Selective Orientation of Needlelike Sepiolite Nanoclay in Polymer Blend for Controlled Properties

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ABSTRACT: Sepiolite nanocray needles have been selectively localized either in the natural rubber (NR) phase or in the carboxylated nitrile rubber (XNBR) phase of the XNBR/NR (50/50) blend prepared by the solution casting method. In a systematic manner, the role of the difference value between the interaction parameter of individual blend components (NR or XNBR)/solvent and the interaction parameter of sepiolite nanoclay/solvent in selectively localizing the sepiolite nanoclay to the NR phase or the XNBR phase of the XNBR/NR (50/50) blend has been explored. A higher percentage of sepiolite nanoclay resides in the dispersed NR phase when the difference value between the interaction parameter of NR/solvent and the interaction parameter of sepiolite nanoclay/solvent is lower than the difference value between the interaction parameter of XNBR/solvent and the interaction parameter of sepiolite nanoclay/solvent. On the other hand, a higher percentage of sepiolite nanoclay resides in the continuous XNBR phase when the difference value between the interaction parameter of XNBR/solvent and the interaction parameter of sepiolite nanoclay/solvent is lower than the difference value between the interaction parameter of NR/solvent and the interaction parameter of sepiolite nanoclay/solvent. It has been shown that by judiciously choosing different solvent combinations to prepare the blend and to disperse nanoclay, it is possible to fine-tune the difference value between the interaction parameter of individual blend components (NR or XNBR)/solvent and the interaction parameter of sepiolite nanoclay/solvent and dictate the selective localization of sepiolite nanoclay to the NR phase or the XNBR phase of XNBR/NR (50/50) blend. This study shows that it is possible to generate a rubber blend with controlled properties by selectively localizing needlelike sepiolite nanoclay in the dispersed phase or the continuous phase of the rubber blend prepared by the solution casting method.

1. INTRODUCTION

Distribution of fillers in polymer blends is important in controlling the physical properties of the final products. In a matrix of incompatible polymer blends, an added filler distributes itself unevenly to each component of the polymer blend. The distribution of filler particles between the two phases of a polymer blend is affected by a number of factors, such as molecular weight, polarity, unsaturation, viscosity, and so on, of the individual polymers of the polymer blend. In general, these filler particles distribute randomly within the incompatible polymer blends, that is, either preferentially accumulate in either of the blend phases or at the blend interface, depending on thermodynamic driving forces and several kinetic factors. In the literature, many researchers have investigated the effect of heterogeneous distribution of fillers in polymer blends.

Over the past few years, incorporation of nanoparticles into polymer blends has also attracted considerable attention because nanoparticles can act as compatibilizers for immiscible polymer blends, control the morphology of polymer blends, change the phase separation temperature, and so on. However, like conventional reinforcing fillers, nanofillers also randomly localize either in the blend phases or at the blend interface and lead to several undesirable properties. Elias et al. have studied the effect of hydrophilic and hydrophobic silica nanoparticles on the morphology and the rheological properties of immiscible polypropylene (PP)/polystyrene (PS) blends. Morphological studies show that the hydrophilic silica tends to confine in the PS phase because of the better interaction between hydrophilic silica and PS. On the other hand, hydrophobic silica tends to locate in the PP phase and at the PP/PS interface. It has been shown that the stabilization mechanism of the PP/PS blend by hydrophilic silica is because of the reduction in the interfacial tension whereas hydrophobic silica acts as a rigid layer preventing the coalescence of PS droplets. Essawy and El-Nashar have investigated the use of montmorillonite (MMT) nanoclay as a reinforcing and compatibilizing filler for the acrylonitrile butadiene rubber/styrene butadiene rubber (SBR) rubber blend. It has been shown that the MMT nanoclay has moderate compatibility with both the blend components, and the nanoclay particles are located at the interface of the blend which induces compatibilization between the blend components.
Hong et al. have investigated the effect of organically modified nanoclay in immiscible polybutylene terephthalate (PBT)/polyethylene (PE) blend. It has been shown that the nanoclay particles selectively localize in the dispersed PBT phase because of their affinity with PBT. This results in effective size reduction and narrowed size distribution of the dispersed phase, which significantly increases the storage modulus of the blend. Ray and Bousmina have investigated the effect of organic modification of MMT nanoclays on the compatibility efficiency in the immiscible polycarbonate (PC)/polymethyl methacrylate (PMMA) blend. It has been found that the nanoclay particles are well dispersed both in the continuous PMMA phase and in the dispersed PC phase. The results show that the increase in the order of d-spacing (average basal spacing or gallery gap observed in layered MMT-based nanoclays) of MMT nanoclays correlates well with the order of particle size reduction of the dispersed phase, which dramatically improves the thermal stability of the PC/PMMA blend.

Bandyopadhyay et al. have studied the distribution of MMT-based nanoclay particles (Cloisite 30B and Cloisite Na+) and its influence on the mechanical properties of nonpolar natural rubber (NR)/polary epoxidized NR (ENR) and nonpolar NR/nonpolar polybutadiene (BR) blends. It has been shown that both Cloisite 30B and Cloisite Na+ nanoclay particles preferentially migrate toward the ENR phase rather than the NR phase in the 50NR/50ENR blend because of the low viscosity of the ENR phase in comparison to the viscosity of the NR phase. The migration of a very high amount of the Cloisite Na+ nanoclay particles toward the ENR phase is because of the interaction between the polar Cloisite Na+ and the pendant epoxy groups present in the ENR phase. Furthermore, it has been shown that both Cloisite 30B and Cloisite Na+ nanoclay particles preferentially migrate toward the NR phase rather than the BR phase in the 50NR/50BR blend because of the low viscosity of the NR phase in comparison to the viscosity of the BR phase.

Cao et al. have investigated the effect of graphene oxide (GO) in polyamide-12 (PA-12)/polyphenylene oxide (PPO) blend with special reference to the compatibilization of blend components. It has been reported that GO is homogeneously distributed throughout the PA-12/PPO blend. It has also been shown that the amphiphilic GO sheets exhibit strong interactions with PA-12 and PPO, which in turn minimizes their interfacial tension, thus leading to notable improvement in mechanical and thermal properties. Chen et al. have studied the effect of modified pristine multiwalled carbon nanotubes (MWCNTs) in high-density PE/polyamide 6 blend. The modified MWCNTs are preferentially found at the interface of the immiscible polymer blend. The MWCNTs at the interface facilitate the chain segments diffusion across the interface, which prevents the propagation of cracks along the interface. Liu et al. have studied the design of high-performance poly-l-lactide (PLLA)/poly-d-lactide graft ethylene-acrylic ester copolymer (EGD)/MWCNTs blends through anchoring MWCNTs at the interface with the aid of stereocomplex crystallization. The anchored MWCNTs function as effective interfacial enhancers to significantly increase the toughness and interfacial strength of PLLA/EGD blends. The anchored MWCNTs also facilitate the formation of an electrical conductive pathway in the network-like PLLA/EGD blends at a much lower percolation threshold. Liu et al. have studied the effect of nanosilica particles on the shape relaxation of dispersed PS droplets in the PP/PS blend. The shape relaxation process of PS droplets from highly elongated fiber toward spheres has been observed in both filled and unfilled systems using an optical microscope. The selective localization of nanosilica on the dispersed PS droplet retards the relaxation process of the deformed PS droplets particularly when nanosilica particles form the network in the dispersed phase. Pawar and Bose have studied the effect of the shape of nanoparticles in preserving the peculiar morphologies in various binary polymer blends. It has been shown that the presence of nanoparticles in the filled phase slows down the relaxation of the filled phase. This helps to preserve the peculiar morphology without altering the interfacial tension between the phases. Zhao et al. have studied the strain relaxation behavior of the dispersed PP droplets in the PP/PS blends in the presence of styrene-ethylene/butylene-styrene (SEBS) triblock copolymer as a compatibilizer. It has been found that the SEBS significantly retards the stress relaxation of the dispersed PP phase by increasing the interfacial adhesion between the blend components.

From a detailed literature review, it is evident that there are few reports in the literature which discuss the methodology to selectively localize nanoparticles in the dispersed phase or continuous phase of rubber blend prepared by the melt mixing method. However, many efforts have not been directed toward understanding the methodologies for selectively localizing nanofillers in the dispersed phase or in the continuous phase of rubber blend generated by dissolving the blend in a solvent and dispersing nanoclay in a solvent (solvent casting method). In our recent publication, a simple and unique thermodynamic approach has been used to preferentially fix layered MMT-based nanoclay particles in a particular phase of incompatible NR and carboxylated nitrile rubber (XNBR) blend prepared by the solvent casting method. It has been shown that by judiciously choosing different solvents for dissolving the rubbers and for dispersing nanoclays, it is possible to preferentially move the MMT nanoclay particles to different phases of the XNBR/NR (50/50) blend. A similar approach needs to be undertaken to validate this thermodynamic approach for preferentially fixing different nanoclay particles (having different structures) in the phases of rubber blends. In this work, the same thermodynamic approach has been used to selectively localize individual sepiolite nanoclay needles either in the NR phase or in the XNBR phase of the incompatible XNBR/NR (50/50) blend prepared by the solvent casting method. It has been shown that the difference value between the interaction parameter of the individual blend components (either XNBR or NR)/solvent and the interaction parameter of sepiolite nanoclay/solvent dictates the localization of sepiolite nanoclay needles either in the NR phase or in the XNBR phase. The abovementioned difference value has been judiciously manipulated by choosing different solvent combinations to prepare the XNBR/NR blend and to disperse sepiolite nanoclay, which consequently gives scope to selectively localize sepiolite nanoclay needles either in the NR phase or in the XNBR phase of the XNBR/NR (50/50) blend.

2. RESULTS AND DISCUSSION

2.1. XNBR/NR (50/50) Blend Dissolved in Toluene and Sepiolite Nanoclay Dispersed in Toluene. 2.1.1. Calculation of the Difference Value between the Interaction Parameter of Rubber (Either XNBR or NR)/Toluene and the Interaction Parameter of Sepiolite Nanoclay/Toluene. The difference value between the interaction parameter of NR—toluene and the interaction parameter of sepiolite nanoclay—

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nanoclay and the values are reported in Table 1.

\[ \chi_{AB/CD} = \chi_{AB} - \chi_{CD} \]  

(1)

where \( \chi_{AB} \) is the interaction parameter of NR–toluene and \( \chi_{CD} \) is the interaction parameter of sepiolite nanoclay–toluene. The \( \chi_{AB} \) (0.056) and \( \chi_{CD} \) (0.104) values have been calculated from Hildebrand equation.\(^{20–22}\) The solubility parameter values of NR, XNBR, sepiolite nanoclay, and toluene are obtained from the standard literature.\(^{20–22}\)

The difference value between the interaction parameter of XNBR–toluene and the interaction parameter of sepiolite nanoclay–toluene has been calculated from the equation below, and the values are reported in Table 1.

\[ \chi_{XY/CD} = \chi_{XY} - \chi_{CD} \]  

(2)

where \( \chi_{XY} \) is the interaction parameter between XNBR–toluene. The \( \chi_{XY} \) (0.179) value has been calculated from the Hildebrand equation.\(^{20–22}\).

The lower interaction parameter value of NR–toluene (\( \chi_{AB} \)) when compared to the interaction parameter value of XNBR–toluene (\( \chi_{XY} \)) confirms the good compatibility between NR and toluene in comparison to the compatibility between XNBR and toluene. Because the difference value between the interaction parameter of NR–toluene and the interaction parameter of sepiolite nanoclay–toluene is lesser than the difference value between the interaction parameter of XNBR–toluene and the interaction parameter of sepiolite nanoclay–toluene, it is predicted that the higher concentration of sepiolite nanoclay should selectively localize in the NR phase when compared to the XNBR phase of the XNBR/NR (50/50) blend. The above prediction regarding the selective localization of a higher percentage of sepiolite nanoclay in the NR phase of the XNBR/NR (50/50) blend has been validated in the forthcoming sections.

2.1.2. Morphological Analysis by Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM), and X-ray Diffraction (XRD). The TEM micrograph of the pristine XNBR/NR (50/50) blend shows uniform dispersion of NR domains (spherical or elliptical shaped) in the continuous XNBR matrix (Figure 1a). The size of the phase-separated NR domains is around 4–5 \( \mu \)m (Figure 1a). In line with the TEM image (Figure 1a), the AFM phase image of the pristine XNBR/NR (50/50) blend also shows uniform dispersion of bright NR domains in the dark XNBR matrix (Figure 1b). The size of the dispersed NR domains is around 4–5 \( \mu \)m (Figure 1b). It is interesting to note here that the TEM micrograph of the XNBR/NR (50/50) blend with 8 phr of sepiolite nanoclay shows the selective localization of a higher percentage of sepiolite nanoclay in the dispersed NR phase (Figure 1c). This observation is consistent with the prediction that higher concentration of sepiolite nanoclay will selectively localize in the NR phase when compared to the XNBR phase if we use toluene as the solvent to prepare the XNBR/NR (50/50) blend and to disperse sepiolite nanoclay. The average length, width, and thickness of the individual sepiolite nanoclay needles are in the range of 450–500, 40–45, and 10–20 nm, respectively (Figure 1c). The dimensions of the sepiolite nanoclay needles reported here are in accord with the dimensions of the sepiolite nanoclay needles reported in the literature.\(^{22–23}\) It is also clear that the sepiolite nanoclay needles show nanodispersion, and there is no sign of aggregation. It should be pointed here that some of the individual sepiolite nanoclay needles are aligned in a way that they are tightly stitching the dispersed NR phase and the continuous XNBR phase (Figure 1c). The AFM phase image of the XNBR/NR (50/50) blend with 8 phr of sepiolite nanoclay shows that a higher percentage of sepiolite nanoclay particles is selectively localized in the dispersed brighter NR phase in comparison to the continuous darker XNBR phase (Figure 1d). The dimensions of the individual sepiolite nanoclay needles as observed in the AFM phase image correlate well with the dimensions of the individual sepiolite nanoclay needles as observed in the TEM micrograph (Figure 1c). From the AFM phase image, it can also be seen that some portion of the

| Sl. no. | system                          | \( \chi_{AB/CD} \) | \( \chi_{XY/CD} \) | \( \chi_{XY/CD} \) | \( \chi_{XY/CD} \) |
|--------|---------------------------------|-------------------|-------------------|-------------------|-------------------|
| 1      | NR/toluene–sepiolite nanoclay/toluene | 0.04              | 0.07              | 0.12              | 0.00              |
| 2      | XNBR/toluene–sepiolite nanoclay/toluene |                |                  |                   |                   |
| 3      | NR/chloroform–sepiolite nanoclay/MEK |                |                  |                   |                   |
| 4      | XNBR/chloroform–sepiolite nanoclay/MEK |                |                  |                   |                   |

Table 1. Difference Value between the Interaction Parameter of Rubber–Solvent and the Interaction Parameter of Sepiolite Nanoclay–Solvent

Figure 1. (a) TEM micrograph of (50NR/50XNBR)\(_T\); (b) AFM phase image of (50NR/50XNBR)\(_T\); (c) TEM micrograph of (50NR/50XNBR)\(_T\)/8SEPT; (d) AFM phase image of (50NR/50XNBR)\(_T\)/8SEPT; and (e) XRD curves of pristine sepiolite nanoclay, NRT/8SEPT, XNBRT/8SEPT, and (50NR/50XNBR)\(_T\)/8SEPT.
individual sepiolite nanoclay needles are protruding into the continuous XNBR phase from the dispersed NR phase. This again confirms that the sepiolite nanoclay needles stitch the dispersed NR phase and continuous XNBR phase of the incompatible XNBR/NR (50/50) blend. This is a very unique observation reported for the first time in the literature. Elias et al. have shown that selective accumulation of nanoparticles at the interface in a polymer blend can significantly decrease the particle size of the dispersed phase and lead to increased compatibility and enhanced properties. However, here, the addition of sepiolite nanoclay to the XNBR/NR (50/50) blend prominently improves the overall properties without reducing the particle size of the dispersed NR phase. The possible reasons for the prominent enhancement of the overall blend properties by the addition of sepiolite nanoclay are because of the selective localization of sepiolite nanoclay in the NR phase (discussed later) and possibly because of the stitching effect produced by individual sepiolite nanoclay needles.

The nanocomposites have been characterized by XRD to understand the dispersion of sepiolite nanoclay in the rubber and rubber blend matrix. The X-ray diffractogram of the pristine sepiolite nanoclay shows a strong peak at 2θ = 7.28° (d-spacing of 1.22 nm) (Figure 1e). This peak mainly arises due to the reflections from the internal channels of the needlelike structure of sepiolite nanoclay. The pristine NR containing 8 phr of sepiolite nanoclay, pristine XNBR containing 8 phr of sepiolite nanoclay, and the XNBR/NR (50/50) blend containing 8 phr of sepiolite nanoclay also register strong XRD peaks in the vicinity of 7.28° (Figure 1e). This is in line with the earlier observations that sepiolite is a non-expandable nanoclay, and exfoliation cannot take place in the polymer matrix. Here, selective localization of sepiolite nanoclay in the NR phase prominently enhances the blend properties (discussed later) in spite of the fact that exfoliation does not take place. It has been shown by various authors that although exfoliation will not take place, sepiolite nanoclay can significantly improve the mechanical properties because it can be very easily dispersed in rubber matrices because of its very low specific surface area. It should be pointed here that there is a decrease in the peak intensity in the case of nanocomposite samples. It is well known that sepiolite nanoclay needles normally show tendency to stick together and form aggregated bundles of fibres. The strong interactions between the blend components (NR and XNBR) and the sepiolite nanoclay needles together with the shear involved during mixing tend to destroy the agglomerated structures. This ultimately leads to the nanodispersion of sepiolite nanoclay and results in the reduction of the peak intensities in the nanocomposite samples.

2.1.3. Dynamic Mechanical Properties. 2.1.3.1. Quantitative Estimation of the Amount of Sepiolite Nanoclay Selectively Localized in the NR Phase and XNBR Phase of the XNBR/XR (50/50) Blend. The dynamic mechanical analysis (DMA) tan δ versus temperature plots for pristine NR, pristine XNBR, and pristine XNBR/NR (50/50) blend are shown in the inset of Figure 2a. Pristine NR presents a peak around −55 °C, showing its glass transition temperature (Tg) (Table 2). It has been observed that the tan δ curve of NR with 8 phr of sepiolite nanoclay is similar to that of pristine NR, except that there is a reduction in the tan δ peak height (Table 2). Pristine XNBR shows a peak at −9 °C, corresponding to its Tg (Table 2). It is clear that the tan δ curve of XNBR with 8 phr of sepiolite nanoclay is similar to that of pristine XNBR, except that there is a reduction in the tan δ peak height (Table 2). It is well known that the reduction in the tan δ peak height by addition of any reinforcing filler can be attributed to the increased population of immobilized rubber chains. The pristine XNBR/NR (50/50) blend presents two peaks around −50 and −6 °C, corresponding to the Tg of NR and XNBR, respectively (Figure 2a). Whereas, the 8 phr sepiolite nanoclay-loaded XNBR/NR (50/50) blend shows the Tg value of NR and XNBR close to −48 and −8 °C, respectively. With the incorporation of sepiolite nanoclay into the XNBR/NR (50/50) blend, the Tg of NR is shown to shift to a higher temperature and the Tg of XNBR shifts to a lower temperature (Table 2). It is expected that sepiolite nanoclay can have good compatibility with both the NR phase and the XNBR phase of the XNBR/NR (50/50) blend. The silanol groups present on the sepiolite nanoclay ends and edges can interact with the carboxyl groups present in the XNBR rubber. Darder et al. have shown that hydrogen bonding can be established between the functional groups present in the polymers and the silanol groups present on the edges of the sepiolite nanoclay needles. It is also well known that sepiolite nanoclay particles show good affinity to NR because the surface energy values of sepiolite and NR are in close vicinity to each other. Accordingly, sepiolite nanoclay has enhanced the interactions and compatibility between XNBR and NR in the NR/XNBR blend, which shifts the Tg of NR to a higher temperature and shifts the Tg of XNBR to a lower temperature. Zhang et al. have studied the effect of incorporation of GO into the XNBR/SBR latex blend. It has been reported that with the addition of GO, the Tg of SBR shifts to a higher temperature and the Tg of XNBR shifts to a lower temperature. Addition of GO introduces interactions between XNBR and SBR, thus improving the miscibility and compati-
bility between the blend components. The tan δ peak heights of NR and XNBR in the pristine XNBR/NR (50/50) blend are 0.75 and 0.45, respectively (Table 2). On the other hand, the tan δ peak heights of NR and XNBR in the XNBR/NR (50/50) blend with 8 phr of sepiolite nanoclay are 0.34 and 0.36, respectively (Table 2). The reduction in the tan δ peak height by the addition of sepiolite nanoclay indicates the enhanced rubber–nanoclay interaction, which results in restricted segmental mobility of polymer chains. The tan δ peak height of NR in the XNBR/NR (50/50) blend with 8 phr of sepiolite nanoclay is in close vicinity to the tan δ peak height of NR in the pristine XNBR/NR (50/50) blend (Table 2). This confirms that sepiolite nanoclay shows greater interaction with the NR phase when compared to the XNBR phase in the XNBR/NR (50/50) blend if we use toluene for dissolving the blend and for preparing sepiolite nanoclay dispersion.

In the literature, it has been shown that from the extent of reduction in the tan δ peak heights corresponding to the continuous phase and dispersed phase (in a polymer blend) by the addition of filler, it is possible to quantitatively estimate the amount of filler present in the phases of the polymer blend using the equation given below:

$$R = \frac{(\tan \delta_{f1})_{\text{max}} - (\tan \delta_{f1})_{\text{max}}}{(\tan \delta_{f})_{\text{max}}}$$

where $\tan \delta_{f1}$ is the tan δ curve peak (maxima in tan δ), and $f_1$ and $f$ correspond to the unfilled (gum) and filler-loaded systems, respectively. $R$ correlates with the filler to weight fraction of polymer ($\omega$) according to the equation given below

$$R = \alpha \omega$$

where $\alpha$ corresponds to the interaction parameter between the polymer/filler. Applying eq 4 for individual polymer and polymer blend systems yields the below equations

$$R_1 = \alpha \omega_1$$

$$R_2 = \alpha \omega_2$$

$$R_{\text{blend}} = \alpha \omega_{\text{blend}}$$

$$R_{\text{blend}} = \alpha \omega_{\text{blend}}$$

$$R_{\text{blend}} = \alpha \omega_{\text{blend}}$$

where subscripts 1 and 2 correspond to the individual blend components, and the notations denoted by prime symbols correspond to the polymer blend system; $\omega_1$ and $\omega_2$ represent the filler weight fraction to total polymer (in polymer blend) distributed in polymer 1 and polymer 2, respectively. Accordingly, the total filler weight fraction, $\omega$, in the polymer blend can be obtained by adding $\omega_1$ and $\omega_2$.

$$\omega = \omega_1 + \omega_2$$

By assuming $\omega_1/\omega_2 = \omega_1'/\omega_2'$, eqs 5 and 8 will yield

$$\frac{\omega_1'}{\omega_2'} = \frac{R_1'R_2}{R_1'R_1}$$

The weight fraction of the filler in the phases of polymer blend ($\omega_1'$) can be determined from eqs 9 and 10 as shown below:

$$\omega_1' = \frac{R_1'R_2\omega}{R_1'R_2 + R_1'R_1}$$

The amount of sepiolite nanoclay selectively localized in the dispersed NR phase and in the continuous XNBR phase of the XNBR/NR (50/50) blend (when we use toluene for dissolving the blend and for preparing sepiolite nanoclay dispersion) has been obtained using eq 11, and the values are shown in Table 3.

### Table 3. Amount of Sepiolite Nanoclay Selectively Localized in the NR Phase and in the XNBR Phase of the XNBR/NR (50/50) Blend

| Sl. no. | sample code                  | amount of nanoclay localized in NR phase (phr) | amount of nanoclay localized in XNBR phase (phr) |
|--------|-----------------------------|-----------------------------------------------|-----------------------------------------------|
| 1      | (50NR/50XNBR)$_{1}$/8SEPt   | 4.97 (62%)                                   | 3.03 (38%)                                   |
| 2      | (50NR/50XNBR)$_{2}$/8SEPM   | 3.18 (39%)                                   | 4.82 (61%)                                   |

It is evident from Table 3 that around 62% of sepiolite nanoclay selectively localizes in the NR phase of the XNBR/NR (50/50) blend. It should be pointed here that this is in accordance with the earlier prediction that a higher percentage of sepiolite nanoclay will selectively localize in the dispersed NR phase when we use toluene for dissolving the blend and for preparing sepiolite nanoclay dispersion. In the literature, several
authors have used the above methodology (DMA tan δ vs temperature plots) to understand the distribution of different fillers in the phases of various rubber blends.14,20,35–41

2.1.3.2. DMA Elastic Modulus Versus Temperature Studies. The elastic modulus, $E'$, versus temperature curves for pristine NR, pristine XNBR, and pristine XNBR/NR (50/50) blend is shown in the inset of Figure 2b. A comparison between pristine NR and pristine XNBR shows that the modulus (at 25 °C) of pristine NR is higher compared to that of pristine XNBR (Table 2). The modulus (at 25 °C) of the pristine blend lies between the modulus of pristine NR and pristine XNBR (Table 2). The modulus (at 25 °C) of NR increases considerably with the incorporation of 8 phr of sepiolite nanoclay (Table 2). This is because NR exhibits excellent compatibility with sepiolite nanoclay when we use toluene for dissolving NR and for preparing sepiolite nanoclay dispersion (as discussed earlier). However, the modulus (at 25 °C) of XNBR does not enhance considerably by incorporating 8 phr of sepiolite nanoclay (Table 2). This is because XNBR exhibits relatively a limited compatibility with sepiolite nanoclay when we use toluene for dissolving XNBR and for preparing sepiolite nanoclay dispersion (as discussed earlier). The elastic modulus versus temperature plots of the pristine XNBR/NR (50/50) blend and the XNBR/NR (50/50) blend with 8 phr of sepiolite nanoclay are shown in Figure 2b. The modulus (at 25 °C) of the XNBR/NR (50/50) blend containing 8 phr of sepiolite nanoclay is around 140% higher than the modulus (at 25 °C) of the pristine XNBR/NR (50/50) blend (see Table 2).

2.1.4. Tensile Property Studies. The stress versus strain curves of pristine NR, pristine XNBR, NR containing 8 phr of sepiolite nanoclay, and XNBR containing 8 phr of sepiolite nanoclay are shown in the inset of Figure 3. It has been observed that the breaking stress and stress at 100% strain of pristine NR are 0.42 and 0.29 MPa, respectively (Table 4). On the other hand, the breaking stress and stress at 100% strain of pristine XNBR are 0.30 and 0.26 MPa, respectively (Table 4). The strain at the break of pristine NR is lower than the strain at the break of pristine XNBR (Table 4). The breaking stress and stress at 100% strain of XNBR significantly enhance by the addition of 8 phr of sepiolite nanoclay (Table 4). On the other hand, the breaking stress and stress at 100% strain of XNBR do not significantly enhance with the incorporation of 8 phr of sepiolite nanoclay (Table 4). The stress versus strain curves of the pristine XNBR/ NR (50/50) blend and the XNBR/NR (50/50) blend with 8 phr of sepiolite nanoclay are shown in Figure 3. The breaking stress, stress at 100% strain, and strain at the break of the pristine XNBR/NR (50/50) blend lie in between the breaking stress, stress at 100% strain, and strain at the break of pristine NR and pristine XNBR (Table 4). The breaking stress, stress at 100% strain, and strain at the break of the pristine XNBR/NR (50/50) blend continuously increase with increasing sepiolite nanoclay content (Table 4). It is very important to understand how the selective localization of a higher percentage of sepiolite nanoclay in the dispersed NR phase of the XNBR/NR (50/50) blend prominently increases the DMA elastic modulus (at 25 °C) and the stress–strain properties (breaking stress, stress at 100% strain, and strain at break) of the incompatible XNBR/NR (50/50) blend. The possible reasons for the above behavior have been discussed in the subsequent paragraph.

Sepiolite nanoclay shows better interaction with the NR phase when compared to the XNBR phase when toluene is used for dissolving the blend and for preparing sepiolite nanoclay dispersion (as discussed earlier). Accordingly, a higher percentage of sepiolite nanoclay selectively localizes in the NR phase of the XNBR/NR (50/50) blend. The well-dispersed sepiolite nanoclay in the NR phase can prominently enhance the strength of NR phase in the XNBR/NR (50/50) blend, which in turn can lead to enhanced blend properties. In addition, the sepiolite nanoclay needles lead to better interaction between the NR phase and XNBR phase (as discussed in DMA studies) by aligning themselves (stitching effect) across the interface in the XNBR/NR (50/50) blend (Figure 1c,d). This can also significantly enhance the overall blend properties.

2.2. XNBR/NR (50/50) Blend Dissolved in Chloroform and Sepiolite Nanoclay Dispersed in Methyl Ethyl Ketone (MEK). 2.2.1. Calculation of the Difference Value between the Interaction Parameter of Rubber (Either XNBR or NR)/Chloroform and the Interaction Parameter of Sepiolite Nanoclay/MEK. To selectively localize a higher amount of sepiolite nanoclay in the XNBR phase of the XNBR/NR (50/50) blend, chloroform is selected as the solvent for preparing the blend, and MEK is selected as the solvent for preparing sepiolite nanoclay dispersion. The difference value between the interaction parameter of NR–chloroform and the interaction parameter of sepiolite nanoclay–MEK has been identified from the equation below and the values are reported in Table 1.

$$\chi_{A'B'}/C'D' = \chi_{A'B'} - \chi_{C'D'}$$

where $\chi_{A'B'}$ is the interaction parameter of NR–chloroform and $\chi_{C'D'}$ is the interaction parameter of sepiolite nanoclay–MEK. The $\chi_{A'B'}$ (0.141) and $\chi_{C'D'}$ (0.012) values have been calculated from the Hildebrand equation.20–22 The solubility parameter values of MEK and chloroform are taken from the literature.20–22

The difference value between the interaction parameter of XNBR–chloroform and the interaction parameter of sepiolite nanoclay–MEK has been identified from the equation below, and the values are shown in Table 1.

$$\chi_{X'Y'}/C'D' = \chi_{X'Y'} - \chi_{C'D'}$$

where $\chi_{X'Y'}$ is the interaction parameter between XNBR–chloroform. The $\chi_{X'Y'}$ (0.020) value has been calculated from the Hildebrand equation.20–22

The lower interaction parameter value of XNBR–chloroform ($\chi_{X'Y'}$) when compared to the interaction parameter value of NR–chloroform ($\chi_{A'B'}$) confirms the excellent compatibility.
between XNBR and chloroform in comparison to the compatibility between NR and chloroform. As the difference value between the interaction parameter of XNBR—chloroform and the interaction parameter of sepiolite nanoclay—MEK is lower than the difference value between the interaction parameter of NR—chloroform and the interaction parameter of sepiolite nanoclay—MEK, it is predicted that the higher concentration of sepiolite nanoclay should selectively localize in the XNBR phase when compared to the NR phase in the XNBR/NR (50/50) blend. The above prediction regarding the selective localization of the higher percentage of sepiolite nanoclay in the XNBR phase of the XNBR/NR (50/50) blend has been validated in the forthcoming sections.

2.2.2. Morphological Analysis by TEM, AFM, and XRD. The TEM micrograph of the pristine XNBR/NR (50/50) blend prepared using chloroform as the solvent shows uniform dispersion of NR domains (having particles size in the range of 5–6 μm) in the continuous XNBR matrix (Figure 4a). In line with the TEM micrograph (Figure 4a), the AFM phase image of the pristine XNBR/NR (50/50) blend prepared using chloroform as the solvent shows a uniform dispersion of NR domains (having particles size in the range of 5–6 μm) in the continuous XNBR matrix (Figure 4b). It is interesting to note here that the TEM micrograph of the XNBR/NR (50/50) blend containing 8 phr of sepiolite nanoclay shows selective localization of a higher percentage of sepiolite nanoclay in the continuous XNBR phase (Figure 4c). This observation is consistent with the prediction that higher concentration of sepiolite nanoclay will selectively localize in the XNBR phase when compared to the NR phase if we use chloroform as the solvent to prepare the XNBR/NR (50/50) blend and if we use MEK as the solvent to disperse sepiolite nanoclay. It should be pointed here that the nanoclay particles are uniformly distributed and show nanodispersion in the XNBR phase. The average length, width, and thickness of the individual sepiolite nanoclay needles are in the range of 450–500, 40–45, and 10–20 nm, respectively (Figure 4c). Because a higher percentage of sepiolite nanoclay needles are localized in the XNBR phase, there is no prominent stitching effect of sepiolite nanoclay needles across the interface (Figure 4c). However, at few places, some portions of the individual sepiolite nanoclay needles protrude into the NR phase from the XNBR phase (Figure 4c). The preferential localization of the higher percentage of sepiolite nanoclay in the XNBR phase does not reduce the particle size of the dispersed NR phase. It is worth mentioning here that there is no considerable enhancement in the blend properties because of selective localization of sepiolite nanoclay in the XNBR phase (discussed later). From the AFM phase image of the XNBR/NR (50/50) blend with 8 phr of sepiolite nanoclay, it is clear that a higher percentage of sepiolite nanoclay particles is present in the XNBR phase in comparison to the brighter NR phase (Figure 4d). The dimension of the individual sepiolite nanoclay needles as observed by the AFM phase image (Figure 4d) correlate well with the dimension of the individual sepiolite nanoclay needles as observed by the TEM micrograph (Figure 4b). The AFM phase image also clearly reveals that there is no prominent stitching effect of the sepiolite nanoclay needles across the phases of the XNBR/NR (50/50)

| Sl. no. | sample code             | breaking stress (MPa) | stress at 100% strain (MPa) | strain at break (%) |
|--------|-------------------------|-----------------------|----------------------------|---------------------|
| 1      | NR                      | 0.42 ± 0.03           | 0.29 ± 0.02                | 459 ± 3             |
| 2      | XNBR                    | 0.30 ± 0.02           | 0.26 ± 0.03                | 853 ± 3             |
| 3      | XNBR/2/8SEP            | 1.55 ± 0.03           | 0.50 ± 0.04                | 690 ± 5             |
| 4      | XNBR/8SEP             | 0.68 ± 0.03           | 0.46 ± 0.03                | 965 ± 3             |
| 5      | (50NR/50XNBR)         | 0.39 ± 0.04           | 0.28 ± 0.02                | 621 ± 4             |
| 6      | (50NR/50XNBR) 2/2SEP   | 1.36 ± 0.03           | 0.43 ± 0.04                | 790 ± 5             |
| 7      | (50NR/50XNBR) 2/4SEP   | 1.67 ± 0.03           | 0.48 ± 0.03                | 828 ± 3             |
| 8      | (50NR/50XNBR) 2/8SEP   | 2.50 ± 0.02           | 0.53 ± 0.04                | 1139 ± 6            |
| 9      | NR                      | 0.38 ± 0.03           | 0.23 ± 0.03                | 474 ± 4             |
| 10     | XNBR                    | 0.31 ± 0.03           | 0.29 ± 0.02                | 905 ± 3             |
| 11     | NR/8SEP               | 0.66 ± 0.03           | 0.27 ± 0.03                | 513 ± 4             |
| 12     | XNBR/8SEP             | 0.97 ± 0.02           | 0.94 ± 0.03                | 1150 ± 4            |
| 13     | (50NR/50XNBR)         | 0.37 ± 0.03           | 0.26 ± 0.02                | 542 ± 4             |
| 14     | (50NR/50XNBR) 8SEP    | 1.98 ± 0.03           | 0.40 ± 0.02                | 980 ± 3             |
blend. The X-ray diffractograms of the nanocomposites have peak positions in the range of 7.28 (2θ) (Figure 4e). The X-ray diffractogram of pristine sepiolite nanoclay also shows a peak at 7.28 (2θ) (Figure 1e). This again confirms the non-expandable nature of sepiolite nanoclay (as discussed earlier). The reduction in the peak intensity in the nanocomposite samples validates the nanodispersion of sepiolite nanoclay in NR, XNBR, and XNBR/NR (50/50) blend.

2.2.3. Dynamic Mechanical Properties. 2.2.3.1. Quantitative Estimation of the Amount of Sepiolite Nanoclay Selectively Localized in the NR Phase and XNBR Phase of the XNBR/NR (50/50) Blend. The tan δ versus temperature plots for pristine NR, pristine XNBR, and pristine XNBR/NR (50/50) blend are shown in the inset of Figure 5a. Pristine NR presents a peak about −55 °C, showing its Tg (Table 2). It has been observed that the tan δ curve of NR with 8 phr of sepiolite nanoclay is similar to that of pristine NR, except that there is a reduction in the tan δ peak height (Table 2). Pristine XNBR shows a peak at −9 °C, corresponding to its Tg (Table 2). The tan δ curve of XNBR with 8 phr of sepiolite nanoclay is similar to that of pristine XNBR, except that there is a reduction in the tan δ peak height (Table 2). The pristine XNBR/NR (50/50) blend presents two peaks around −50 and −6 °C, corresponding to Tg of NR and XNBR, respectively (Table 2). It is interesting to note that the 8 phr sepiolite nanoclay-loaded XNBR/NR (50/50) blend shows Tg values of NR and XNBR at −50 and −6 °C, respectively (Figure 5a). With the incorporation of sepiolite nanoclay, there is no shift in the Tg of XNBR to lower temperature (Table 2). This can be due to the existence of minimum interactions between the blend components (NR and XNBR) because of the selective localization of sepiolite nanoclay needles in XNBR phase and also due to the absence of a prominent stitching effect of the sepiolite nanoclay needles. The tan δ peak heights of NR and XNBR in the pristine XNBR/NR (50/50) blend are 0.68 and 0.52, respectively (Table 2). On the other hand, the tan δ peak heights of NR and XNBR in the pristine XNBR/NR (50/50) blend with 8 phr of sepiolite nanoclay are 0.55 and 0.28, respectively (Table 2). The tan δ peak height of XNBR in the XNBR/NR (50/50) blend with 8 phr of sepiolite nanoclay is much lower than the tan δ peak height of XNBR in the pristine XNBR/NR (50/50) blend (Table 2). On the other hand, the tan δ peak height of NR in the XNBR/NR (50/50) blend with 8 phr of sepiolite nanoclay is in close vicinity to the tan δ peak height of NR in the pristine XNBR/NR (50/50) blend (Table 2). This confirms that sepiolite nanoclay shows excellent interaction with the XNBR phase when compared to the NR phase in the XNBR/NR (50/50) blend when we use chloroform as the solvent for preparing the blend, and MEK as the solvent for preparing the sepiolite nanoclay dispersion.

The amount of sepiolite nanoclay selectively localized in the dispersed NR phase and in the continuous XNBR phase of the XNBR/NR (50/50) blend (when we use chloroform as the solvent for preparing the blend and MEK as the solvent for preparing sepiolite nanoclay dispersion) has been identified using eq 11, and the values are shown in Table 3.

It is evident from Table 3 that around 61% of sepiolite nanoclay selectively localizes in the XNBR phase of the XNBR/NR (50/50) blend. It should be pointed here that this is in accordance with the earlier prediction that a higher percentage of sepiolite nanoclay will selectively localize in the continuous XNBR phase when we use chloroform as the solvent for preparing the blend and MEK as the solvent for preparing the sepiolite nanoclay dispersion.

2.2.3.2. DMA Elastic Modulus Versus Temperature Studies. The elastic modulus (E′) versus temperature curves for pristine NR, pristine XNBR, and pristine XNBR/NR (50/50) blend is shown in the inset of Figure 5b. A comparison between pristine NR and pristine XNBR shows that the modulus (at 25 °C) of pristine NR is higher compared to that of pristine XNBR (Table 2). The modulus (at 25 °C) of the pristine blend lies between the modulus of pristine NR and pristine XNBR (Table 2). The modulus (at 25 °C) of XNBR enhances considerably by the incorporation of 8 phr of sepiolite nanoclay (Table 2). This is because XNBR exhibits excellent compatibility with sepiolite nanoclay when we use chloroform for dissolving XNBR and MEK for preparing sepiolite nanoclay dispersion (as discussed earlier). On the other hand, the modulus (at 25 °C) of NR does not enhance considerably by the incorporation of 8 phr of sepiolite nanoclay (Table 2). This is because NR exhibits limited compatibility with sepiolite nanoclay when we use chloroform for dissolving NR and MEK for preparing sepiolite nanoclay dispersion (as discussed earlier). The elastic modulus versus temperature plots of the pristine XNBR/NR (50/50) blend and the XNBR/NR (50/50) blend with 8 phr of sepiolite nanoclay are shown in Figure 5b. The modulus (at 25 °C) of the 8 phr sepiolite nanoclay-loaded XNBR/NR (50/50) blend is around 39% higher than the modulus (at 25 °C) of the pristine XNBR/NR (50/50) blend (see Table 2). It is worth mentioning here that selective localization of a higher percentage of sepiolite nanoclay in the XNBR phase does not prominently enhance the modulus (at 25 °C) of the XNBR/NR (50/50) blend. On the other hand, as discussed earlier, selective localization of a higher
percentage of sepiolite nanoclay in the NR phase significantly enhances the modulus (at 25 °C) of the XNBR/NR (50/50) blend. The reasons for the above behavior have been explained in the forthcoming section.

2.2.4. Tensile Property Studies. The stress versus strain curves of pristine NR, pristine XNBR, NR containing 8 phr of sepiolite nanoclay, and XNBR containing 8 phr of sepiolite nanoclay are shown in the inset of Figure 6. It has been observed that the breaking stress and stress at 100% strain of pristine NR are 0.38 and 0.23 MPa, respectively (Table 4). The breaking stress and stress at 100% strain of pristine XNBR are 0.31 and 0.29, MPa respectively (Table 4). The strain at the break of pristine NR is lower than the strain at the break of pristine XNBR (Table 4). The breaking stress and stress at 100% strain of XNBR significantly increase with the addition of 8 phr of sepiolite nanoclay (Table 4). On the other hand, the breaking stress and stress at 100% strain of NR do not significantly enhance with the incorporation of 8 phr of sepiolite nanoclay (Table 4). The stress versus strain curves of the pristine XNBR/NR (50/50) blend and the XNBR/NR (50/50) blend/sepiolite nanocomposite. Inset: Tensile properties of pristine NR, pristine XNBR, NR/sepiolite nanocomposite, and XNBR/sepiolite nanocomposite.

Figure 6. Tensile properties of the pristine XNBR/NR (50/50) blend and the XNBR/NR (50/50) blend/sepiolite nanocomposite. Inset: Tensile properties of pristine NR, pristine XNBR, NR/sepiolite nanocomposite, and XNBR/sepiolite nanocomposite.

because a major portion of sepiolite nanoclay has migrated to the XNBR phase. The extent of reduction in the strength of the NR phase by losing sepiolite nanoclay overcomes the extent of enhancement in the strength of the XNBR phase by accumulating sepiolite nanoclay. This ultimately does not contribute to the improvement of the blend properties to a greater extent. In addition, the presence of a higher percentage of sepiolite nanoclay in the XNBR phase does not increase the interaction between the NR phase and XNBR phase (as discussed in DMA studies) because there is no prominent stitching effect of the sepiolite nanoclay needles across the interface. Accordingly, there is no prominent increase in the overall blend properties.

3. CONCLUSIONS

1. A unique approach for selectively localizing needle-shaped sepiolite nanoclay in the dispersed NR phase and in the continuous XNBR phase of the incompatible XNBR/NR (50/50) blend and its effect on the overall blend properties have been studied by considering various thermodynamic governing factors. It has been found that 62% of sepiolite nanoclay (at 8 phr) selectively localizes in the dispersed NR phase when toluene is used as the solvent for dissolving the XNBR/NR (50/50) blend and for preparing the sepiolite nanoclay dispersion. This is because the difference value between the interaction parameter of NR–toluene and the interaction parameter of sepiolite nanoclay–toluene is low (\(\chi_{XNBR/toluene} - \chi_{sepiolite nanoclay/toluene} = 0.04\)) in comparison to the difference value between the interaction parameter of XNBR–toluene and the interaction parameter of sepiolite nanoclay–toluene (\(\chi_{XNBR/toluene} - \chi_{sepiolite nanoclay/toluene} = 0.07\)). Selective localization of sepiolite nanoclay in the dispersed NR phase increases the strength of the NR phase in the XNBR/NR (50/50) blend because of the excellent compatibility between NR and sepiolite nanoclay when toluene is used as the solvent for dissolving the XNBR/NR (50/50) blend and for preparing sepiolite nanoclay dispersion. This significantly increases the tensile properties and the DMA elastic modulus (at 25 °C) value of the incompatible XNBR/NR (50/50) blend. Morphological studies reveal that the sepiolite nanoclay needles are aligned in a way that the continuous phase (XNBR) and the dispersed phase (NR) of the incompatible XNBR/NR (50/50) blend are tightly stitched together by the needle-shaped sepiolite nanoclay. This increases the interactions between the blend components and prominently improves the overall blend properties.

2. It has been observed that 61% of sepiolite nanoclay selectively localizes in the XNBR phase when chloroform is used as the solvent for dissolving the XNBR/NR (50/50) blend and MEK is used as the solvent for preparing the sepiolite nanoclay dispersion. This is because the difference value between the interaction parameter of XNBR–chloroform and the interaction parameter of sepiolite nanoclay–MEK is lower (\(\chi_{XNBR/chloroform} - \chi_{sepiolite nanoclay/MEK} = 0.00\)) when compared to the difference value between the interaction parameter of NR–chloroform and the interaction parameter of sepiolite nanoclay–MEK (\(\chi_{NR/chloroform} - \chi_{sepiolite nanoclay/MEK} = 0.12\)). The selective localization of
sepiolite nanoclay in the XNBR phase does not significantly improve the tensile properties and the DMA elastic modulus (at 25 °C) value of the XNBR/NR (50/50) blend. This is attributed to the reduction in the strength of the NR phase in the incompatible XNBR/NR (50/50) blend when a higher percentage of sepiolite nanoclay localizes in the XNBR phase. The extent of reduction in the strength of the NR phase by losing sepiolite nanoclay overcomes the extent of enhancement in the strength of the XNBR phase by accumulating sepiolite nanoclay. This ultimately does not contribute to the improvement of the blend properties to a greater extent. In addition, localization of the higher percentage of sepiolite nanoclay in the XNBR phase reduces the stitching effect of the sepiolite nanoclay needles across the phases of the XNBR/NR (50/50) blend. This reduces the interactions between the blend components and does not contribute to the prominent enhancement of the overall blend properties.

4. EXPERIMENTAL PROCEDURE

4.1. Sample Materials. Kynmac X 750 (XNBR), having 7.0% acid groups and 27.0 ± 1.5% acrylonitrile groups, Mooney viscosity, ML1+4 at 100 °C = 47 ± 5, specific gravity = 0.99, was purchased from Lanxess, Cologne, Germany. ISNR 3CV (NR), having Mooney Viscosity, ML1+4 at 100 °C = 63 ± 5, was purchased from Rubber Research Institute of India, Kottayam, India. Pangel B20 (sepiolite nanoclay) was procured from Tolsa S.A., Empres, Mercedes, Spain. Pangel B20 sepiolite nanoclay is an organophilic needlelike nanoclay containing ribbons of 2:1 phyllosilicate structure with a significant number of silanol groups (SiOH) at its edges. Individual sepiolite fibres generally range from 10 nm to 5 μm in length, 10–30 nm width, and 5–10 nm thickness with an aspect ratio ranging from 100 to 300.22−24,26,42 Solvents were procured from Sigma-Aldrich, New Delhi, India.

4.2. Synthesis of Samples. 4.2.1. Synthesis of Pristine Rubber Samples and Rubber Nanocomposite Samples. XNBR (4 g) or NR (4 g) was swollen in a known amount (80 mL) of solvent (toluene or chloroform) and stirred thoroughly by using a magnetic stirrer for 10 h (1000 rpm at 25 °C). Once the stirring was completed, the rubber solution was poured into a glass Petri dish and dried for 4 days at room temperature until there was no weight change. For preparing rubber nanocomposite samples, the neat rubber solutions were prepared as per the procedure described above. Nanoclay was dispersed in a desired solvent (either MEK or toluene) by an ultrasonicator for 1 h at a frequency of 25 kHz at 25 °C. The dispersion of nanoclay was incorporated into the prepared rubber solution. The stirring was continued again for 9 h using a magnetic stirrer (1000 rpm at 25 °C). Once the stirring was completed, the rubber nanocomposite solution was poured into a glass Petri dish and dried for 4 days at room temperature until there was no weight change. The samples prepared are shown in Table 5.

4.2.2. Synthesis of Pristine Rubber Blend Samples and Rubber Blend Nanocomposite Samples. XNBR (2 g) and NR (2 g), to prepare the XNBR/NR (50/50) blend, was swollen in a known amount (80 mL) of solvent (toluene or chloroform) and stirred thoroughly for 10 h using a magnetic stirrer (1000 rpm at 25 °C). Once the stirring was completed, the rubber blend solution was poured into a glass Petri dish and dried for 4 days at room temperature until there was no weight change. For preparing rubber blend nanocomposite samples, the neat rubber blend solutions were prepared as per the procedure described above. Nanoclay was dispersed in a desired solvent (either MEK or toluene) by an ultrasonicator for 1 h at a frequency of 25 kHz at 25 °C. The dispersion of nanoclay was incorporated into the prepared rubber blend solution. The stirring was continued again for 9 h using a magnetic stirrer (1000 rpm at 25 °C). Once the stirring was completed, the rubber blend nanocomposite solution was poured into a glass Petri dish and dried for 4 days at room temperature until there was no weight change. The samples prepared are reported in Table 5.

4.3. Characterization Techniques. TEM was used to study the bulk morphology of the samples. The sample preparation for TEM was done by ultra-cryomicrotomy at −100 °C (which was well below the glass transition temperature (Tg) values of NR and XNBR). A JEOL 2011 instrument (Japan) with a LaB6 electron source operating at 200 kV was used for TEM imaging. AFM was used to study the surface morphology of the samples. A multimode AFM instrument from Bruker Dimension Icon SPM (Massachusetts, USA) was used. Phase images were captured in the PeakForce tapping mode at a set point ratio of 100 pN, using a long tapping mode etched silicon probe (LTESP) tip with a ScanAssyst-Fluid probe (spring constant in the range of 1.4 N/m). The cantilever was oscillated...
at a resonance frequency ($\omega_0$) of 180 kHz. XRD patterns were measured at 25 °C using a Rigaku Mini-flex Diffractometer (Tokyo, Japan). The instrument was equipped with a Cu filter under the following conditions: scan range ($2\theta$) = 2°–10°; scan rate = 0.5°/min; and Cu Kα radiation ($\lambda$) = 1.54 Å. A dynamic mechanical analyzer (DMA Q800, TA Instruments, New Castle, DE, USA) instrument was used to study the dynamic mechanical property of the samples. Experiments were carried out in tension mode at a strain amplitude of 0.01%, at a constant sinusoidal frequency of 1 Hz, from −100 to 100 °C at a heating ramp of 2 °C/min under a nitrogen atmosphere. The selective localization of the sepiolite nanoclay needles in the continuous phase and in the dispersed phase of the XNBR/NR (50/50) blend was estimated from the DMA tan δ versus temperature curves. The tensile stress−strain properties of the samples were estimated using a universal testing machine (UTM, Zwick/Roell Z010, Ulm, Germany) having a 10 kN load cell at a crosshead speed of 50 mm/min. The experiments were conducted according to the ASTM D 412−98 test method using dumbbell-shaped tensile specimens.

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Notes

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