

Poly(vinyl alcohol) Nanocomposite Films: Thermo-optical Properties, Morphology, and Gas Permeability

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ABSTRACT: Poly(vinyl alcohol) (PVA)/saponite nanocomposites were prepared with various clay concentrations with the solution intercalation method. The intercalations of the polymer chains in the clay were examined with wide-angle X-ray diffraction and transmission electron microscopy. The variations of the dispersion, morphology, thermal properties, and gas permeability of the nanocomposites with clay concentrations in the range of 0–10 wt % were examined. Up to a 5 wt % clay loading, the clay particles were highly dispersed in the PVA matrix without any agglomeration of particles. However, some agglomerated structures formed in the polymer matrix above a 7 wt % clay concentration. The thermal stability of the hybrids increased linearly with increases in the clay loading up to 10 wt %. To

measure the oxygen permeability and optical properties of the PVA hybrid films, the PVA hybrid solutions were coated onto both biaxially oriented polypropylene and poly(ethylene terephthalate) films, which were used as polymer substrates. The oxygen permeability values monotonically decreased with increases in the clay loading in the range of 0–10 wt %. The optical properties, such as the haze and gloss of the hybrid films when coated onto the matrix films, were nearly constant, that is, independent of the clay loading. These improvements arose because of the largely nanometer-scale dispersion of the clay layers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 591–596, 2006

Key words: films; nanocomposites; organoclay

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a water-soluble polymer extensively used in paper coating, textile sizing, and flexible water-soluble packaging films, yet not without some disadvantages. These problems have produced the current interest in improving the mechanical, thermal, and permeability properties of thin PVA films by the fabrication of PVA nanocomposite films, ultimately with the hope of retaining the optical clarity of PVA.^{1–4} PVA nanocomposite materials offer viable alternatives to heat-treated or conventionally filled PVA materials.

PVA nanocomposites with clay have been studied in many laboratories.^{5–9} In PVA nanocomposites, the clay layers retain a colloidal distribution.^{9,10} In the wet state or after mild drying, the clay layers are distributed and embedded in the 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 of the PVA matrix impede reaggregation of all the clay layers; some remain in the dispersed state.⁹ The preparation of nanocomposites is designed to create amorphous

domains with uniformly distributed mineral layers, but the preparation of PVA/clay nanocomposites from solutions is difficult because of the reaggregation of the layers.¹¹

In previous research, Lopez et al.¹² reported on synthetic methods used to prevent particle aggregation. To avoid the agglomeration of fillers, they prepared magnetic nanoparticles by *in situ* precipitation within an ion-exchange sulfonated polystyrene. Strawhecker and Manias¹³ also synthesized PVA nanocomposites to improve the processability and thermomechanical properties of pure PVA and PVA/montmorillonite hybrids, with the emphasis on application-relevant, low-silicate-concentration hybrid materials. Even at low clay concentrations (≤ 10 wt %), the thermomechanical properties could be substantially increased, whereas the gas permeability rate was reduced.

In this study, we investigated the effects of the clay loading on the properties of PVA/clay hybrids. The properties of the hybrids were studied in the film form as a function of the clay concentration in the matrix polymer. The clay concentration of the composites was varied from 0 to 10 wt %. We also examined the relationship between the properties and structures of the PVA/clay hybrid films with wide-angle X-ray diffractometry, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The morpho-

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logical properties of the hybrids were investigated with transmission electron microscopy (TEM).

Although the enhancements of gas-barrier properties are well known in polymer-clay nanocomposites, their dependence on factors such as the relative orientation of the sheets in the matrix and the state of aggregation and dispersion is not well understood.^{14–16} Biaxially oriented polypropylene (BOPP) and poly(ethylene terephthalate) (PET) films are widely used as packaging materials. However, these films do not exhibit attractive gas-barrier properties. To improve their gas-barrier properties, BOPP and PET films can be coated with barrier coating materials such as PVA and poly(vinylidene chloride) (PVDC). However, most barrier films and bottles are prepared through extrusion, and the cost of manufacturing these films is high because of the large investments required and difficulties in process control. In addition, PVDC produces dioxins when it is burnt at low temperatures. In contrast, PVA has excellent gas-barrier properties, is inexpensive, and does not produce environmental pollution. The second objective of this study was to investigate the possibility of casting PVA hybrid films onto BOPP and PET films to enhance their barrier and optical properties.

EXPERIMENTAL

Materials

The source clay, Na⁺-saponite (SPT), was obtained from Kunimine Industry Co. (Tokyo, Japan) By screening the SPT with a 325-mesh sieve to remove impurities, we obtained a clay with a cation-exchange capacity of 100 mequiv/100 g. PVA with 88% saponification (average degree of polymerization = 500) was purchased from Aldrich Chemical Co. (Seoul, Korea) and was used as received. Common reagents were used without further purification.

Preparation of the PVA/SPT hybrid films

The suspensions in distilled water with various weight percentages of SPT were heated to 70–80°C to dissolve PVA. To investigate their O₂ permeability, each PVA/SPT hybrid solution was cast onto thin polymer film substrates; the BOPP and PET films were 20 and 12 μm thick, respectively. These thicknesses of the two substrate films are commonly used in packaging. Before the casting, polyurethane primer was applied to prevent the separation of the coating films from the substrate films and dried at 90°C for 2–3 min in a vacuum oven. The solvent was evaporated in a vacuum oven at 70°C for 2 days. The films were then cleaned in an ultrasonic cleaner three times, each for 5 min. Once the solvent had been removed, the films were dried again in a vacuum oven at 50°C for 2 days.

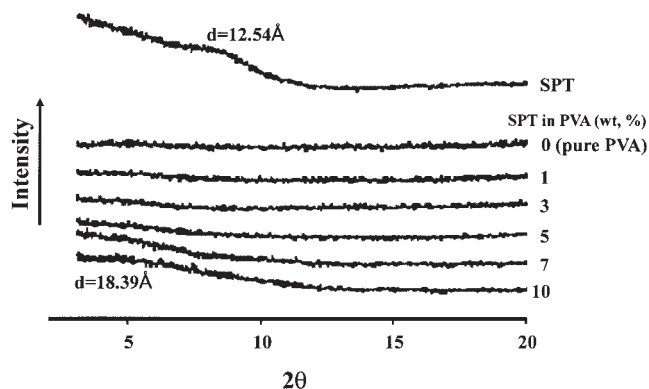


Figure 1 XRD patterns of the clay and PVA hybrids with different clay concentrations.

Characterization

The thermal behavior of the SPT/PVA hybrid films was studied with the combined DuPont (New York, NY) model 910 DSC and TGA apparatus at a heating rate of 20°C/min under a flow of N₂. X-ray diffraction (XRD) measurements were performed at room temperature on a Rigaku D/Max-III B X-ray diffractometer (Tokyo, Japan) with Ni-filtered Co K α radiation. The scanning rate was 2°/min over a range of 2 θ = 2–20°.

The samples for TEM were prepared by the placement of the PVA hybrid films into epoxy capsules and then the curing of the epoxy at 70°C for 24 h *in vacuo*. The cured epoxies containing the PVA hybrids were then microtomed into 90-nm-thick slices, and a layer of carbon, about 3 nm thick, was deposited onto each slice on a 200-mesh copper net. TEM photographs of ultrathin sections of the polymer/clay hybrid samples were obtained with an EM 912 Omega TEM (Tokyo, Japan) instrument with an acceleration voltage of 120 kV.

The O₂ permeability of the films was measured according to ASTM E 96 with a Mocon DL 100 (New York, NY). The values of the O₂ transmission rate were obtained at 23°C, 0% relative humidity, and 1 atm of pressure. The gloss and haze of the films were also measured according to ASTM D 985 and ASTM D 1310, respectively.

RESULTS AND DISCUSSION

Dispersion of the clay in PVA

Figure 1 shows the XRD curves of the pristine clay, SPT, in the 2 θ region of 2–20°. The d_{001} reflection of the SPT was found at 2 θ = 8.18°, which corresponds to an interlayer distance of 12.54 Å. Figure 1 also shows the XRD curves of PVA hybrid films with various clay concentrations in the range of 0–10 wt %. For the PVA hybrids with clay concentrations less than or equal to 5 wt %, no clay peaks appeared in the XRD results,

and this indicated that the clay in those hybrids dispersed homogeneously into the polymer matrix, producing exfoliated nanocomposites. Further evidence of the clay dispersion into PVA on a nanometer scale was obtained with TEM (see the following section).

In contrast to the hybrids with low clay concentrations, a small diffraction peak corresponding to the basal spacing was observed at $2\theta = 4.80^\circ$, corresponding to an interlayer distance of 18.39 Å, for a higher loading of the clays (≥ 7 wt %) in the PVA matrix. In these hybrid systems, the location of the peak indicated an increase in the basal interlayer spacing over that in SPT, and there was a shift of the diffraction peak toward lower values of 2θ ;^{17,18} this indicated that the clay was intercalated in polymer chains. With increases in the clay concentration from 7 to 10 wt %, this peak increased in intensity (see Fig. 1); this suggested that increases in the amount of the clay aggregation occurred with increased clay concentration.

Morphology

More direct evidence for the formation of a true nanoscaled composite was provided by the TEM analysis of ultramicrotomed sections. The micrographs are presented in Figure 2. The dark lines are the intersections of 1-nm-thick clay sheets, and the spaces between the dark lines are the interlayer spaces. For low clay concentrations (≤ 5 wt %), the clay layers in Figure 2(a,b) were exfoliated and dispersed randomly into the PVA matrix. The clay sheets were estimated to be approximately 1 nm thick and approximately 50–100 nm long. This TEM photograph demonstrates that most of the clay layers were exfoliated and dispersed homogeneously into the PVA matrix. The clay layers were also shown to be well dispersed in the PVA hybrids by the XRD profiles, as discussed previously. For high clay concentrations (≥ 7 wt %), however, some of the clays were well dispersed in the PVA matrix, and some of them were agglomerated at size levels of approximately 10–20 nm [see Fig. 2(c)]. From these results, we can conclude that agglomerated structures form and become denser in the PVA matrix above a critical clay concentration of 7 wt %.^{19–21} The presence of peaks in the XRD patterns of these samples should be attributed to these agglomerated layers (see Fig. 1).

Thermal properties

Table I presents the thermal properties of pure PVA and its hybrid films obtained with the solution intercalation method with various clay concentrations. The endothermic peak of pure PVA appears at 197°C, which corresponds to the melting-transition temperature (T_m). The maximum transition peaks of the PVA hybrids with various clay concentrations were found

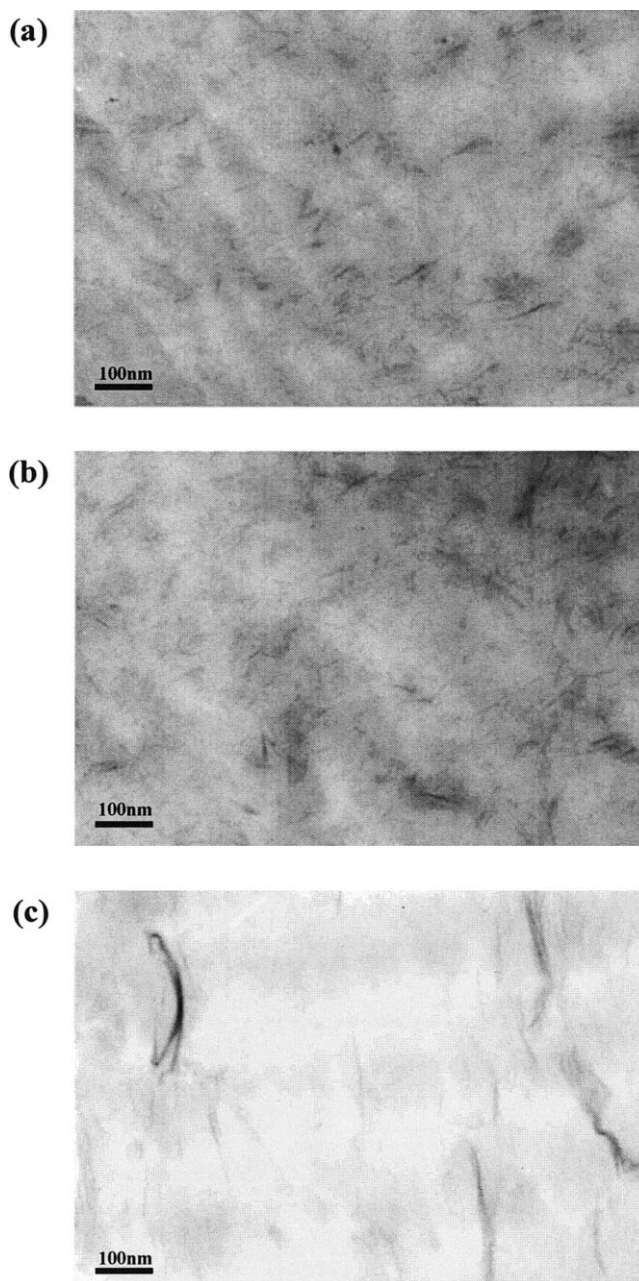


Figure 2 TEM micrographs of PVA hybrids containing (a) 3, (b) 5, and (c) 7 wt % clay.

in the DSC thermograms to be virtually unchanged from this value for organoclay loadings in the range of 3–10 wt %. This implies that varying the clay concentration did not result in a good insulation effect of the clays in the PVA matrix, as is evident in Table I.

In contrast to the results for T_m , the PVA hybrids exhibited improved thermal degradation properties. The TGA results for pure PVA and PVA hybrids with 0–10 wt % SPT are shown in Table I. Table I shows that the initial thermal degradation temperature (T_D^i) of the PVA hybrid films increased with the amount of organoclay. T_D^i (2% weight loss) was in the range of

TABLE I
Thermal Behavior of PVA and PVA Hybrid Films

Clay (wt %)	T_m (°C)	T_D^i (°C) ^a	wt_R^{600} (%) ^b
0 (pure PVA)	197	300	1
3	198	306	8
5	197	308	10
7	196	313	13
10	197	316	22

^a For 2% weight loss.

^b Weight percentage of the residue at 600°C.

300–316°C for clay concentrations in the range of 0–10 wt %, with the largest difference between pure PVA and the hybrids occurring for the 10 wt % PVA hybrid (i.e., 16°C higher than that of pure PVA). This enhancement in the thermal stability was due to the presence of the clay nanolayers, which acted as barriers that maximized the heat insulation and minimized the permeability of volatile degradation products in the material.^{22–25} This enhancement was also due to the decreased permeability of oxygen, which resulted from the dispersion of clay in the polymer/clay composites.

It is notable that even small amounts of clay were effective in improving the weight residues of the hybrids. The char yield at 600°C of the hybrids with various clay loadings was 7–21 wt % higher than that of pure PVA. This enhancement of the char formation was ascribed to the high heat resistance exerted by the clay. On the basis of the aforementioned results, we conclude that the thermal stability of the hybrids was improved by the presence of the dispersed clay nanolayers over that of pure PVA. The thermal stability of the PVA hybrids with different clay loadings is plotted in Figure 3.

Oxygen permeability

The introduction of an inorganic material had a clear effect on the gas permeability. In general, the gas

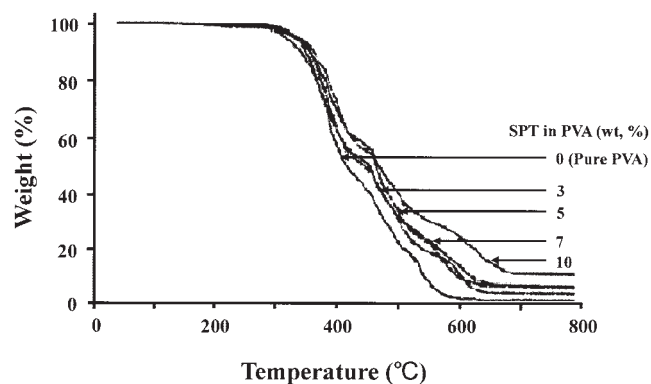


Figure 3 TGA thermograms of PVA hybrids with different clay concentrations.

TABLE II
O₂ Permeability of PVA Hybrid Films Cast onto Two Substrate Films^a

Clay (wt %)	O ₂ permeability (cc m ⁻² day ⁻¹)	
	BOPP	PET
0 (pure PVA)	4.35	5.55
1	3.65	—
3	3.12	4.13
5	1.91	2.63
7	1.65	2.23
10	1.30	1.67

^a The PVA hybrid films coated onto the BOPP and PET films were 1.2 and 2.0 μm thick, respectively. The BOPP and PET films were 20 and 12 μm thick, respectively.

permeabilities of the hybrid films were lower than those of the pure polymer films, and this was independent of the specific gas. This behavior could be attributed to the presence of the high aspect ratio and rigid platelet clay in the polymer matrix.^{26–29}

The permeability of O₂ through the PVA hybrid films is presented as a function of the clay concentration in Table II. PVA hybrid solutions with various clay concentrations were cast onto thin BOPP and PET films. It is well known that the O₂ permeabilities of pure BOPP and PET films are about 2000–2500 and 100–150 cc/m²/day, respectively. The PVA films coated onto the BOPP and PET films were 1.2 and 2.0 μm thick, respectively. With increases in the clay loading from 0 to 10 wt %, the O₂ permeabilities of the PVA hybrid films decreased linearly from 4.35 to 1.30 cc/m²/day for BOPP and from 5.55 to 1.67 cc/m²/day for PET. The permeabilities of the hybrids containing 5 wt % or more clay were less than half the corresponding values of the pure films. When the clay was loaded to 10 wt %, the O₂ permeability of the hybrid was less than one-third of that of the ordinary film in both cases.

This result was due to increases in the lengths of the tortuous paths followed by the gas molecules and to the interaction between the oxygen and clay molecules.^{15,27} Furthermore, films containing higher amounts of clay seemed to be much more rigid, and this contributed to a decrease in their gas permeability.

Models for the gas permeability of polymer composites must consider the shape and spatial orientation of the dispersed phase. The permeability of composites consisting of filler particles dispersed in a polymer matrix can be predicted by the Maxwell model.³⁰ The platelet morphology of the clays significantly reduced the gas permeability in comparison with the spherical droplet morphology in nanocomposites.³¹ Clay is a mineral consisting of stacked silicate sheets measuring 1 nm thick and about 100–2000

TABLE III
O₂ Permeability of PVA and PVA Hybrid Films
Cast onto BOPP Films^a

Thickness (μm) ^b	O ₂ permeability ($\text{cc m}^{-2} \text{ day}^{-1}$)	
	Pure PVA	PVA hybrid ^c
1.2	4.35	1.91
2.0	2.95	1.47
2.4	2.20	1.10
3.0	1.25	0.55

^a BOPP was 20 μm thick.

^b Thickness of the PVA film cast onto the BOPP film.

^c PVA hybrid film containing 5 wt % clay.

nm long. It possesses a high aspect ratio and a platy morphology.^{32,33}

Table III shows the O₂ permeability results as a function of the thickness of the coating layer for both pure PVA and the PVA hybrid containing 5 wt % clay cast onto the BOPP film. With the increase in the thickness of the PVA coating layer from 1.2 to 3.0 μm , its O₂ permeability changed from 4.35 to 1.25 $\text{cc/m}^2/\text{day}$. The PVA hybrid film containing 5 wt % SPT exhibited similar behavior. For example, when the thickness of the coating layer was increased to 3.0 μm , its O₂ permeability was 0.55 $\text{cc/m}^2/\text{day}$, less than half that of pure PVA (1.25 $\text{cc/m}^2/\text{day}$). It is evident in Tables II and III that the mass-transfer process for the respective penetrants is highly dependent on the clay loading as well as the thickness of the coating layer.

PVA is a very sensitive and reactive polymer under highly humid conditions. Increases in the humidity result in an increase in water sorption due to an increased hydrophilic volume and thus in an increase in O₂ transport because the path of the diffusing molecules is less tortuous. The O₂ permeabilities of the pure PVA and PVA hybrid films are shown as functions of time (min) in Figure 4. The relative humidity

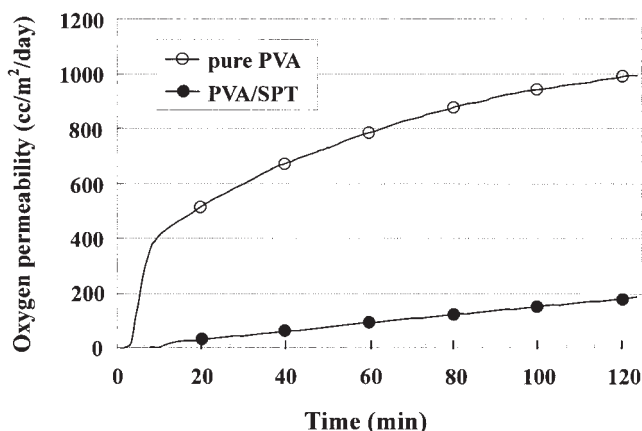


Figure 4 Effect of time on the O₂ permeability under 80% relative humidity of PVA hybrid films cast onto BOPP films.

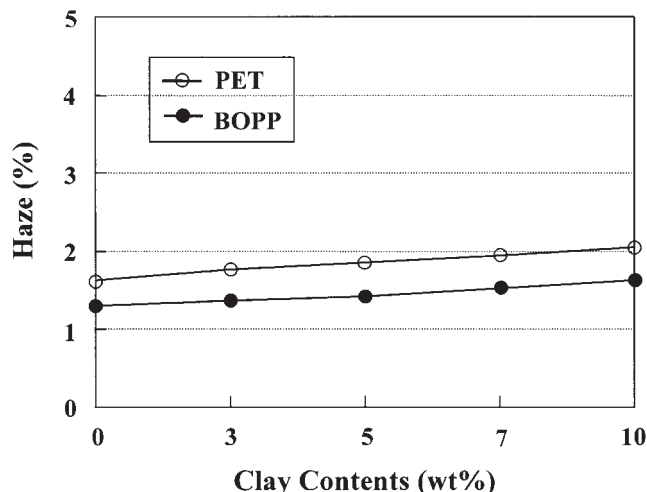


Figure 5 Effect of the clay concentration on the haze of PVA hybrid films cast onto substrate films.

in the feed compartment was maintained at 80%. For periods up to 120 min, the O₂ permeabilities of the PVA and PVA hybrid films increased linearly. The O₂ transmittance of the PVA hybrid film was much lower than that of pure PVA throughout this period. From these results, we can conclude that the introduction of inorganic components into organic polymers improves their barrier properties because the clay layers have high aspect ratios and provide gas-transport barriers to the volatile gases under high humidity.

Optical properties

Figure 5 shows the variation of the haze of the films with the clay concentration. The haze increased slightly with increasing clay concentration up to 10 wt % for PVA hybrid films coated onto the PET and BOPP substrates. In contrast to these results, the glosses of the two samples decreased with increases in the clay loading from 0 to 10 wt %, as shown in Figure 6.

The haze and gloss of the two systems were only slightly changed when the clay loading was increased from 3 to 10 wt %. The haze and gloss of the PVA hybrid films were not significantly different from those of pure PVA (0 wt % clay).

CONCLUSIONS

PVA nanocomposites with various clay concentrations were synthesized. PVA hybrid films with a higher clay concentration exhibited improved thermal stability and O₂-barrier properties, whereas the clay concentration had no effect on T_m . TEM showed that for a low clay concentration (≤ 5 wt %), most of the clay layers were exfoliated and dispersed homogeneously in PVA. In this work, the addition of small amounts of

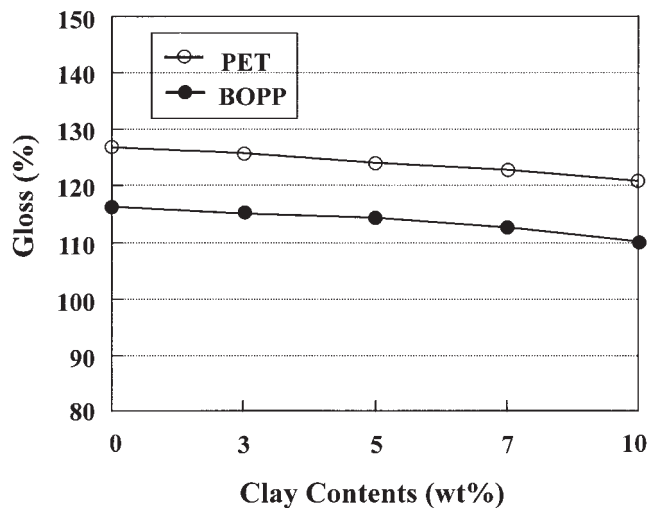


Figure 6 Effect of the clay concentration on the gloss of PVA hybrid films cast onto substrate films.

clay was found to be sufficient to improve the properties of PVA.

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