Dynamic viscoelastic behavior and molecular mobility of acrylonitrile–butadiene copolymer nanocomposites with various organoclay loadings

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Received 3 January 2007; received in revised form 21 September 2007; accepted 17 October 2007

Available online 30 October 2007

Abstract

Layered silicate nanostructures of NBR nanocomposites prepared using the various organoclays (OCs) and silicate loadings were investigated by analyzing the viscoelastic behavior, activation energy ($E_a$), and average relaxation times ($\tau_{HN}$) obtained from dynamic mechanical measurements. Viscoelastic behavior revealed that NBR nanocomposite with OC having polar organic modifier (NBROC30B) has the highest elasticity in NBR nanocomposites, indicating the formation of the largest gallery height. In addition, $E_a$ and $\tau_{HN}$ showed that the mobility of NBROC30B was the closest to that of NBR, providing further evidence that NBROC30B has the largest gallery height. Interestingly, viscoelastic behavior, $E_a$ and $\tau_{HN}$ of the nanocomposites with silicate loadings in excess of 7 wt% were remarkably higher than those of the nanocomposites with silicate loadings below 7 wt%. These results imply the sudden change of silicate structure and suggest the formation of three-dimensional network-like percolated silicate structure at NBR nanocomposites with silicate loadings over 8 wt%, which was consistent with HR-TEM results.

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Keywords: Dynamic mechanical thermal analysis (DMTA); A. Layered structure; Molecular mobility; Nanoclay; A. Nano composites

1. Introduction

Recently, clay-based polymer nanocomposites have attracted considerable attention due to their markedly superior mechanical and thermal properties compared to conventional composites, even at low clay loadings [1]. Thus, an increasing number of studies have been performed with the aim of improving the properties of nanocomposites [2–7]. In general, it is well-known that exfoliated nanocomposites, where individual layers are irregularly delaminated and dispersed in a continuous polymer matrix [8], show higher physical properties than intercalated nanocomposites. Thus, it is important to analyze the silicate structure in nanocomposites in order to understand their characteristics. Nanocomposite structure has generally been investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Although both of these methods are powerful tools for directly obtaining structural data, they do not provide information on the relation between the properties of a nanocomposite and its silicate structure. Recently, dynamic mechanical analysis (DMA) has been increasingly used to study nanocomposites, because this technique provides information about the characteristics of the dispersed phase as well as the silicate structure [9–11]. Lee et al. [10] investigated the rheological properties of ethylene–vinyl acetate copolymer (EVA) nanocomposites with increasing the silicate loading and then, they reported the enhancement of elasticity of EVA nanocomposites with increasing silicate contents due to the interaction and
dispersion of the clay in the polymer matrix. In addition, they found that EVA nanocomposites with clay contents over 7.5% had a three-dimensional network structure. These results clearly show that DMA is very useful tool to investigate the silicate structure of nanocomposites. However, few studies have evaluated the degree of expansion of the gallery height between silicate layers and three-dimensional structure of the silicate of nanocomposites by DMA. In the present work, acrylonitrile–butadiene copolymer (nitrile rubber or NBR) nanocomposites with organoclays (OCs) having different intercalants were prepared with various silicate loadings by the melt mixing process. Then, we investigated the degree of expansion of the gallery height depending on the variations of the intercalant architecture and verified the change in the silicate structure with silicate loading by means of DMA.

2. Experimental

2.1. Materials

Uncrosslinked NBR containing approximately 34 wt% acrylonitrile was obtained from Kumho Petrochemical Co. Ltd. The OCs composed of sodium montmorillonite (MMT) and intercalant were obtained from Southern Clay Products, Inc. under the trade names Closite®20A (OC20A), Closite®25A (OC25A), and Closite®30B (OC30B). The chemical structures of NBR and the intercalants used in this study are shown in Fig. 1.

![Chemical structures of NBR and intercalants](image)

Fig. 1. Chemical structures of the NBR and intercalants used in this study: (a) pure NBR, (b) intercalant in OC20A (dimethyl dehydrogenated tallow ammonium), (c) intercalant in OC25A (dimethyl hydrogenated tallow 2-ethylhexyl), and (d) intercalant in OC30B (methyl tallow bis(2-hydroxyethyl)).

2.2. Preparation of NBR nanocomposites

NBR nanocomposites were prepared with various silicate loadings (1, 3, 5, 7, and 10 wt%) by the melt mixing method using a Haake internal mixer with Banbury blades under 100 rpm at 90 °C for 600 s. Then, the nanocomposites were annealed at 90 °C for 100 min. The nanocomposites with OC20A, OC25A, and O30B are referred to herein as NBROC20AX, NBROC25AX, and NBROC30BX, respectively (where X is the silicate loading).

2.3. Characterization

XRD measurements were performed on a MAC Science MXP 18A-HF X-ray diffractometer with Cu Kα radiation (λ = 0.154 nm) at 40 kV and 100 mA. The diffraction angle was scanned from 1° to 10° at a rate of 3°/min. Specimens for XRD measurement were prepared by pressing at 100 °C for 2 min, followed by quenching to room temperature. Dynamic oscillatory shear measurements were carried out on a Rheometrics Mechanical Spectrometer Model 800 (RMS-800) with a torque transducer capable of performing measurements over the range of 2–2000 g cm. Then, dynamic isothermal frequency sweeps were performed using a 25-mm-diameter parallel disk geometry with a gap setting of 2 mm. The angular frequency ranged from ω = 10⁻¹ to 10² rad s⁻¹. The measuring temperature was set to 60–180 °C in increasing intervals of 20 °C under N₂ atmosphere. High-resolution transmission electron microscopic (HR-TEM) analysis was performed with a Jeol JEM 3010CX at 300 kV. For the HR-TEM observation, ultra-thin cross-sections of the specimens were carried out by using a Leica Ultracut UCT ultracryomicrotome.

3. Results and discussion

Fig. 2 shows the XRD peak profiles for the OCs and NBR nanocomposites with various intercalant and silicate loadings. From the peak positions in these profiles, the gallery heights of the NBROC20As, NBROC25As, and NBROC30Bs can be seen to increase by ~0.9, 1.1, and 2.1 nm with respect to those of OC20A, OC25A, and OC30B, respectively. In particular, NBROC30B exhibited the greatest increase in gallery height among the NBR nanocomposites. However, NBROC20A and NBROC25A exhibited a weak peak at 2θ = 4.6 and 5.3, respectively, indicating the collapse of the gallery spacing to form a more deeply ordered silicate structure [11]. These results indicate that the polar interaction between NBR and OC30B plays a critical role in the expansion of the gallery height. In spite of the distinct increase in gallery height in each nanocomposite, the XRD data indicated that each nanocomposite still had the same peak position, regardless of the silicate loading, as results reported by Krishnamoorti and Giannelis [11,12]. This finding indicates that although X-ray data can be used to determine the gallery
height, it gives no information on the silicate structure with silicate loading. Thus, we investigated viscoelastic properties of the nanocomposites so as to analyze the silicate structure with silicate loading. In Fig. 3, the loss modulus, $G''(\omega)$, versus storage modulus, $G'(\omega)$, curves indicate that NBROC30B05 is slightly more elastic than the other nanocomposites with 5 wt% silicate loading. This can be ascribed to NBROC30B05 having a larger gallery height than NBROC20A05 and NBROC25A05. In addition, the $G''(\omega)$ versus $G'(\omega)$ curves of the three nanocomposites with 5 wt% silicate loading and NBR at varying temperatures fall onto a single curve, implying that the nanocomposites do not have a structural heterogeneity and change. Similar results were obtained for the nanocomposites with other silicate loadings (data not shown). This indicates that time–temperature superposed master curves of each nanocomposite can be formed by only frequency shift factor, $\alpha_T$, as shown in Fig. 4. From Fig. 4, NBROC30B05 exhibits the highest moduli, implying that NBROC30B05 was more elastic than the other nanocomposites. This is consistent with the findings above $G''(\omega)$ versus $G'(\omega)$ plots, and reveals that NBROC30B05 has the largest gallery height in the nanocomposites with 5 wt% silicate loading due to polar interaction between the NBR and the intercalant of OC30B. In Fig. 5, $G'$ and $G''$ master curves for NBROC20A increase monotonically with increasing silicate loading. Moreover, the frequency dependence of

![Fig. 2. X-ray diffraction profiles for (a) OC20A and NBROC20As, (b) OC25A and NBROC25As, and (c) OC30B and NBROC30Bs.](image)

![Fig. 3. Plots of log $G''$ versus log $G'$ both taken at the same frequency for NBR, NBROC20A05, NBROC25A05, and NBROC30B05 at various temperatures (60–180°C).](image)
the master curve decreased in the low frequency region, which became more dominant as the silicate loading increased. These indicate that viscoelastic behavior of the nanocomposites was shifted toward solid-like as the increase of silicate loading. The master curves for NBROC25A and NBROC30B also showed trends similar to that obtained for NBROC20A. (The master curves for NBROC25A and NBROC30B with silicate loading are not shown in this paper.)

Fig. 4. Time–temperature superposed (a) storage modulus and (b) loss modulus master curves of NBR nanocomposites at silicate loading of 5 wt%.

where $C_1$ and $C_2$ are constants and $T_0$ is the reference temperature, in this case 120 °C. Then, apparent activation energies, $E_a$, which is quantitative measure to evaluate the molecular mobility, can be determined by substituting the WLF equation into the frequency shift factor in the Arrhenius equation, as follows:

$$E_a = R \left( \frac{d \ln \alpha_i}{dT(1/T)} \right) = 2.303 R \left[ \frac{C_1 C_2 T^2}{(C_2 + T - T_0)^2} \right].$$

where $C_1$ and $C_2$ are determined by the nonlinear curve fitting using the WLF equation and $R$ is universal gas constant. $E_a$ at 333.15 K, as shown in Table 1, decrease in the order NBROC20A > NBROC25A > NBROC30B > NBR. Giannelis et al. found that, in small-amplitude
oscillatory shear measurements, the storage modulus for the exfoliated nanocomposites displayed frequency dependence similar to that of the pure polymer, in spite of a monotonic increase in the magnitude of the moduli with increasing silicate loading [5]. This was attributed to the relaxation of the polymer chains in the exfoliated nanocomposites not being affected by the presence of the silicate layers, at least within the sensitivity of the dynamic mechanical measurements. Thus, we conclude that NBROC30B, which had activation energy closer to that of NBR than did NBROC20A and NBROC25A, had a larger gallery height than the NBROC20As and NBROC25As. As another quantitative measure for evaluating the nanocomposites, suggesting that NBROC30B has a larger single average relaxation time, $\tau_{HN}$, of the pure polymer among the nanocomposites, that percolation of silicate tactoids, in which some tactoids are connected, can occur over specific silicate loadings. Moreover, they suggested that the percolation of nanoscopic fillers leads to the increase of solid-like.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$T_0$ (°C)</th>
<th>$E_a$ (kJ/mol)</th>
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<tbody>
<tr>
<td>Pure NBR</td>
<td>6.6</td>
<td>350</td>
<td>120</td>
<td>58.2</td>
</tr>
<tr>
<td>NBROC20A</td>
<td>01</td>
<td>4.2</td>
<td>232</td>
<td>70.0</td>
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<tr>
<td></td>
<td>02</td>
<td>3.2</td>
<td>187</td>
<td>77.7</td>
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<tr>
<td></td>
<td>03</td>
<td>2.8</td>
<td>167</td>
<td>86.3</td>
</tr>
<tr>
<td></td>
<td>05</td>
<td>2.6</td>
<td>159</td>
<td>91.9</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>3.6</td>
<td>165</td>
<td>115.9</td>
</tr>
<tr>
<td>NBROC25A</td>
<td>01</td>
<td>4.3</td>
<td>259</td>
<td>60.5</td>
</tr>
<tr>
<td></td>
<td>03</td>
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<tr>
<td></td>
<td>05</td>
<td>4.1</td>
<td>206</td>
<td>83.3</td>
</tr>
<tr>
<td></td>
<td>07</td>
<td>4.4</td>
<td>207</td>
<td>89.7</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>4.9</td>
<td>196</td>
<td>111.2</td>
</tr>
<tr>
<td>NBROC30B</td>
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<td>5.1</td>
<td>293</td>
<td>58.8</td>
</tr>
<tr>
<td></td>
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<td>4.2</td>
<td>234</td>
<td>68.3</td>
</tr>
<tr>
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<td>05</td>
<td>4.1</td>
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</tr>
<tr>
<td></td>
<td>10</td>
<td>5.9</td>
<td>232</td>
<td>97.3</td>
</tr>
</tbody>
</table>

* Calculated at 333.15 K.

$$G' = G' + iG'' = G_\infty + (G_0 - G_\infty) / [1 + (i\omega \tau_{HN})^\beta]$$

where $G'$ is the complex shear modulus, and $G_\infty$ and $G_0$ are the unrelaxed and relaxed moduli, respectively. $\omega$ is the frequency and $\tau_{HN}$ is single average relaxation time. The parameters $\alpha$ and $\beta$, ranging from 0 to 1, are shape parameters that account for the symmetric and asymmetric relaxation time distribution, respectively. Considering the real and imaginary parts of Eq. (3), the storage modulus may be derived as

$$G'(\omega) = G_\infty + (G_0 - G_\infty) x$$

$$\frac{\cos(\beta \omega \tau_{HN})}{[1 + 2(\omega \tau_{HN})^\alpha \cos(\pi x/2) + (\omega \tau_{HN})^{2\beta}]}$$

Thus, $\tau_{HN}$ values can be acquired by a nonlinear curve fitting of the $G'(\omega)$ master curve using Eq. (4). Fig. 7 shows that $\tau_{HN}$ of the nanocomposites increased with silicate loading. Moreover, the NBROC30B nanocomposites exhibit $\tau_{HN}$ values closest to those of pure NBR among the nanocomposites, suggesting that NBROC30B has a larger gallery height than the other nanocomposites. Interestingly, $E_a$ and $\tau_{HN}$ for all nanocomposites with silicate loadings in excess of 7 wt% increased remarkably compared to those for the nanocomposites with silicate loadings below 7 wt%, as shown in Table 1 and Fig. 7, respectively. Krishnamoorti et al. [11] reported that mesoscopic structure consisting of silicate tactoid is present in intercalated nanocomposites and that percolation of silicate tactoids, in which some tactoids are connected, can occur over specific silicate loading. Moreover, they suggested that the percolation of nanoscopic fillers leads to the increase of solid-like
behavior of nanocomposites. Lu et al. also reported that great improvement of solid-like behavior in highly filled nanocomposites is mainly due to the network formation of clay layers [15]. Thus, the drastic increases of $E_a$ and $\tau_{HN}$ over silicate loading of 8 wt% are considered to be ascribed to the sudden change of silicate structure such as the formation of network-like percolation of silicate tactoids. To verify the change of silicate structure predicted from molecular mobility results of the nanocomposites, we carried out the morphological analysis by means of HR-TEM. As shown in Fig. 8, it was found that network-like silicate structure was formed in NBROC30B10, whereas no network-like silicate structure was observed in NBROC30B05. These are consistent with the results expected from evaluation of molecular mobility of NBR nanocomposites.

4. Conclusions

In this study, NBR nanocomposites containing OCs with a polar intercalant, nonpolar intercalant with short chain length, or nonpolar intercalant with long chain length were prepared with various silicate loadings (1, 3, 5, 7, and 10 wt%) by the melt mixing process. The XRD data showed that all of the NBR nanocomposites had an intercalated structure and that NBROC30B had the largest gallery height among the NBR nanocomposites due to the polar interaction between the intercalant and NBR chain. However, X-ray pattern did not show evidence of a structural change as a function of silicate loading. From analysis of viscoelastic properties, it was revealed not only that the nanocomposites became solid-like with increasing silicate loading but also that NBROC30B was the most elastic of the NBR nanocomposites. In addition, it was found that the $E_a$ and $\tau_{HN}$ values of NBROC30B were much closer to those of NBR than the other nanocomposites. These results indicate that NBROC30B had the largest gallery height among the nanocomposites tested. Moreover, the $E_a$ and $\tau_{HN}$ values of all of the nanocomposites with silicate loadings over 8 wt% were markedly higher than those of the nanocomposites with silicate loadings below 7 wt%. These results suggest that the layered silicate in the NBR nanocomposites with silicate loadings over 8 wt% formed a network-like percolated structure, and were consistent with HR-TEM results.

Acknowledgements

The authors are grateful to the Korea Science and Engineering Foundation (KOSEF) for support of this study through the Hyperstructured Organic Materials Research Center (HOMRC).

References


