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Preparation and characterization of poly(vinyl butyral)/Na$^+$-montmorillonite nanocomposite

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Polymer/clay hybrid nanocomposite materials, in which a small amount of inorganic filler is added into the polymer matrix, have been extensively investigated because of their superior physical, mechanical, and electrical properties in comparison to conventional polymer composites [1–8]. The clay gallery used in polymer/clay nanocomposites has a layered smectite group, in which each smectite is constructed from a tetrahedral alumina sheet sandwiched between two tetrahedral silicate sheets, exhibiting negative charge on the smectite surface which enables them to absorb cations such as Na$^+$ and Ca^{++} [9]. Because of the large aspect ratio of smectites, physical and chemical reactions were possible on the surface of smectites or between smectites. The preparation methods of polymer/clay nanocomposites including solvent intercalation, melt mixing, and *in-situ* polymerization are known [10–12]. In this letter, both solvent intercalation and *in-situ* reaction were adopted to prepare poly(vinyl butyral) (PVB)/Na$^+$-montmorillonite (MMT) nanocomposite (PVBN).

Preparing a mixture of hydrophobic polymer and hydrophilic inorganic species without a sufficient affinity between the two is our main concern [8]. The poly(vinyl butyral) (PVB) was prepared by an acetalization of poly(vinyl alcohol) (PVA)/Na$^+$-MMT nanocomposite [13]. Initially, Na$^+$-MMT was suspended in de-ionized water and the clay-suspended solution was sonicated to make the clay swell better. Poly(vinyl alcohol) (PVA) powder (Polynol, Oriental Chemistry, Korea) was then added into the stirred swollen clay solution at 25 °C. The degrees of hydrolysis and polymerization of PVA were about 99% and 1700, respectively. The mixture of PVA powder and swollen clays was heated up to the solvation temperature of 90 °C. After solvation, the temperature was reduced to 10 °C. A small amount of HCl was then added to make the solution acidic before the addition of *n*-butyl aldehyde (nBA, Aldrich, USA). The reactants were slowly heated from 10 to 55 °C for 3 h. Further agitation was applied for 3 h. The synthesized PVB/MMT particles were then neutralized by adding NaOH and filtered via an aspirator. Two different PVB/MMT nanocomposites of PVBN 3 and PVBN 5 were thus prepared from two different Na$^+$-MMT contents in wt% of 3 and 5%, respectively. For the Fourier transform infrared spectrum (FT-IR, Bruker, Germany) analysis, the samples were pelletized using KBr. For characterization methods such

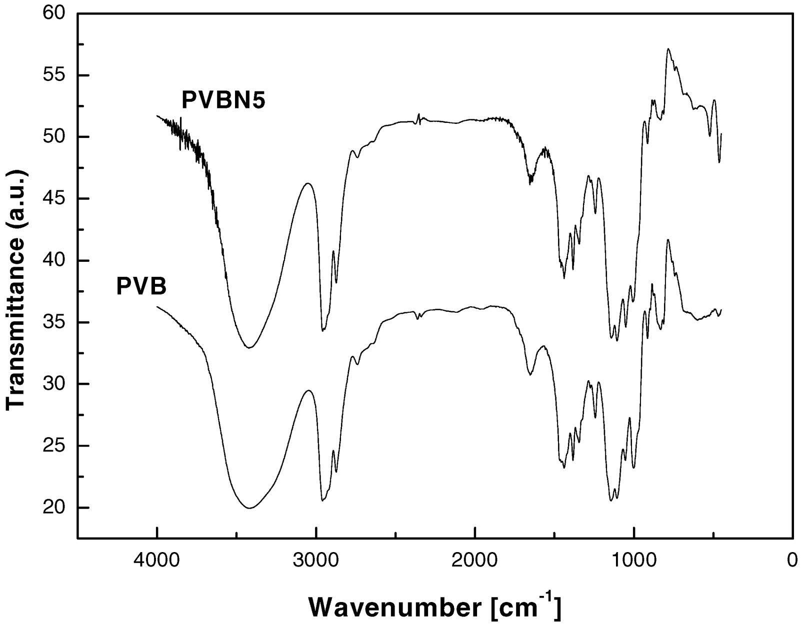

Figure 1 FT-IR spectra of PVB and PVBN5.

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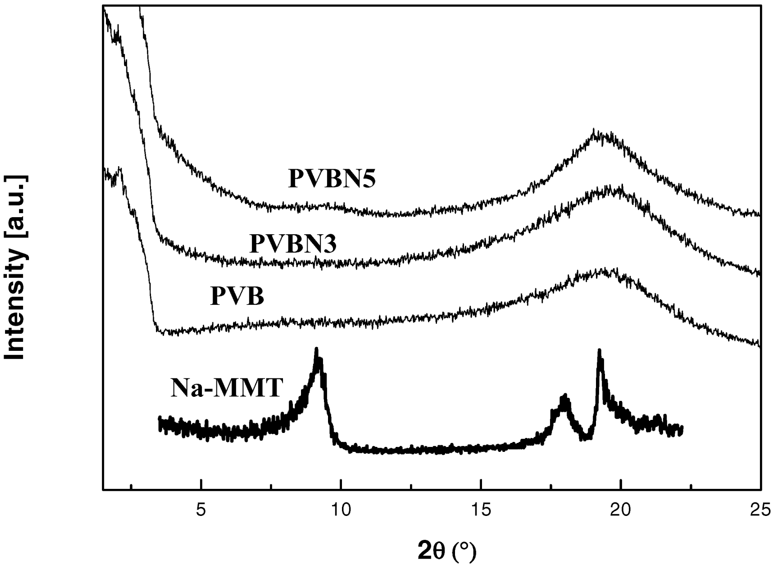

Figure 2 XRD patterns of Na-MMT, PVB, and PVBN series.

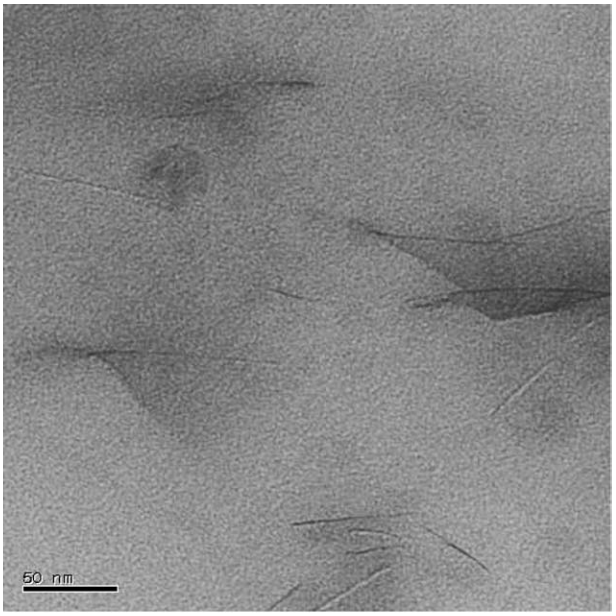

Figure 3 TEM micrograph of PVBN5.

as X-ray diffraction (XRD) and transmission electron microscopy (TEM) hot pressed films were prepared by applying 10 MPa of pressure at 200 °C. In addition, epoxy molding and micro-sectioning methods were used to prepare the sample for the TEM measurement.

Fig. 1 shows the FT-IR spectra of both PVB and PVBN series. Broad peaks at 1700 cm^{-1} for both samples indicate the —OH group of unreacted PVA resulting from uncompleted acetalization. On the other hand, a peak at 2400 cm^{-1} in both spectra represents the cyclic acetal group of PVB, and the peak positioned at 3200 cm^{-1} in PVBN5 indicated the Al—O of Na^+-MMT [14].

The XRD results of Na^+-MMT, PVB, and PVBN series are represented in Fig. 2. The internal distance between each smectite clay (the d-spacing) was about 1 nm and was confirmed by the XRD peak at 9 °. In both PVBN3 and PVBN5, the characteristic peak of the clay was not observed, implying that the clay regularity was disappeared because of an exfoliated structure. Strong

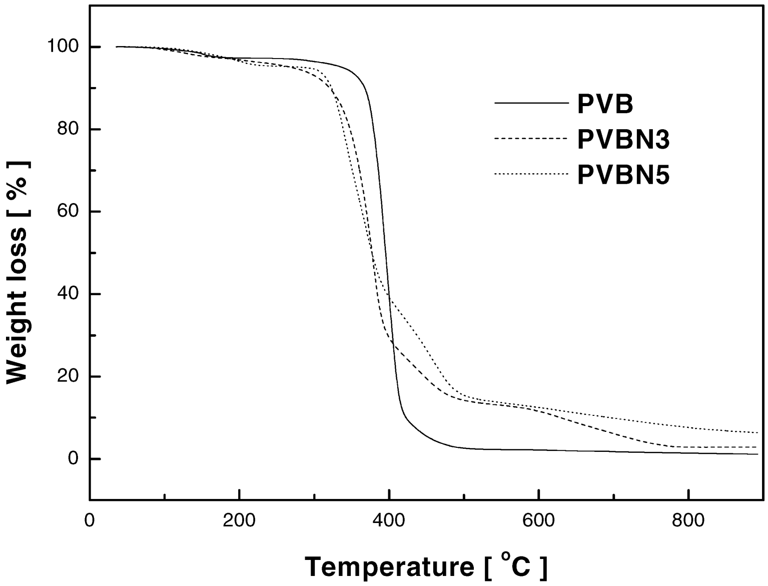

Figure 4 TGA results of pristine PVB and PVBN series.

hydrogen bonding between —OH of the PVB and Al—O of the clay surface enables the polymer chains to contact the clay surface. Repulsive force between hydrophobic butyral group and hydrophilic clay surface cause the clay layers to delaminate. Additional evidence of the exfoliation of PVBN is found from the TEM image. Fig. 3 is a TEM image of PVBN5. The Bright back ground field represents the PVB matrix and the black lines are the clay layers. Clay layers are not aligned, but are detached separately.

Fig. 4 shows the thermogravimetric analysis (TGA) results for the PVB and PVBN series. The decomposition temperature of the polymer/clay hybrid materials becomes higher than that of pristine matrix polymers because of the high thermal stability of clays and interaction between clays and polymers [15]. However the opposite trend was observed in our TGA results. The thermal degradation temperature of our PVBN series decreased with the addition of clays. Ogata *et al.* [16] reported that the clay hinders the polymer degradation at low temperature, while it accelerates the polymer decomposition at high temperature. Accelerated decomposition at high temperature results in a weaker thermal stability of PVBN [17, 18].

In summary, a PVB nanocomposite with a hydrophilic clay was synthesized, which exhibits an exfoliated dominant structure. However, the thermal stability of PVBN decreased compared to the pristine PVB matrix due to the acceleration of polymer decomposition by the addition of clays.

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