

Poly(vinyl alcohol) Nanocomposites with Different Clays: Pristine Clays and Organoclays

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ABSTRACT: Poly(vinyl alcohol) (PVA)/clay nanocomposites were synthesized using the solution intercalation method. Na ion-exchanged clays [Na⁺-saponite (SPT) and Na⁺-montmorillonite (MMT)] and alkyl ammonium ion-exchanged clays (C₁₂-MMT and C₁₂OOH-MMT) were used for the PVA nanocomposites. From the morphological studies, the Na ion-exchanged clay is more easily dispersed in a PVA matrix than is the alkyl ammonium ion-exchanged clay. Attempts were also made to improve both the thermal stabilities and the tensile properties of PVA/clay nanocomposite films, and it was found that the addition of only a small amount of clay was sufficient for that purpose. Both the ultimate tensile strength and the initial modulus for the nanocomposites increased gradually with clay loading up to 8 wt %. In C₁₂OOH-MMT, the maximum enhancement of

the ultimate tensile strength and the initial modulus for the nanocomposites was observed for blends containing 6 wt % organoclay. Na ion-exchanged clays have higher tensile strengths than those of organic alkyl-exchanged clays in PVA nanocomposites films. On the other hand, organic alkyl-exchanged clays have initial moduli that are better than those of Na ion-exchanged clays. Overall, the content of clay particles in the polymer matrix affect both the thermal stability and the tensile properties of the polymer/clay nanocomposites. However, a change in thermal stability with clay was not significant. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3208–3214, 2003

Key words: nanocomposites; organoclay; intercalation

INTRODUCTION

Recently, due to the development of nanotechniques, there has been growing interest in the field of nanocomposites and their special properties. At present, polymer/clay hybrids are one of the most important classes of synthetically engineered materials.^{1–4} They can be transformed into new materials possessing the advantages of both organic materials, such as light weight, flexibility, and good moldability, and inorganic materials, such as high strength, heat stability, and chemical resistance. Materials incorporating polymer/clay hybrids can attain enhanced degrees of stiffness, strength, and gas-barrier properties with the addition of far less inorganic content than is used in conventionally filled polymer composites.^{3–6} They are, therefore, lighter weight. They also exhibit two-dimensional stability. The higher the degree of exfoliation in the polymer/clay hybrids, the greater is the enhancement of their properties.^{5–9}

Poly(vinyl alcohol) (PVA) is a water-soluble polymer extensively used in paper coating, textile sizing, and flexible water-soluble packaging films.^{10,11} These applications stimulate interest in improving the mechanical, thermal, and permeability properties of thin nanocomposite films, ultimately with the hope of retaining the optical clarity of PVA. PVA nanocomposite materials may offer a viable alternative for these applications to heat treatments or conventionally filled PVA materials.

PVA/clay nanocomposites have been studied in many laboratories.^{12–14} In the presence of PVA, the layers remain in a colloidal distribution.^{14,15} In the wet state or after mild drying, the clay layers are distributed and embedded in a PVA gel. This state corresponds to a true nanoscaled hybrid material. However, drying *in vacuo* causes certain portions of the clay layers to reaggregate. The steric constraints, due to the PVA matrix, impedes reaggregation of all the clay layers; some remain in the dispersed state.¹⁴ Interest in preparing nanocomposites lies in the amorphous domains with uniformly distributed mineral layers, but the behavior of PVA/montmorillonite poses a serious obstacle during preparation of nanocomposites from solutions because it is difficult to avoid reaggregation of the layers.

This article presents characterizations of the thermal and tensile properties of PVA hybrids with various

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clays: Na ion-exchanged clays and alkyl ammonium ion-exchanged clays. These properties of the hybrids in film form were studied as functions of the clay content in the matrix polymer. We also examined the relationship between the properties and the structures of PVA/clay hybrid films using wide-angle X-ray diffraction measurements. The morphological properties of the hybrids were studied using scanning electronic microscopy (SEM) and transmission electronic microscopy (TEM).

EXPERIMENTAL

Materials

Source clays, Kunipia-F [Na^+ -montmorillonite (Na^+ -MMT)] and Saponite [Na^+ -saponite (Na^+ -SPT)] were obtained from Kunimine Ind. Co. (Tokyo, Japan). By screening the Na^+ -MMT and the Na^+ -SPT with a 325-mesh sieve to remove impurities, we obtained a clay having a cationic exchange capacity of 119 meq/100 g for MMT and 100 meq/100 g for SPT. PVA, dodecylamine, and 12-aminolauric acid were purchased from the Aldrich Chemical Co. (Seoul, Korea) and were used as received. Commercially available solvents were purified by distillation; *N,N*-dimethylacetamide (DMAc) was purified and dried over molecular sieves before use. Common reagents were used without further purification.

Preparations of organo-MMTs and PVA/organo-MMT hybrid films

A dispersion of Na^+ -MMT was added to solutions of ammonium salts of dodecylamine (C_{12} -) and of 12-aminolauric acid (C_{12}OOH -). Modifications of MMT by dodecylammonium chloride and 12-aminolauric acid ammonium chloride were obtained through a multistep route^{3,16} and were termed C_{12} -MMT and C_{12}OOH -MMT, respectively.

Since the synthetic procedures for PVA/ C_{12} -MMT or C_{12}OOH -MMT hybrids with different weight percents of organoclay are very similar, only a representative example for the preparation of PVA/ C_{12} -MMT (2 wt %) is given. A 50.0 g mixture of the DMAc dispersion containing 0.08 g of C_{12} -MMT, 4.0 g of a PVA, and excess DMAc was stirred vigorously at room temperature for 1 h. The solution was cast onto glass plates, and the solvent was evaporated in a vacuum oven at 50°C for 2 days. The films were then cleaned in an ultrasonic cleaner three times for 5 min each time. These films with the solvent removed were dried again in a vacuum oven at 50°C for 1 day.

Na^+ -MMT and Na^+ -SPT hybrid films were cast from a water suspension where PVA was dissolved. The suspensions were heated to 70°C to dissolve the PVA and sonicated for 5 min, and, finally, films were

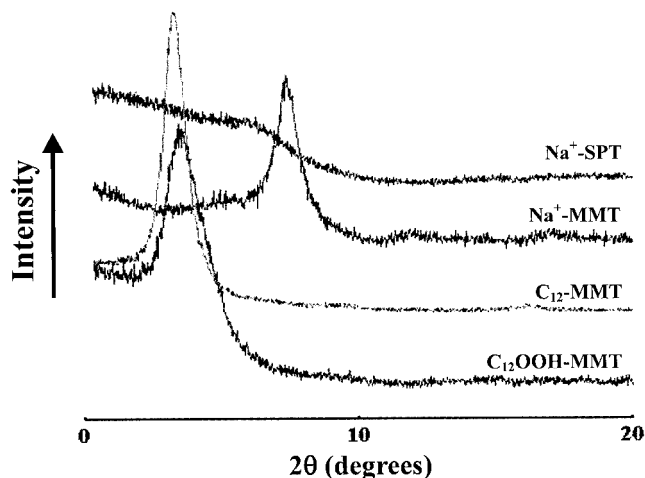


Figure 1 XRD patterns of the clays.

cast in a closed oven at 40°C for 2 days. The film thicknesses were 10–15 μm .

Characterization

Thermogravimetric analyses (TGA) were performed using a DuPont 910 instrument with a heating rate of 20°C/min under a N_2 flow. Wide-angle X-ray diffraction (XRD) measurements were performed at room temperature on a Rigaku (D/Max-III B) X-ray diffractometer using Ni-filtered $\text{CoK}\alpha$ radiation. The scanning rate was 2°/min over a range of $2\theta = 2$ –20°.

The tensile properties of the solution-cast films were determined using an Instron mechanical tester (Model 5564) at a cross-head speed of 5 mm/min at 25°C. The specimens were prepared by cutting strips 5 mm wide and 70 mm long. All measurements were done in 10 replicates, and the values were averaged. The experimental uncertainties in the tensile strength and modulus were ± 5 MPa and ± 0.2 GPa, respectively.

The morphologies of the fractured surfaces of the films were investigated using SEM with a Hitachi S-2400 electron microscope. All samples were fractured in liquid nitrogen in a direction perpendicular to the stretch direction, and the fractured surfaces were sputter-coated with gold using an SPI sputter coater for enhanced conductivity. TEM photographs of ultra-thin sections of the polymer/organo clay hybrid samples were taken on an EM 912 OMEGA transmission electron microscope using an acceleration voltage of 120 kV.

RESULTS AND DISCUSSION

Dispersibility of clay and organoclay in PVA

Figure 1 shows XRD curves of Na^+ -SPT, Na^+ -MMT, C_{12} -MMT, and C_{12}OOH -MMT in the region from $2\theta = 2$ –20°. Basal spacings were measured using XRD

TABLE I
Interlayer Spacings of Clay Modified
with Various Intercalation Agents

Clay	2θ	d -spacing (Å)	Interlayer spacing (Å)
Na ⁺ -SPT	8.18	12.54	2.54
Na ⁺ -MMT	8.56	11.99	1.99
C ₁₂ -MMT	6.14	16.69	6.69
C ₁₂ OOH-MMT	6.40	16.02	6.02

analysis. Each curve had one peak corresponding to basal spacings of 12.54 Å for Na⁺-SPT, 11.99 Å for Na⁺-MMT, 16.69 Å for C₁₂-MMT, and 16.02 Å for C₁₂OOH-MMT.⁷ The thickness of the clay layer was 10 Å, while the interlayer spacings were 2.54 Å for SPT, 1.99 Å for MMT, 6.69 Å for C₁₂-MMT, and 6.02 Å for C₁₂OOH-MMT. The interlayer spacing clearly changed with the size of the exchanged cation. The interlayer spacings were calculated from the XRD measurements and are summarized in Table I.

Figure 2 shows XRD curves of PVA hybrids with different clays at a 4 wt % clay content. In the cases of the Na⁺-MMT and the Na⁺-SPT hybrids, these curves show no peaks, that is, the peak corresponding to the basal spacing has disappeared. This shows that the clay in those hybrids was dispersed homogeneously into the polymer matrix. Some chemical interaction between the PVA and the clays might occur. In the hybrid with C₁₂-MMT, the diffraction at $2\theta = 6.14^\circ$ shifted to $2\theta = 4.25^\circ$, corresponding to a basal spacing of 24.11 Å. At the same weight percent loading of PVA with C₁₂OOH-MMT, the peak appeared at $2\theta = 4.43^\circ$, corresponding to a d -spacing of 21.55 Å. This increase in the basal spacing suggests intercalation of the matrix polymers into clay galleries.

With higher loading of the clays (8 wt %) in PVA, diffractions corresponding to the basal spacing were

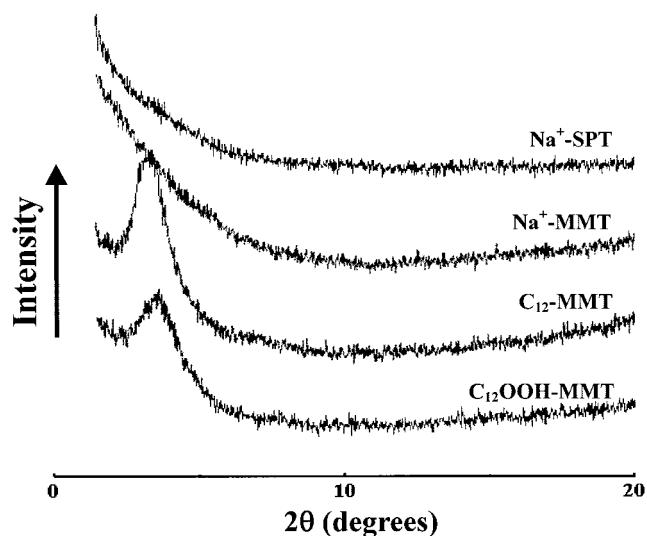


Figure 2 XRD patterns of 4 wt % clay/PVA hybrid films.

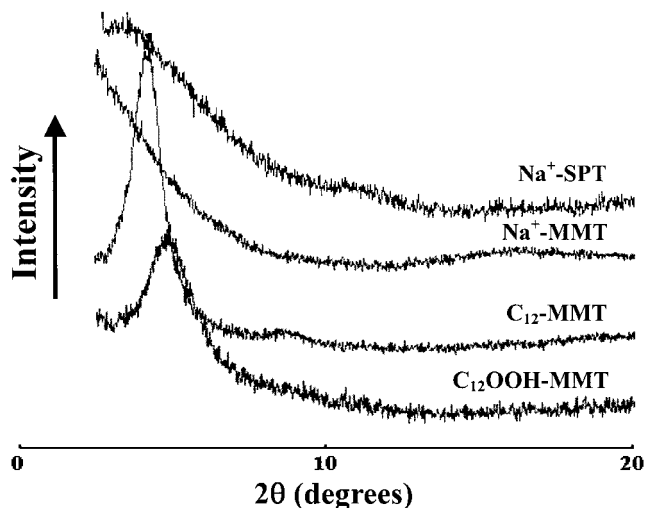


Figure 3 XRD patterns of 8 wt % clay/PVA hybrid films.

observed (see Fig. 3). As with the C₁₂-MMT and the C₁₂OOH-MMT hybrids, a sharp peak existed in the region of $2\theta = 4\text{--}5^\circ$, and the peak increased in intensity with an increasing clay content from 4 to 8 wt % (see Figs. 2 and 3), suggesting that some portion of the organophilic clay aggregated.

The clay peaks did not appear in the Na⁺-clay hybrids shown in Figures 2 and 3, indicating that the PVA/Na⁺-clay samples became exfoliated nanocomposites. Further evidence of Na⁺-clay dispersion into PVA on a nanometer scale can be provided by TEM studies.

Morphology

Scanning electron micrographs of the fractured surfaces of PVA hybrid films prepared with different clays are compared in Figure 4. The fractured surfaces of Figure 4(a,b) show not only the smooth surfaces due to the finely dispersed clay particles but also no trace of clay particles with an increasing clay content from 4 to 8 wt %. Conversely, the fractured surfaces of Figure 4(c,d) show voids, and some deformed parts, which may result from the coarseness of the fractured surface, can be found. However, the fractured surfaces were more deformed when organophilic-MMT was used in the hybrids [see Fig. 4(c,d)]. This is probably a consequence of the agglomeration of clay particles.¹⁶⁻¹⁸ In conclusion, pristine clays can be dispersed better than can organoclays in a water-soluble polymer.

More direct evidence for the formation of a true nanoscaled composite was provided by TEM analysis of ultramicrotomed sections. The micrographs are presented in Figure 5. XRD profiles showed the expected results: well-dispersed layers in both the PVA/Na⁺-SPT and the PVA/Na⁺-MMT hybrids. The dark lines

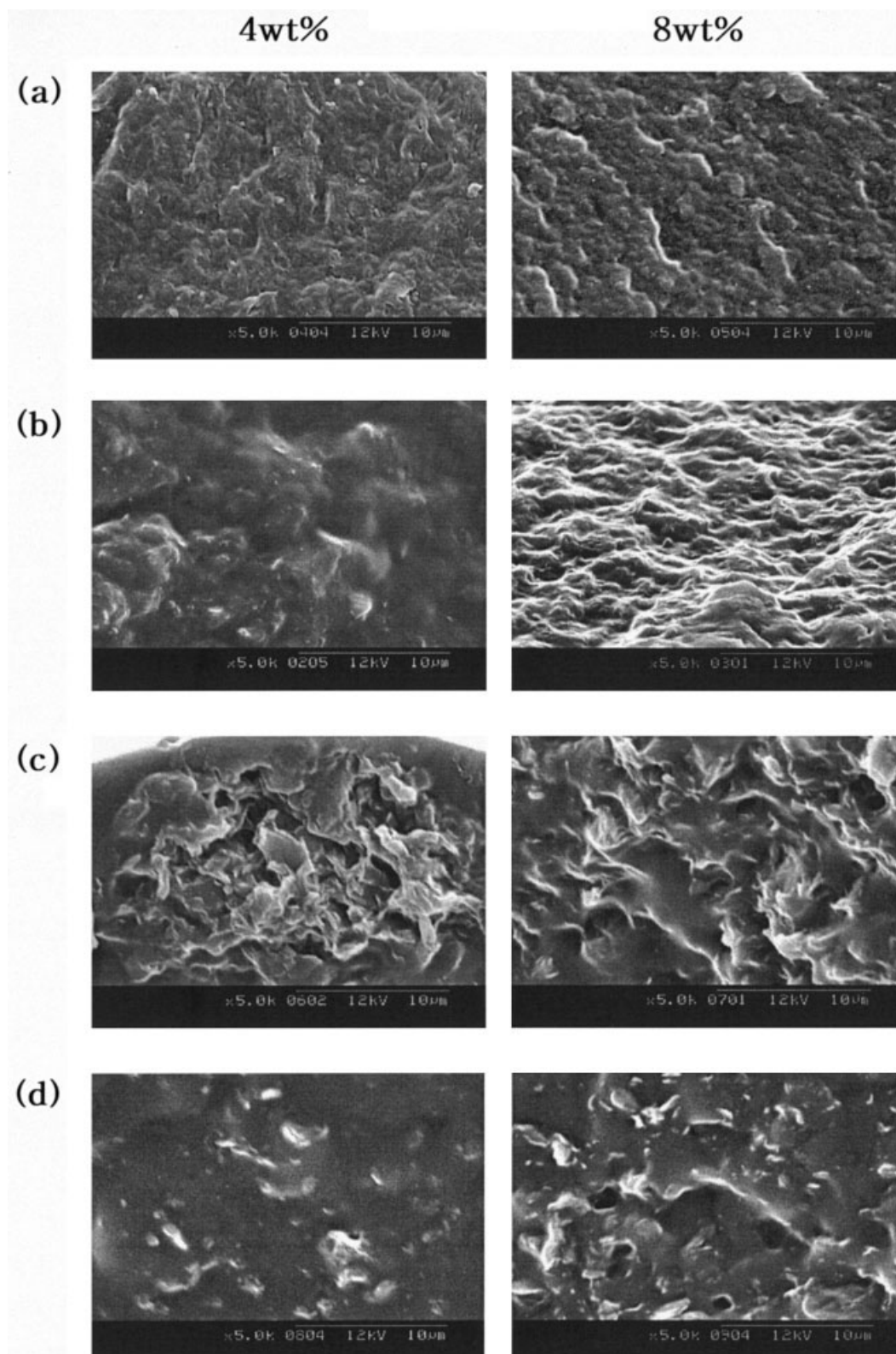


Figure 4 SEM photographs of PVA hybrids as a function of clay loading ($\times 5000$): (a) Na^+ –SPT; (b) Na^+ –MMT; (c) C_{12} –MMT; (d) C_{12}OOH –MMT.

are the intersections of 1-nm-thick clay sheets, and the spaces between the dark lines are the interlayer spaces. The clay layers of Figure 5(a,b) are exfoliated and dispersed randomly in the PVA matrix. The esti-

mated size of the clay sheet is about 1 nm in thickness and about 40–100 nm in length. These TEM photographs prove that most of the clay layers of organoclays were exfoliated and dispersed homogeneously

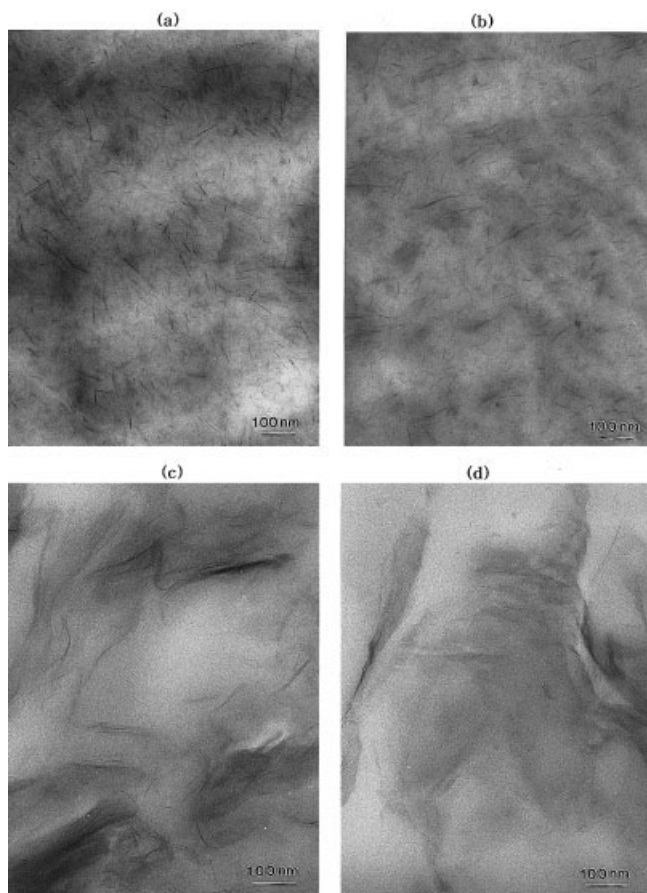


Figure 5 TEM photographs of PVA hybrids containing 4 wt % clay: (a) Na⁺-SPT; (b) Na⁺-MMT; (c) C₁₂-MMT; (d) C₁₂OOH-MMT.

into the PVA matrix. This is consistent with the XRD results shown in Figures 2 and 3.

Unlike hybrids containing Na ion-exchanged clays, the alkyl ammonium ion-exchanged clay hybrids show poor formation of nanoscale structures because of intercalation [see Fig. 5(c,d)] and are composed of anisotropic laminated layers where individual clay layers are bonded together by the PVA matrix. A comparison of the morphology results leads to the conclusion that Na ion-exchanged clay is more easily dispersed in a PVA matrix than is alkyl ammonium ion-exchanged clay. This implies that the hydrophilic character of clay promotes dispersion of inorganic crystalline layers in water-soluble polymers. Similar results were observed by many research groups in water-soluble polymers such as poly(vinyl alcohol)^{10,19} and poly(ethylene oxide).^{20,21} This is consistent with the XRD results, shown in Figure 2, and will be cross-checked in the Tensile Properties section using the ultimate tensile strength.

As seen in Table I, greater interlayer spacing should be advantageous in the intercalation of the polymer chains. It should also lead to easier dissociation of the clay, which should result in hybrids with better dis-

persion of clays. However, the relationship between intercalation and interlayer spacing was not followed in our system.

Thermal properties

Figure 6 shows TGA curves of PVA/clay hybrids with identical clay contents (4 wt %) under a N₂ flow. The onset degradation temperature of the hybrids was slightly increased by the incorporation of the clay. The nanocomposite had higher thermal stability than that of PVA. The initial decomposition temperature (T_D^i) at a 2% weight loss for all the hybrids was 7–15°C higher than that of pure PVA. This enhancement in the thermal stability is due to the presence of clay nanolayers, which act as barriers to maximize the heat insulation and to minimize the permeability of volatile degradation products to the material.^{16,22,23} Also, it can be attributed to the decreased permeability of oxygen caused by the dispersed clay in the polymer/clay composites.

It is notable that only small amounts of clay are effective in improving the weight residues for hybrids. This enhancement of char formation is ascribed to the high heat resistance exerted by the clay itself. The char yield at 600°C increased by 4–10 % with a 4 wt % clay loading in the hybrids. Among the hybrids, the char yields of the Na ion-exchanged clay (Na⁺-SPT and Na⁺-MMT) hybrids were higher than those of the alkyl ammonium ion-exchanged clay (C₁₂-MMT and C₁₂OOH-MMT) hybrids. A comparison of the char formation leads to the conclusion that the organic alkyl groups of alkyl ammonium ion-exchanged clays thermally decompose more easily than do hybrids of Na ion-exchanged clay. On the basis of the aforementioned results, the thermal stabilities of the hybrids are improved by the presence of dispersed clay nanolayers and are greater than those of pure PVA.

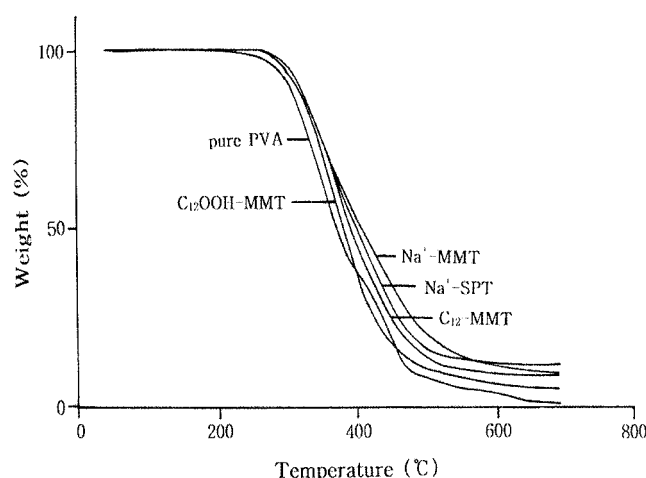


Figure 6 TGA thermograms of 4 wt % clay/PVA hybrid films.

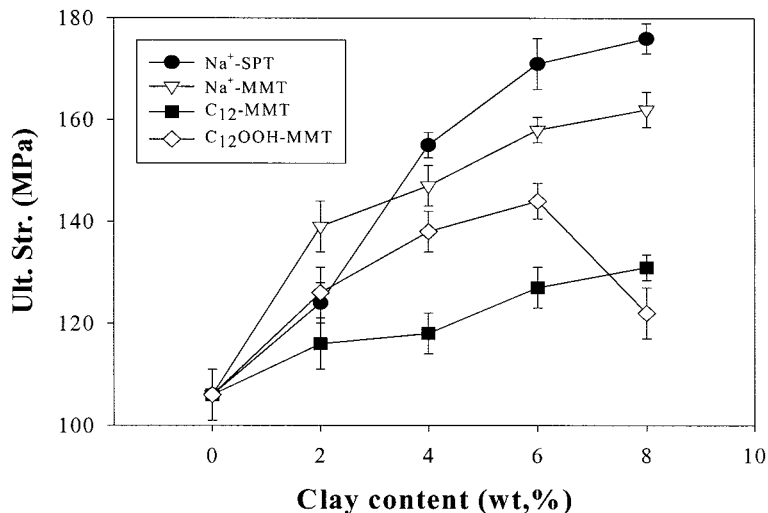


Figure 7 Effects of the clay loading on the ultimate tensile strength of the hybrid films.

Tensile properties

Figures 7–9 show the tensile properties of PVA hybrids with different clay contents. The ultimate tensile strength of the PVA/clay hybrids increases with an increasing clay content from 0 to 8 wt %. On the other hand, the strength of the PVA/C₁₂OOH–MMT hybrid increases gradually with increasing organoclay loading and has a maximum value at 6 wt % C₁₂OOH–MMT content, as shown in Figure 7. This unique strength–mechanical behavior of the C₁₂OOH–MMT-modified hybrid is largely due to the agglomeration of organoclay particles, as seen in Figure 4(d) and Figure 5(d). This result appears to be related to the lack of interfacial interactions between the clay and the matrix polymers; thus, many defects and agglomerations occur in areas of the interphase. Similar trends were observed in studies of other polymer hybrids.^{18,24,25}

The above results suggest that the ultimate tensile strength of the Na ion-exchanged clay hybrids was greater than that of the alkyl ammonium ion-exchanged clay hybrids because the Na ion-exchanged clays are more effectively dispersed than are the organic alkyl-exchanged clays by intercalation in a PVA matrix. This evidence of organoclay agglomeration in a matrix polymer was provided by the TEM measurements [Fig. 5(a,b) versus 5(c,d)].

The modulus values increased with an increasing clay content up to 8 wt %, and the organic alkyl-exchanged clay had a better initial tensile modulus than that of the Na ion-exchanged clay (see Fig. 8). It can be deduced that flexible alkyl groups in clay produce a better orientation of the polymer chains in a composite. Thus, the initial modulus of the hybrids with organic alkyl-exchanged clays is higher than that

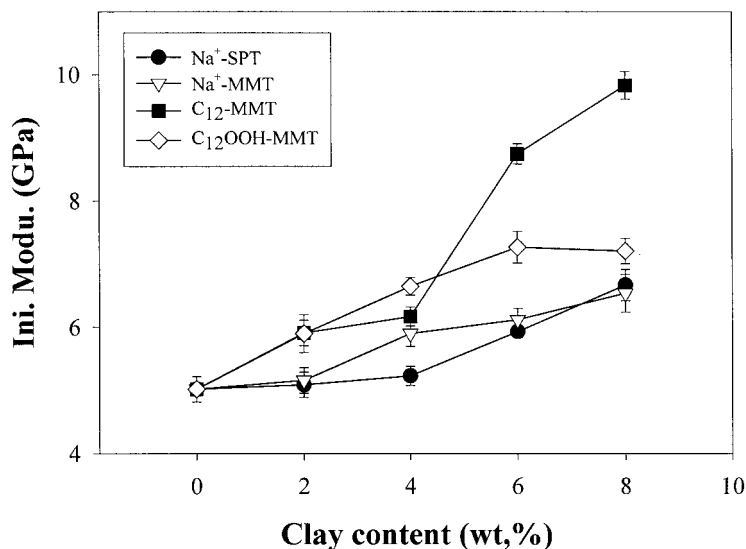


Figure 8 Effects of the clay loading on the initial tensile modulus of the hybrid films.

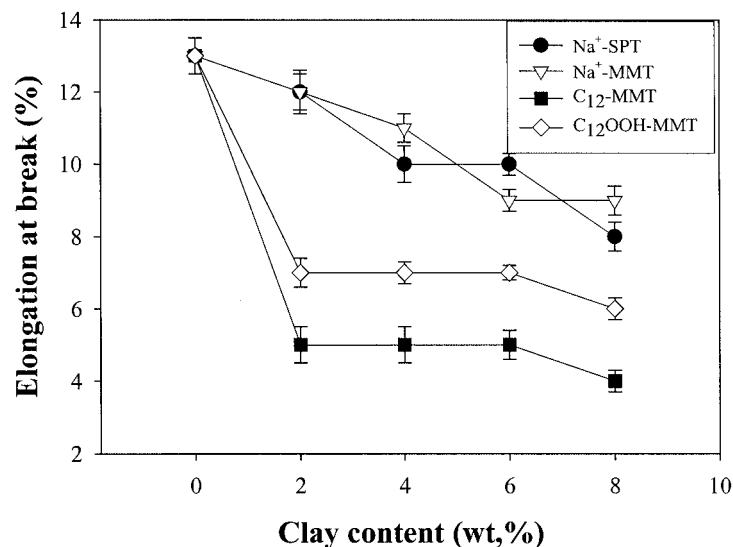


Figure 9 Effects of the clay loading on the elongation at break of the hybrid films.

of hybrids with Na ion-exchanged clays. The modulus value of the 8 wt % C₁₂OOH-MMT-modified hybrid was twice higher than that of the pure PVA polymer.

The elongations at break of the hybrid films with various clays are shown in Figure 9. The elongations at break of PVA hybrids clearly decreased with the introduction of the clay and with an increase in the clay content. Similar to the result of the ultimate tensile strength, the elongation at break of the Na ion-exchanged clay hybrids was greater than that of the alkyl ammonium ion-exchanged clay hybrids.

CONCLUSIONS

The purpose of this study was to investigate the structure of PVA nanocomposites, with the focus on the layered filler dispersion, as well as on the changes of the thermomechanical properties due to the inorganic-layered fillers. Various clays (Na⁺-SPT, Na⁺-MMT, C₁₂-MMT, and C₁₂OOH-MMT) were employed to investigate the properties of PVA hybrid films. From the thermal stability studies, the initial decomposition temperatures and the char yields of the hybrids were slightly higher than those of pure PVA. The morphological study showed that the hybrids of the alkyl ammonium ion-exchanged clay had more fractured surfaces, voids, and aggregated parts than those of the Na ion-exchanged clays at the same weight percent clay loading. In terms of the tensile properties, the Na ion-exchanged clays in hybrid films had better ultimate strengths, but the alkyl ammonium ion-exchanged clays had superior initial moduli.

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