. On the other hand, the nanocomposites containing RH compatibiliser depicted an increase in the maximum torque value than that of the RH-free nanocomposites. The maximum torque of nanocomposite rubbers depends on both the extents of crosslinking and reinforcement caused by the nanoclays. Several researchers have suggested that organoclay is not only a reinforcing agent for final NBR products, but also acts as an effective accelerant or co-curing agent in NBR vulcanisation process. Table 2 shows that the highest maximum torque value and torque difference occurred at 3 phr content of RH compatibiliser. Also, the scorch and cure times showed minimum values and the calculated cure rate index has an optimum value at RH compatibiliser concentration of 3 phr. Curing is generally accelerated by alkaline additives, amines and inorganic bases. Therefore, it can be concluded that the RH compatibiliser played a role as a basic co-curing agent in the vulcanisation process, enhancing the cure behaviour of the NBR nanocomposites. However, no significant change in the cure characteristics of NBR nanocomposites is observed by further increasing the RH concentration to 5 phr.

The XRD patterns of the nanoclay and prepared nanocomposites are as shown in Fig. 2. It can be estimated the change of a gallery distance for the organoclay before and after intercalation, through the peak shift in the XRD patterns. The nanoclay (Cloisite 30B) indicated an intense peak around 2θ = 4.881° corresponding to the basal spacing of 18.08 Å (d₅₀0₁). The XRD patterns of nanoclay

![Graph](image-url)
in the NBR nanocomposites depicted that the $d_{001}$ main diffraction peak has been shifted towards the lower angles in comparison with the nanoclay. It can be seen that the XRD pattern of nanoclay in the nanocomposites containing 3 phr of RH compatibiliser reaches an intense peak of around $2\theta = 2.14^\circ$, corresponding to the basal spacing of 41.28 Å. It may be due to the RH compatibiliser that facilitates the intercalation of rubber chains into the interlayer galleries of organoclay which contributes for increasing the interaction between NBR and Cloisite 30B during the processes of mixing and vulcanisation. In parallel, the assigned figure shows that additional contents of RH compatibiliser has no more effect on the intercalation of silicate layers. However, XRD analysis is not completely consistent in determination of the intercalation/exfoliation state of silicate layers. Therefore, using TEM photomicrographs along with XRD patterns show the nanostructure of the NBR nanocomposites. TEM micrograph of the cryogenically fractured surface of the sample containing 0 and 3 phr of RH compatibiliser is as shown in Fig. 3. Narrow stacks of clay, displayed as dark lines in this image, suggest the formation of nanostructured composites due to proper break up and exfoliation of silicate layers in nanocomposites containing 3 phr of RH compatibiliser.

The mechanical properties of nanocomposites are as depicted in Figs. 4 and 5. Several studies have shown that the mechanical properties of nanocomposites depend on various parameters like rubber–clay interactions, compounding conditions and clay content. From Fig. 4, in all prepared nanocomposites, modulus improved by increasing the RH compatibiliser content up to 3 phr, attributing this improvement to the state of intercalation/exfoliation of the nanocomposites and also the confinement of rubber chains arising from the presence of silicate layers in the matrix. However, the hardness results as shown in Fig. 4 have no obvious changes with respect to the concentrations of RH compatibiliser. The nanocomposites containing 1 and 3 phr of RH compatibiliser showed 10 and 30% increase in tensile strength, respectively, compared to the nanocomposite without RH compatibiliser as shown in Fig. 5. It can be investigated that the RH compatibiliser serves to enhance the interface interaction between the NBR macromolecular chains and silicate layers, so the improvement in tensile strength is more significant which is consistent with the literature.

| Sample code | Min. torque (lb f.in) | Max. torque (lb f.in) | Torque difference (lb f.in) | $t_2$ (min) | $t_90$ (min) | Cure rate index |
|-------------|----------------------|----------------------|-----------------------------|-------------|-------------|----------------|
| RH0         | 9.95                 | 32.40                | 22.60                       | 2.82        | 11.74       | 11.21           |
| RH1         | 9.93                 | 35.87                | 25.92                       | 2.50        | 10.00       | 13.33           |
| RH3         | 9.90                 | 41.58                | 31.65                       | 1.57        | 8.96        | 13.53           |
| RH5         | 9.80                 | 39.92                | 30.02                       | 1.68        | 9.12        | 13.44           |

*Scorch time.

*Time required for optimum cure.

![2 XRD patterns of pure organoclay and prepared nanocomposites](image1)

![3 TEM micrograph of nanocomposite containing a 0 phr b 3 phr of RH compatibiliser](image2)
The enhanced interface interaction in the cured NBR nanocomposites also result in the reduction of elongation and resilience as shown in Fig. 5. The nanocomposites containing 1 and 3 phr of compatibiliser showed about 10 and 15% decrease in resilience, respectively, compared to the nanocomposite without RH compatibiliser. This phenomenon is in agreement with the previous works of Zhu and Wool. The enhancement in the mechanical properties is due to the better dispersion of nanoclay in the NBR matrix and rubber–clay interaction as corroborated from XRD and TEM results.

The swelling ratios of the prepared nanocomposites in toluene are as shown in Fig. 6. The percentage of solvent uptake was considerably decreased for NBR nanocomposite containing 3 phr of RH compatibiliser compared to other nanocomposites. The higher reinforcement of nanoclay in the NBR matrix restricts the extensibility of the rubber chains induced by swelling. Hence, the nanocomposites containing 3 phr of RH compatibiliser have higher solvent resistance and additional RH compatibiliser has no considerable improvement.

The uniaxial stress–strain data were imported into ABAQUS software and the behaviour of prepared nanocomposites is compared with Ogden and Mooney–Rivlin models. Material parameters of these models were as presented in Table 3 for different nanocomposites. The initial shear modulus or shear modulus at very low shear strains is calculated from the following equation and presented in Table 3:

\[ G_0 = \sum_{i=1}^{N} \mu_i \]  

4 100, 300% modulus and hardness of the nanocomposites

5 Tensile, elongation and resilience of prepared nanocomposites
From the results presented in the Table 3 it can be concluded that more dispersion of silicate layers of organo-clay via introduction of a compatibiliser in the NBR matrix leads to higher initial shear modulus of prepared nanocomposites. It is investigated that enhancement of the interactions between rubber chains and silicate layers leads to more resistance of the nanocomposites to the shear forces at the initial strains. We can see from Table 3 that the errors of fitting experimental results and theoretical models gradually increase via introducing of RH complex into the formulations. It seems that the RH complex can raise the interactions between NBR matrix and organoclay, leading to more fitting deviations from the experimental data.

To investigate the effect of compatibiliser content on the applicability of used hyperelastic models, nominal stress versus nominal strain obtained from experimental and model predictions for NBR-RH-Cloisite 30B nanocomposites were as illustrated in Figs. 7 and 8. According to the obtained results for prepared nanocomposites, it can be pointed that Ogden model has some deviations from experimental data in middle and large deformations. This behaviour is in agreement with previous works of Naderi and co-workers. It can be seen from Fig. 7 that the increasing of RH content up to 3 phr leads to increasing of model predictions from experimental data especially at large deformations. The Mooney–Rivlin investigations have more deviations from experimental data in middle and large deformations. The Mooney–Rivlin model containing more parameters of matrix and nanoparticles like Poisson’s ratio, elastic and shear modulus of the matrix and inclusions. Therefore, the predicted modulus of nanocomposites using Mori–Tanaka theory has lesser deviations from experimental data. As expected from the Mori–Tanaka theory, increasing the intercalation of silicate layers leads to decreasing of differences between model predictions and experimental data. For more realisation of RH role in the increasing gallery distance, an effective particle volume is defined and employed to represent the inherently discrete nanoclay.

| Model          | Parameters | RH content (phr) | Error |
|----------------|------------|------------------|-------|
|                | µ1         | 0.006            | 0.012 | 0.019 |
|                | µ2         | 2.526            | 2.681 | 3.359 |
|                | α1         | 4.092            | 4.465 | 4.506 |
|                | α2         | -4.51            | -4.757| -4.379|
|                | Error      | 0.013            | 0.014 | 0.013 |
| Initial shear modulus (MPa) | 2.532     | 2.692            | 3.378 |
| Mooney–Rivlin  | C10        | 1.106            | 1.604 | 1.845 |
|                | C01        | -0.456           | -1.01 | -0.923 |
|                | Error      | 0.08             | 0.09  | 0.1   | 0.09  |
structure on the basis of previous works of Boyce and co-workers\textsuperscript{45} The particle thickness can be related to the number of silicate layers through the following equation

\[ t = (N - 1)d_{(001)} + d_s \]  

(8)

where \( d_s \) is the silicate sheet thickness, \( d_{(001)} \) is the inter-layer spacing and \( N \) is the number of silicate layers in each particle and expected to reduce with RH-increasing concentration or better dispersion of nanoparticles. The elastic properties of an isotropic effective particle can be estimated as

\[ E_p = \chi E_{\text{silicate}} + (1 - \chi)E_{\text{gallery}} \]

\[ v_p = \chi v_{\text{silicate}} + (1 - \chi)v_{\text{gallery}} \]  

(9)

where \( \chi \) is the volume fraction of the silicate in the effective particle as the following equation

\[ \chi = \frac{V_{\text{silicate}}}{V_p} = \frac{N d_s}{t} \]  

(10)

We have used the molecular characterisation of Cloisite 30B lattice cell for investigation of elastic properties of the effective particle with different number of silicate layers and then calculated the elastic modulus of prepared nanocomposites using Mori–Tanaka theory. Figure 10 represents the modulus of nanocomposites with respect to the number of silicate layers in each effective particle. From the results of the Fig. 10, it can be estimated that the more interactions of organoclay and rubber chains by addition of different concentrations of RH complex could change the number of silicate layers in each effective particle for instance the modulus of nanocomposite which containing 3 phr of RH lies between the graphs related to \( N = 2 \) and 3. It can be concluded that the number of silicate layers in an effective particle should not necessarily be an integer and it can be a real number. This means that the silicate layers should not necessarily lie in parallel with each other and cover all surface of surrounding silicate layers and could cover only a certain percent of other surfaces. Therefore, the parameter of \( N \) should be related to the sum of areas which are covered by other silicate layers in an effective particle volume. Figure 11 depicts
the modulus of nanocomposites with respect to different numbers of silicate layers that completely cover each other or real contents of N.

Conclusion

The nanocomposites of NBR and Cloisite 30B prepared by introduction of a compatibiliser consists of RH in the mixing process. It is investigated that the RH compatibiliser increases the interactions between rubber matrix and silicate layers. Consequently, these interactions may improve the interfacial combination between the NBR and Cloisite 30B thus promote the intercalation/exfoliation of silicate layers in rubber matrix. The mechanical properties of the NBR-RH-Cloisite 30B nanocomposites were far superior to those of corresponding NBR-Cloisite 30B nanocomposites especially at large deformations and have an optimum quantity with respect to RH loading. Investigations of the effect of compatibiliser content on the applicability of Ogden and Mooney–Rivlin hyperelastic models show that the Ogden model has some deviations from experimental data in large deformations but Mooney–Rivlin has more deviations from experimental data in all deformations in comparison to Ogden model. As expected from the Mori–Tanaka theory, increasing the intercalation of silicate layers leads to decrease of differences between model predictions and experimental data for modulus of prepared nanocomposites. Effective particle volume method was used for more realisation of the effect of compatibiliser on the exfoliation/intercalation of silicate layers and its effect on the modulus of the nanocomposites. The results show that the average number of silicate layers in each effective particle volume may be decreased due to addition of RH compatibiliser.

Supplemental data

Supplemental data for this article can be accessed here at doi:10.1080/14658011.2016.1212967.

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