

## Effect of Paramagnetic Fe<sup>3+</sup> on T<sub>1</sub><sup>H</sup> in PVA/montmorillonite-clay Nanocomposites

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The relation between T<sub>1</sub><sup>H</sup> values of PVA/montmorillonite-clay nanocomposites and an iron content in a few different kinds of montmorillonite clays is examined. The T<sub>1</sub><sup>H</sup> values for PVA in the PVA/montmorillonite-clay nanocomposites decreased drastically with the amount of the montmorillonite clay, and the decrement depends on the iron content in the montmorillonite clay.

Organic-polymer/inorganic-clay nanocomposites have a potential to show a great improvement of gas barrier and mechanical or thermal properties, when the nanocomposites take exfoliate or intercalated states.<sup>1</sup> It is, hence, very important to detect the dispersion of clay and to investigate morphology or interaction between a polymer and a clay mineral. In the few past years, several solid-state NMR studies for the nanocomposites have been reported widely to investigate polymer structures, morphology, and interaction between the organic and the inorganic materials.<sup>2,3</sup> VanderHart et al.<sup>3</sup> showed that the <sup>1</sup>H spin-lattice relaxation (T<sub>1</sub><sup>H</sup>) curves of nylon-6 in the nylon-6/montmorillonite nanocomposites give morphological information, depending on the amounts of paramagnetic Fe<sup>3+</sup> ion naturally contained in montmorillonite clay. This implies that there is a possibility of detection of clay dispersion and/or clay's identity by measuring T<sub>1</sub><sup>H</sup>.

In this study, we investigate the efficiency of Fe<sup>3+</sup> ion on the T<sub>1</sub><sup>H</sup> values for the well-exfoliated system, poly(vinyl alcohol) (PVA)/montmorillonite nanocomposites.<sup>4,5</sup>

PVA/montmorillonite nanocomposites (PVA/mnt NnC's) are prepared by casting the water solutions at respective mnt weight concentration as mentioned by other researchers.<sup>4,5</sup> To detect difference of amount of Fe<sup>3+</sup> ions affecting on T<sub>1</sub><sup>H</sup>, we prepared the nanocomposites with three kinds of mnt clays and a synthetic saponite clay. Amounts of Fe<sup>3+</sup> ion (as Fe<sub>2</sub>O<sub>3</sub>) in those clays by elemental analysis are 2.7% in mnt-1, 3.5% in mnt-2, 4.4% in mnt-3, and 0.0% in saponite clay, respectively.<sup>6</sup> The PVA/mnt NnC's are prepared at the weight ratio of 100/1, 100/2, 100/4, 100/6, 100/8, and 100/10.

The dispersion of the mnt clay is characterized by the X-ray diffraction (XRD) measurement as shown in Figure 1. Because of our instrumental limitation, the XRD pattern at angle below 2θ = 5.0 could not be observed. The observed XRD patterns show that the characteristic peaks at 2θ = 7.2 and 28.4 for mnt disappeared for the PVA/mnt NnC's. We confirmed that the simple mixing of PVA and mnt clay powders at 100/10 clearly shows the two peaks on its XRD pattern. These suggest that the space distance of mnt clay layers becomes larger than 1.8 nm by nano-composing at least, as is calculated from θ = 2.5 and λ = 0.154 nm, indicating that the PVA/mnt NnC's are well-exfoliated state; Strawhecker and Manias<sup>5</sup> have reported that the space distance of the clay layers for the PVA/mnt NnC's with clay ratio less than 20 wt % is larger than 5 nm.

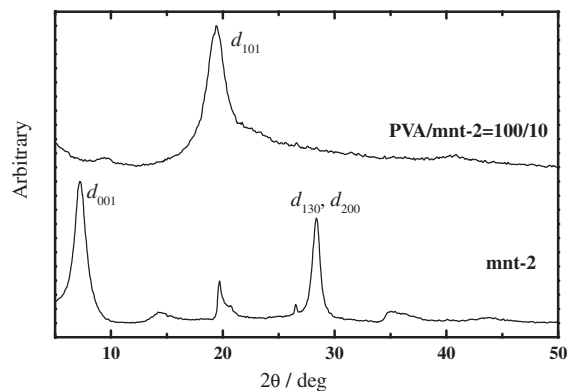
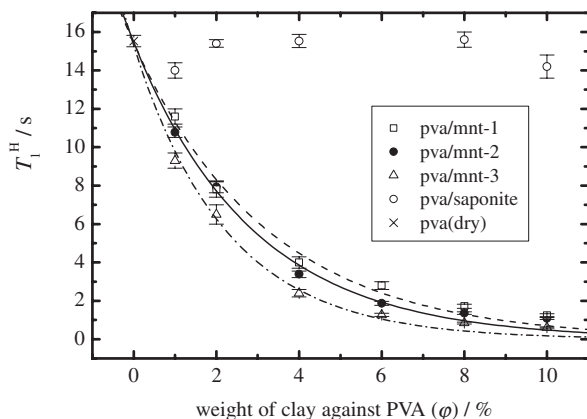


Figure 1. XRD spectra of mnt-2 and PVA/mnt-2 = 100/10 NnC samples.

Figure 2 shows the indirectly obtained T<sub>1</sub><sup>H</sup> values of PVA/clay NnC's by observing the well-resolved <sup>13</sup>C CPMAS (cross-polarization with magic-angle-spinning) NMR against the weight ratio of clay (φ) in the nanocomposites. Here, the abscissa indicates the weight of clay that is mixed with 100 g of PVA: e.g., for PVA/mnt = 100/10, the T<sub>1</sub><sup>H</sup> value is plotted at φ = 10. The T<sub>1</sub><sup>H</sup> values are estimated from the whole integral of both CH<sub>2</sub> and CH signals.

The T<sub>1</sub><sup>H</sup> value of PVA is extremely affected by moisture. For example, the T<sub>1</sub><sup>H</sup> value of dried PVA film is over 15 s, while that of the wet PVA film, which is cast from the water solution and just dried under atmosphere, is less than 3 s. Here, we use the dried PVA and PVA/clay NnC's that are prepared under the same condition. The PVA and the PVA/clay NnC films are firstly dried under vacuum at 80 °C for 3 days after casting the water solution and further dried under vacuum at 80 °C for 12 h after inserting the films in the solid-state NMR sample tube. The water content of those samples is less than 0.3 wt %, which is obtained by a Mettler Toledo HG53 Halogen Moisture Analyzer. On the other hand, since PVA is semicrystalline polymer, we may detect both intrinsic T<sub>1</sub><sup>H</sup> values of crystalline and amorphous phases. However, the fast <sup>1</sup>H spin diffusion between the crystalline and amorphous phases makes those different values equal. Furthermore, the clay did not affect the crystalline/amorphous ratio as mentioned in a case of nylon-6/mnt NnC's.<sup>3b</sup>

All the observed T<sub>1</sub><sup>H</sup> decays are single-exponential. The obtained T<sub>1</sub><sup>H</sup> value of PVA is 15.5 ± 0.2 s: the error is σ. Figure 2 shows that the T<sub>1</sub><sup>H</sup> values for PVA/saponite clays are mostly the same as that of PVA, while those of the PVA/mnt NnC's are largely affected and decrease steeply with the amount of mnt clay. Furthermore, the decrease ratio differs among the kind of mnt clay. These results suggest that the mixing of inorganic clay to PVA is not effective on T<sub>1</sub><sup>H</sup> but the Fe<sup>3+</sup> ions naturally contained in the mnt clay play a very important role to alter the T<sub>1</sub><sup>H</sup> values of PVA in the nanocomposites.



**Figure 2.** Observed  $T_1^H$  values of the various PVA/mnt and PVA/saponite NnC's vs weight of clay against PVA. The broken, solid and dotted-broken lines are the best-fit curves to the respective observed data points, respectively.

The effect of  $\text{Fe}^{3+}$  ions on  $T_1^H$  of PVA reaches to the neighboring PVA thin phase only.<sup>3</sup> The  $T_1^H$  value of the PVA thin phase becomes extremely short. The very short  $T_1^H$  relaxation averages out the original  $T_1^H$  values of the bulk PVA by the fast  $^1\text{H}$  spin diffusion occurring in PVA. Therefore, well dispersed state of clay is very important to observe a single-exponential  $T_1^H$  decay. On the contrary, a non-single-exponential  $T_1^H$  decay suggests the poor dispersion of mnt in a nanocomposite. In fact, in a case of PVA/mnt = 100/20 or 100/30, we observed the non-single-exponential decay curves. The present  $T_1^H$  single-exponential decay means the good dispersion of clay. This is consistent with the results of the XRD study.

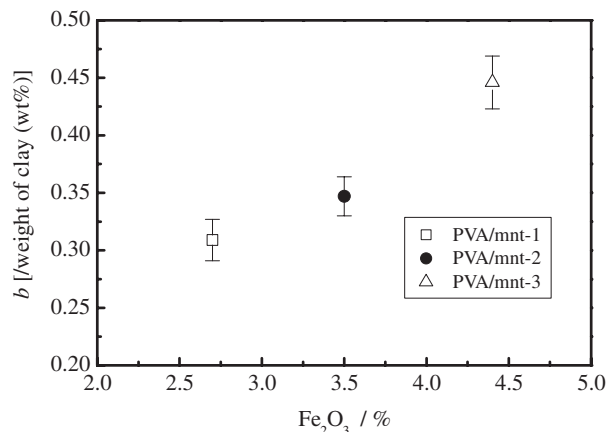
Figure 2 shows that the paramagnetic effect on  $T_1^H$  relates to the kind of mnt clay because the degree of  $T_1^H$  decrease is clearly different, especially for the range of PVA/mnt = 100/0 to 100/4. This suggests that the quantitative evaluation of the degree of  $T_1^H$  decrease can identify clay minerals if the contribution factor is known. Furthermore, the clay dispersion is also given by the contribution factor.

To analyze the contribution factor quantitatively, we fit the observed  $T_1^H$  for PVA/mnt NnC's using the following simple exponential decay function:

$$T_1^H(\varphi) = T_1^H(0) \cdot \exp(-b \cdot \varphi).$$

Here  $b$  is the paramagnetic contribution factor to  $T_1^H$ , which is depending on a kind of clay, and  $\varphi$  is the weight of clay against PVA in PVA/clay NnC's. Since clay layers are distributed in PVA matrix homogeneously, and since a resulting distance between the exfoliated layers in PVA decreases abruptly with the small amount of clay, the paramagnetic effect on  $T_1^H$  appears exponentially. Detailed discussion will be published elsewhere.

Each  $T_1^H(\varphi)$  data set is successfully least-square fitted and the results are shown in Figure 2 as broken, solid, and broken-dotted lines, respectively. The obtained  $b$  values ( $\text{wt}\%^{-1}$ ) are  $0.31 \pm 0.02$ ,  $0.35 \pm 0.02$ , and  $0.45 \pm 0.02$  for PVA/mnt-1, -2, and -3, respectively. Since the paramagnetic susceptibility of  $\text{Fe}^{3+}$  ions contributing to  $T_1^H$  is equal among the kinds of the montmorillonite clays, these obtained  $b$  values correspond to the mass fraction of  $\text{Fe}^{3+}$  ions in the respective mnt clays: the larger  $b$  value is the greater mass fraction of  $\text{Fe}^{3+}$  ions. Thus, the contribution factor will be comparable to the  $\text{Fe}_2\text{O}_3$  contents.



**Figure 3.** The paramagnetic contributing factor against the  $\text{Fe}_2\text{O}_3$  content obtained from elementary analysis. The symbols are the same as Figure 2.

The comparison between the paramagnetic contributing factor and the  $\text{Fe}_2\text{O}_3$  content is plotted in Figure 3.

Figure 3 shows that the correlation between the obtained  $b$  factor and the  $\text{Fe}_2\text{O}_3$  content in mnt clays is very good. This good relation suggests that the  $\text{Fe}_2\text{O}_3$  content of clay can be estimated by just measuring  $T_1^H$ . Therefore, the  $T_1^H$  values are not only affected by weight fraction of clay in NnC's but also by concentration of  $\text{Fe}_2\text{O}_3$ . Furthermore, the dispersion of clay is also detectable by  $T_1^H$ , because the  $b$  factor is affected by the dispersion. On the other hand, in this study, only the exfoliate PVA/mnt NnC's are examined. Therefore, it is necessary to measure a lot of nanocomposites with the various clay dispersion and different types of clay containing the paramagnetic-ion center to apply more complicated cases. Establishing a database of the contributing factor will be useful to analyze the amount of paramagnetic ion, a producing district, and clay dispersion for the various organic-inorganic nanocomposites nondestructively.

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