

Effect of Clay Concentration on the Oxygen Permeability and Optical Properties of a Modified Poly(vinyl alcohol)

Jaime C. Grunlan, Ani Grigorian, Charles B. Hamilton, Ali R. Mehrabi

Avery Dennison Corporation, Avery Research Center 2900 Bradley Street, Pasadena, CA 91107

Received 30 October 2003; accepted 28 December 2003

DOI 10.1002/app.20564

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The effect of clay concentration on the oxygen permeability and optical properties of a modified poly(vinyl alcohol) (PVOH) was studied. Sodium montmorillonite (MMT- Na^+), at a concentration of 10 wt %, was found to decrease the oxygen permeability of the PVOH below 0.001 $\text{cc} \cdot \text{mil}/\text{m}^2/\text{day}$ at 55% relative humidity. This low permeability is attributed to the strong interaction between PVOH and clay, as evidenced by an increase of more than 10°C in the glass transition temperature at this concentration. Transmission electron microscopy images show the high level of clay exfoliation that results from the strong affinity to PVOH. Haze and clarity were optical properties that changed significantly with increasing clay concentration.

These values were 0.4 and 100%, respectively, in the absence of clay, but became 80 and 23% with 10 wt % MMT- Na^+ . Transmission did not change as considerably, reaching a low of 73% with a clay concentration of 10 wt %. The ability to reduce the oxygen permeability of PVOH-based systems at elevated humidity may prove advantageous for applications in food and flexible electronics packaging, where moisture sensitivity currently prevents them from being used. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1102–1109, 2004

Key words: water-soluble polymers; gas permeation; clay; composites; TEM

INTRODUCTION

Polymeric films containing some amount of alcohol functionality, of which poly(vinyl alcohol) (PVOH) and poly(ethylene-co-vinyl alcohol) (EVOH) are most common, are known to be excellent barriers to oxygen under low humidity [$< 35\%$ relative humidity (RH)] conditions.^{1–4} This low permeability to oxygen, from less than 0.001 to nearly 7 $\text{cc} \cdot \text{mil}/\text{m}^2/\text{day}$ depending on composition (higher values typically correspond to less vinyl alcohol content), is attributed to the large inter- and intramolecular cohesive energy that results from the highly polar alcohol ($-\text{OH}$) functionality.⁵ As the relative humidity is increased beyond 35%, these films show a dramatic increase in oxygen permeability (P_{O_2}).^{1,3,4} It is this same polar nature of the alcohol groups that makes these polymers very hydrophilic and susceptible to plasticization in an elevated humidity environment. As moisture is absorbed at high polarity sites, polymer cohesion is weakened, which results in increased oxygen permeability.^{2,6} Other, less polar, polymers are often used as oxygen barriers (e.g., polyacrylonitrile⁷ or polyvinylidene chloride⁸) due to their lower susceptibility to moisture, but these materials also tend to exhibit higher intrinsic oxygen per-

meability at low humidity ($> 1 \text{ cc} \cdot \text{mil}/\text{m}^2 \cdot \text{day}$).⁹ Despite the issue of moisture susceptibility, alcohol-based films are widely used for food packaging applications.^{5,10,11} Organic electronics, whose biggest challenge is flexible high barrier packaging,¹² could also benefit from these polymers if the issue of moisture sensitivity was overcome.

There are a variety of techniques used to reduce the P_{O_2} and/or water susceptibility of packaging polymers. Sandwiching the water-sensitive polymer between relatively hydrophobic layers is one of the most common methods used to maintain oxygen barrier at high humidity.^{4,13–15} This type of construction, usually formed via coextrusion, is often used in retortable food packaging. The outer layers of the sandwich are comprised of polypropylene, polyethylene, or some other hydrophobic polymer. For example, EVOH sandwiched between symmetrical layers of polyethylene did not exceed its 0% RH oxygen permeability value ($\sim 0.009 \text{ cc} \cdot \text{mil}/\text{m}^2 \cdot \text{day}$) until the relative humidity exceeded 80%.¹⁶ Without hydrophobic polymer protection, the EVOH film would be expected to exhibit a permeability beyond its 0% RH value at 60% RH, when tested at room temperature.² This level of improvement is modest, but sufficient for many food packaging applications. More recently, melt blends of EVOH with polypropylene^{17,18} or PET¹⁹ have been used to create laminar dispersions with relatively low oxygen permeability. These blended structures have been able to reduce the P_{O_2} of polypropylene by an order of magnitude (i.e., from 3,634 down to 366 $\text{cc} \cdot$

Correspondence to: J. C. Grunlan (jaime.grunlan@averydennison.com).

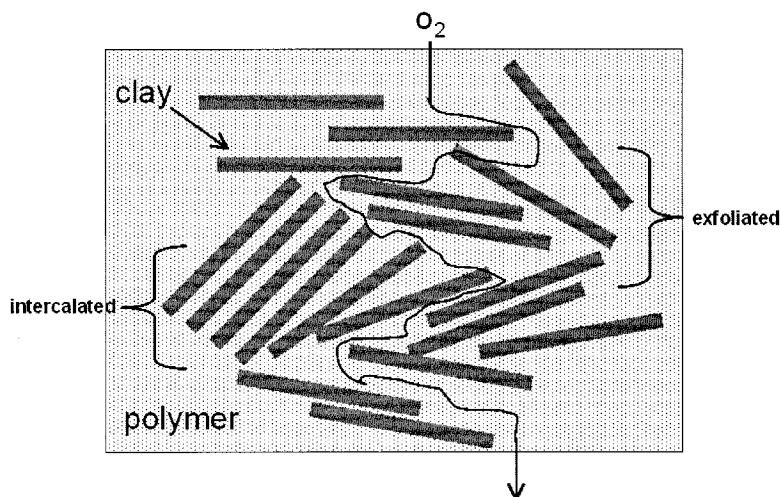


Figure 1 Schematic representation of tortuous path that oxygen gas must take to diffuse through clay-filled polymer. Differences between intercalation and exfoliation are highlighted.

mil/m² · day),¹⁷ although this level of permeability is orders of magnitude greater than EVOH alone.

Increasing polymer crystallinity is another way to improve oxygen barrier. In general, increasing crystallinity results in reduced gas solubility and a more tortuous path for the diffusing species.²⁰ The oxygen permeability of PET can be reduced from 250 to 62 cc · mil/m² · day by increasing its crystalline volume fraction (ϕ_c) from 0.01 to 0.39.²¹ Permeability values for EVOH are much lower than for PET, typically 0.095–1.8 cc · mil/m² · day,²² due to a combination of strong hydrogen bonding and a high level of crystallinity. Pure PVOH has even lower oxygen permeability than standard EVOH compositions at 0% RH,⁴ but this value rises to 25.5 cc · mil/m² · day at 50% RH.²³ Crystallinity alone is not sufficient to prevent significant degradation of the oxygen barrier of water-soluble polymers at high humidity.

Adding oxygen-impermeable filler to polymers has a similar effect to increasing crystallinity. Layered silicates (e.g., clay) have been especially effective for improving polymer gas barrier and a variety of other properties (e.g., modulus, tensile strength, thermal stability, etc.).^{24,25} Clay minerals have been used in a variety of polymers to reduce oxygen permeability,^{26–28} along with talc^{29,30} and mica.^{30,31} These platelet-type fillers have very large surface areas and high aspect ratios that allow them to significantly alter the behavior of the polymer matrix at very low concentration. For example, 2 wt % organomontmorillonite (MMT) was able to reduce the P_{O_2} of poly(amic acid) more than an order of magnitude (from 182.3 to 9.22 cc · mil/m² · day).²⁸ When adequately intercalated and/or exfoliated, these impermeable platelets serve to create a microscopic obstacle course, also known as a “tortuous path” (shown schematically in Fig. 1),³² that dramatically increases the time necessary for the

oxygen to diffuse through the polymer. Although there have been some studies involving platelet-type fillers and water-soluble polymers,^{33–35} the oxygen permeability of these systems has not been evaluated.

In the present study, the effect of clay concentration on the oxygen permeability and optical properties of a PVOH, modified with itaconic acid, is examined. This polymer (see Fig. 2) was chosen due to its low P_{O_2} relative to more common PVOH compositions (see Table I). The addition of sodium montmorillonite (MMT- Na^+) was found to dramatically reduce the oxygen permeability of this PVOH, referred to as the “terpolymer” due to its three different repeat units, at 35 and 55% RH. This improvement in oxygen barrier is accompanied by reasonable transparency, although films with significant levels of clay (>5 wt %) are very hazy.

EXPERIMENTAL

Materials

Three PVOH powders, containing some amount of vinyl acetate and/or itaconic acid, were purchased

TABLE I
Oxygen Permeability of Varying Forms of Poly(vinyl alcohol)

PVOH (wt %)	Thickness (μm)	O_2 Permeability (cc · mil/m ² ·day) ^a			
		0% RH	35% RH	55% RH	90% RH
87–89	6	0.130		0.721	6.024
99	6	0.020		0.040	5.906
97 ^b	6	<0.001 ^c	0.006	0.021	5.693

^a Permeability is the product of film thickness and oxygen transmission rate (OTR) measured at 23°C.

^b The terpolymer contains 97 wt % vinyl alcohol, 2 wt % vinyl acetate, and 1 wt % itaconic acid.

^c The MOCON instrument has an OTR sensitivity limit of 0.005 cc/m² · day.

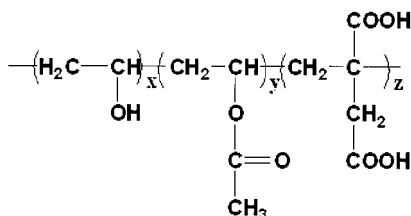


Figure 2 Chemical structure of poly(vinyl alcohol-co-vinyl acetate-co-itaconic acid), shown in order from left to right. The values for x , y , and z are 97, 2, and 1, respectively.

from Aldrich (Milwaukee, WI). Two of these powders are traditional copolymers with vinyl acetate having degrees of hydrolysis of 87–89% and 99%, respectively. Both of these polymers had a M_w of 85,000–146,000 g/mol. The third polymer, referred to as the terpolymer or modified PVOH, contained itaconic acid along with vinyl alcohol and vinyl acetate. The M_w of this terpolymer is 4,300–4,400 g/mol and its chemical structure is shown in Figure 2. Cloisite Na⁺, a natural MMT clay, was purchased from Southern Clay Products (Gonzales, TX). MMT has a monoclinic structure with the formula Na_{0.33}(Al,Mg)₂Si₄O₁₀(OH)₂ · n H₂O and a density of 2.86 g/cm³ (Fig. 3). Most of the MMT platelets are 2–13 μm in length and 1 nm in thickness, although several sheets are often bunched together to give a thickness of several nanometers.

Composite film preparation

Aqueous polymer solutions containing 10 wt % of a given PVOH were prepared by adding 10 g of polymer powder to 90 g of deionized water. This mixture was then simultaneously stirred and heated at 60°C until the polymer was completely dissolved. Clay was slowly added to this aqueous mixture as the polymer was dissolving. Higher clay concentrations required longer time periods to achieve exfoliation. Typical mixtures were stirred 4–8 h with heat and then left to stir overnight at room temperature. In some cases a mixture had to be placed on a roller for an additional 24 h to completely disperse aggregated clay. Once adequately mixed, the liquid precomposites were coated onto 2-mil (50.8 μm) PET substrates using the 4-mil opening of a Byrd bar, purchased from Paul N. Gardner (Pompano Beach, FL). The wet coatings were dried at 70°C for 30 min to achieve a final dry thickness of 6 μm.

Instrumental analysis

Dry composite microstructures were imaged using a JEOL CXII TEM. Glass transition temperatures (T_g) were obtained for each composite using a Shimadzu DSC-50 (Kyoto, Japan). The temperature was in-

creased at a rate of 10°C/min for this analysis, starting at 25°C. Haze and clarity of the composite films were evaluated using a BYK-Gardner haze-gard plus instrument (Columbia, MD). The haze measurement provides the amount of wide-angle scattering, which is the percentage of light that deviates from the incident beam by more than 2.5° as specified by ASTM D1003. Clarity provides a measure of small-angle (< 2.5°) scattering and conforms to ASTM D1746. Films that have a large haze value (> 10%) tend to have a milky appearance, while low clarity values tend to make objects appear distorted or unclear. Visible light transmission for each terpolymer-based film was evaluated using a μQuant UV-Vis instrument made by Bio-Tek (Winooski, VT). The oxygen transmission rate (OTR), used to obtain permeability when normalized by thickness, of PVOH-based films were measured using a MOCON OX-TRAN 2/20 instrument (Minneapolis, MN) that conforms to ASTM F1927.

RESULTS AND DISCUSSION

Composite microstructure

The quality of oxygen barrier for a clay-filled composite is largely determined by the extent to which the clay platelets are dispersed in the polymer matrix. For a given concentration of platelet-type filler, the relative permeability ($P_{\text{composite}}/P_{\text{polymer}}$) decreases as the ratio of platelet length to thickness increases.^{26,27,29,37} This behavior is the result of an increasingly tortuous path for oxygen as the clay sheets become more completely delaminated (i.e., exfoliated), as shown in Figure 1. Figure 4 shows TEM images of the terpolymer (see structure in Fig. 2) filled with 1 and 10 wt % MMT-Na⁺. At low magnification [Figs. 4(a) and (c)], it

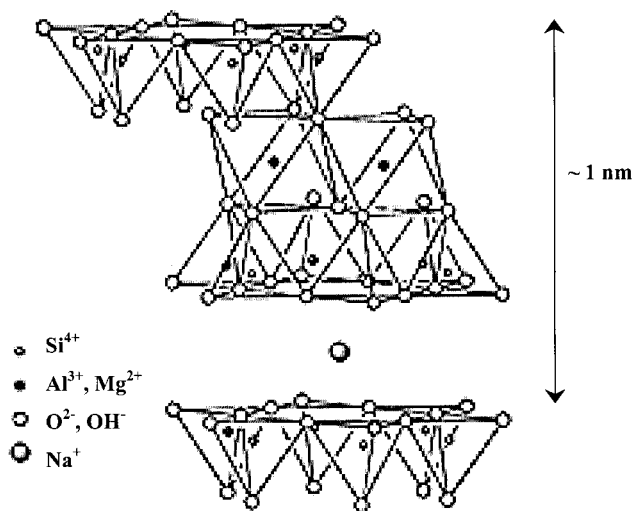


Figure 3 Monoclinic crystal structure of MMT-Na⁺ clay (modified from www.apchem.nagoya-u.ac.jp/ketuzai/english/study-e.html)

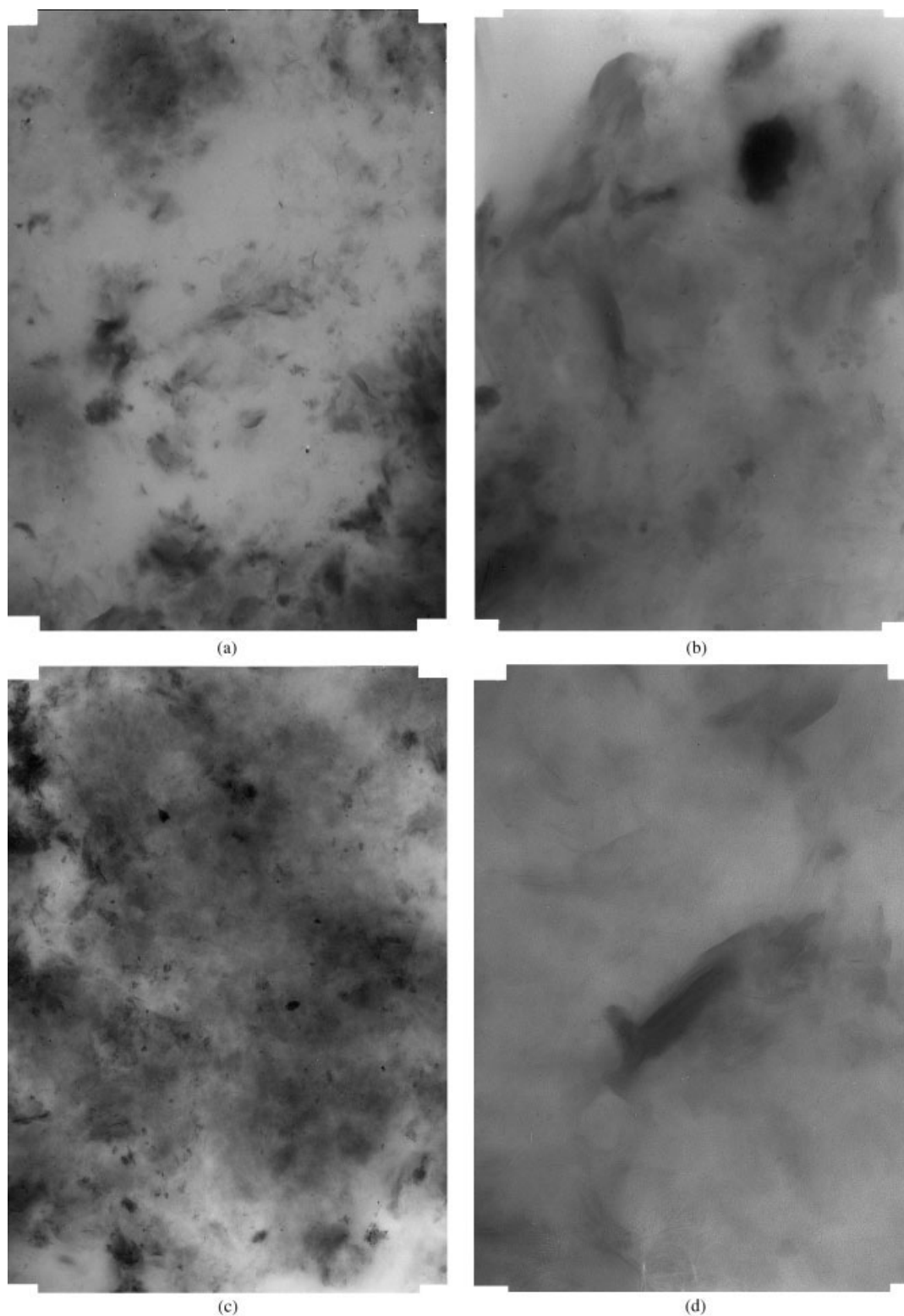


Figure 4 TEM micrographs of the terpolymer filled with 1 wt % (a and b) and 10 wt % (c and d) MMT-Na⁺. (a) 0.4 in = 1.26 μm; (b) 0.4 in = 505 nm; (c) 0.4 in = 1.26 μm; (d) 0.4 in = 150 nm.

is apparent that the clay exists in varying states of dispersion for both concentrations. The darkest aggregates seen in these micrographs consist of platelets whose galleries, between individual sheets, are only

slightly swollen with polymer. One of these aggregates is shown at high magnification in Figure 4(d), where the closely packed parallel sheets can be discerned. This condition is referred to as intercalation,

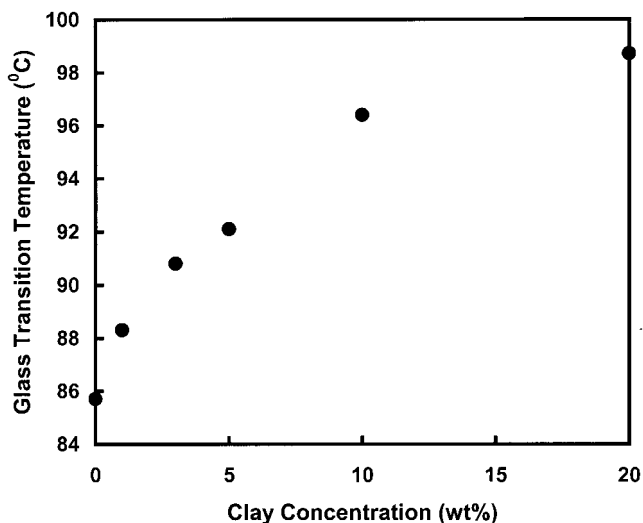


Figure 5 Effect of clay concentration on the glass transition temperature of the terpolymer.

whereas exfoliation refers to clay platelets that are completely separated from one another with no apparent stacking arrangement (difference shown schematically in Fig. 1).³⁸ Complete exfoliation of clay in a polymer is very rare and the level of dispersion shown here is very comparable to other well-mixed, clay-filled systems.^{26–28} The higher magnification images [Figs. 4(b) and (d)] show a number of highly exfoliated sheets, seen as very thin lines pointing in all directions. This level of dispersion suggests strong interaction between the terpolymer and clay.

Another evidence of the strong interaction between polymer and clay is the increase in glass transition temperature observed with increasing clay concentration, shown in Figure 5. The terpolymer has a T_g of 85.7°C in the absence of clay, which is in close agreement with that reported for unmodified PVOH.²³ The terpolymer T_g rises to 88.3°C with the addition of only 1 wt % MMT- Na^+ . This increase in T_g is due to the adsorption energy created between polymer and filler that must be overcome prior to polymer softening. The magnitude of the glass transition temperature increase has been attributed to the level of polymer–filler interaction and normalized surface area of the filler.³⁹ MMT platelets have a very large surface area covered with electronegative oxygen and hydroxide species (see Fig. 3) that immobilize PVOH, which has a strong tendency to hydrogen bond to itself and to other species containing highly electronegative substituents.⁴⁰ Additional clay produces a further increase in the glass transition temperature, but the magnitude of this effect diminishes with increasing clay concentration. In general, a higher degree of aggregation accompanies an increased clay concentration,²⁶ which results in a reduced effective surface area per unit concentration and less polymer–clay interaction.

Oxygen permeability

A PVOH containing 1 wt % itaconic acid (i.e., the terpolymer) was chosen as the composite matrix in this study due to its low intrinsic oxygen permeability relative to unmodified forms of PVOH (see Table 1). The terpolymer permeability is shown, relative to the two most common forms of PVOH with 87–89% and 99% hydrolysis, in Figure 6. At 0% RH, the terpolymer has a permeability below the detection limit of the measurement instrument, which suggests it is more than an order of magnitude lower than 99% hydrolyzed PVOH. This superior barrier behavior is likely due to a combination of low molecular weight, which typically enhances crystallinity, and stronger hydrogen bonding supplied by carboxylic acid groups on each itaconic acid unit. Poly(acrylic acid) has a higher density ($\rho = 1.41 \text{ g/cm}^3$)⁴¹ and surface energy ($\gamma = 67 \text{ mJ/m}^2$)⁴² than PVOH ($\rho = 1.33 \text{ g/cm}^3$ and $\gamma = 62.4 \text{ mJ/m}^2$),^{23,43} suggesting that –COOH functionality exhibits stronger H-bonding than –OH. At 55% RH, the permeability difference between the terpolymer and fully hydrolyzed PVOH is much smaller. The same factors that give the terpolymer such a low permeability at 0% RH (low molecular weight and stronger H-bonding) also increase its water susceptibility at elevated humidity. PVOH with 87–89% hydrolysis has an oxygen permeability that is nearly an order of magnitude greater than its fully hydrolyzed counterpart at both levels of humidity. It is the increased vinyl acetate content accompanying lower levels of hydrolysis that creates reduced hydrogen bonding, without

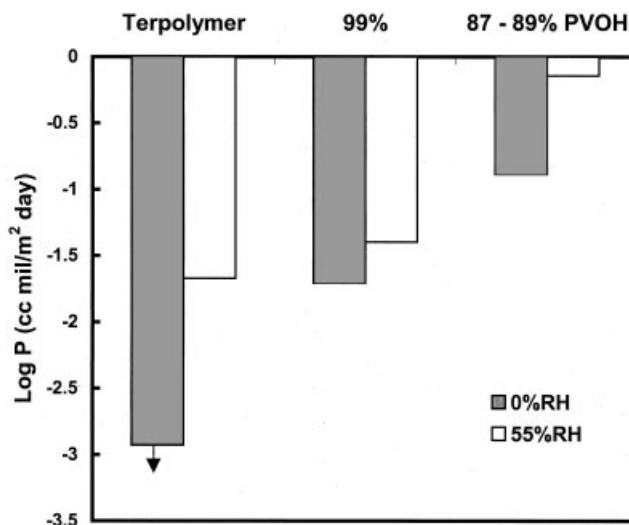


Figure 6 Comparison of oxygen permeability (P_{O_2}) for the terpolymer and two forms of PVOH, one with 99% and the other with 87–89% hydrolysis. Measurements were performed on 6- μm films on 2-mil PET at 23°C. At 0% RH, the terpolymer permeability cannot be detected, but is shown as the lowest detectable value ($0.001 \text{ cc} \cdot \text{mil}/\text{m}^2 \cdot \text{day}$) and denoted with a downward arrow (\downarrow).

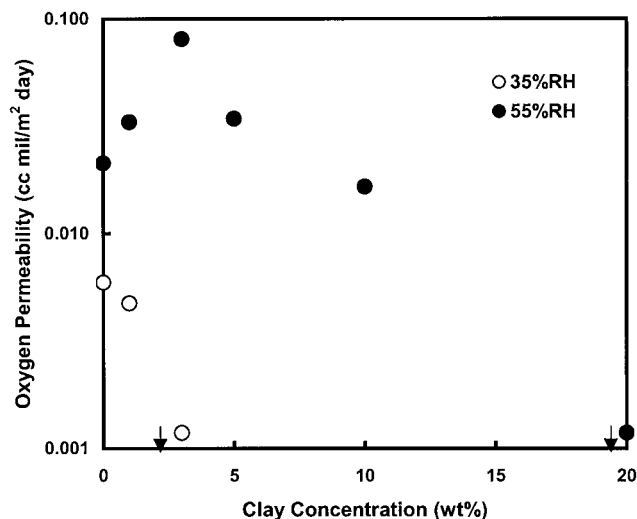


Figure 7 Oxygen permeability as a function of clay concentration for the terpolymer (see Fig. 2) at 35 (○) and 55% RH (●). Two data points are marked with downward arrows (↓) to indicate undetectable OTR, which suggests that $P_{O_2} < 0.001 \text{ cc} \cdot \text{mil} / \text{m}^2 \cdot \text{day}$.

significantly decreasing water susceptibility due to lack of interaction between polymer chains.¹ The addition of clay, which is impermeable to oxygen and relatively water insensitive, is one method that appears to improve barrier behavior at elevated humidity.

Figure 7 shows oxygen permeability as a function of clay concentration for the terpolymer. At 55% RH, the P_{O_2} initially increases with clay concentration, reaching a peak at 3 wt %. It is not until 10 wt % that the oxygen permeability is less than that of the terpolymer alone. The addition of clay to the terpolymer disrupts crystallinity and occupies hydroxyl groups that would normally be involved in hydrogen bonding with oxygen. When the concentration of clay is very low, the benefit of the tortuous path (see Fig. 1) cannot out-

weigh these adverse factors. At concentrations beyond 10 wt %, the tortuous path is very extensive and becomes the dominant factor controlling permeability. This can be seen visually when comparing Figures 4(a) and (c) with 1 and 10 wt % clay, respectively. In Fig. 4(a) there are relatively large areas containing no clay, but the distribution of platelets is much more dense and homogeneous in Figure 4(c). There is no possible way to draw a straight line through Figure 4(c) without intersecting numerous clay particles. At 35% RH the benefit of clay is realized at only 1 wt % and oxygen permeability can no longer be detected at 3 wt %, as shown in Table II.

Optical behavior

Table II summarizes the optical behavior of the clay-filled terpolymer films. The modified PVOH is completely transparent in the absence of clay (it actually has a transmission greater than 100% due to the planarizing effect it has on its PET substrate). As the concentration of clay is increased to 10 wt %, the transmission [shown graphically in Fig. 8(a)] decreases nearly linearly to less than 75%. This level of degradation in transparency is comparable to that observed in other MMT-filled polymers^{26,33} and is attributed to incomplete exfoliation of platelets and their random orientation. Clarity exhibits a much more negative linear trend with clay concentration [Fig. 8(b)], changing from nearly 100% without clay to 23% at 10 wt %. Greater clay concentration results in a rougher surface and more internal sites for light scattering. These factors have a dramatic effect on the narrow-angle scattering that clarity evaluates and results in a significant loss of resolution (i.e., sharpness of detail) despite maintaining relatively high transparency. Haze, which is a measure of wide-angle scattering, shows a sharply positive change as clay is increased [Fig. 8(c)]. When haze becomes greater than 10%,

TABLE II
Oxygen Permeability and Optical Properties of the Clay-Filled Terpolymer

Clay (wt %)	Thickness (μm)	O_2 Permeability ($\text{cc} \cdot \text{mil} / \text{m}^2 \cdot \text{day}$) ^a		Haze (%)	Clarity (%)	% T ^b
		35% RH	55% RH			
0	6	0.006	0.021	0.44	99.7	101.2
1	6	0.005	0.033	14.9	86.7	97.2
3	6	<0.001 ^d	0.080	45.9	62.1	93.9
5	6		0.034	53.0	54.7	82.9
10	6		0.017	79.6	23.1	72.7
20	6		<0.001 ^d	70.4	26.5	73.6

^a Permeability is the product of film thickness and oxygen transmission rate (OTR) measured at 23°C.

^b % Transmission was measured at 550 nm, but the values are within 2% of those at 400 and 700 nm.

^c % Transmission is slightly greater than 100 due to planarizing effect of terpolymer on 2-mil PET.

^d The MOCON instrument has an OTR sensitivity limit of $0.005 \text{ cc} / \text{m}^2 \cdot \text{day}$.

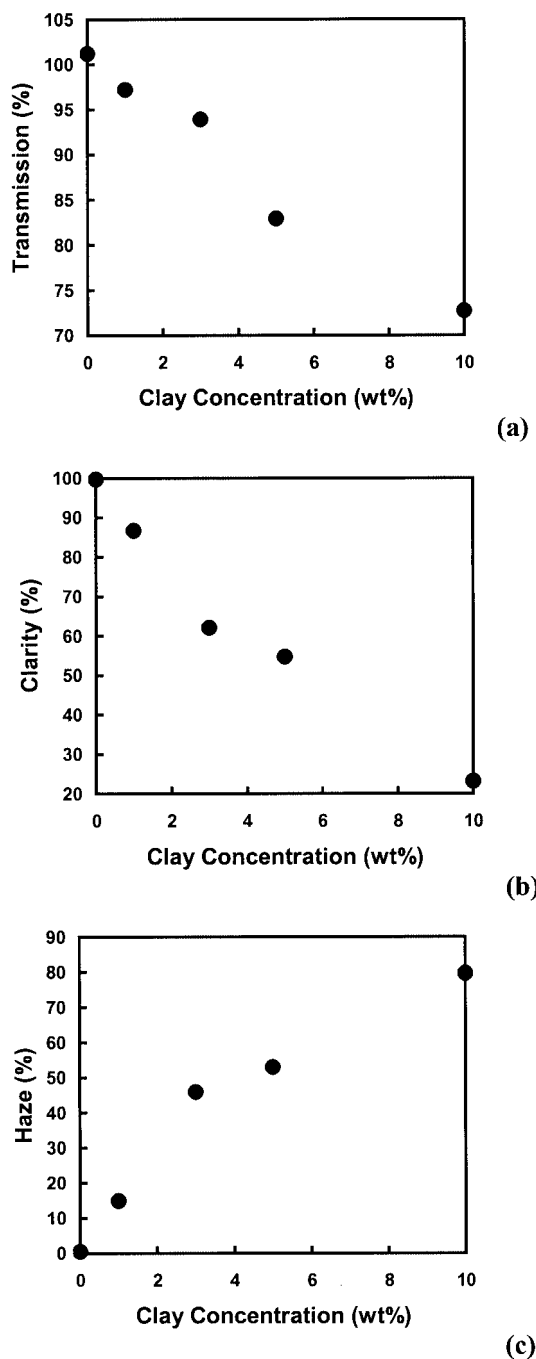


Figure 8 Transmission (a), clarity (b), and haze (c) as a function of clay concentration within the terpolymer (see Fig. 2).

cloudiness can be observed visually. At a level of 80%, achieved with 10 wt % clay, the film is very milky in appearance. Better overall optical behavior could potentially be achieved through more complete exfoliation and alignment of the clay.

CONCLUSION

Adding clay to PVOH is an effective method of reducing oxygen permeability at least up to 55% RH. At 35%

RH, this modified PVOH had an oxygen permeability of $0.006 \text{ cc} \cdot \text{mil}/\text{m}^2 \cdot \text{day}$ in the absence of clay, but permeability was undetectable ($< 0.001 \text{ cc} \cdot \text{mil}/\text{m}^2 \cdot \text{day}$) with the addition of only 3 wt %. When the relative humidity was raised to 55%, 10 wt % clay was required to achieve an undetectable permeability, although this was more than an order of magnitude decrease from the value without clay ($0.021 \text{ cc} \cdot \text{mil}/\text{m}^2 \cdot \text{day}$). An increasing glass transition temperature with clay concentration demonstrated the strong interaction with the PVOH, which allowed the clay to become highly exfoliated. The large surface area of these clay platelets served to occupy many of the PVOH hydroxyl groups that contribute to water sensitivity. At the same time the platelets are impermeable to oxygen and act as barriers that create a much longer diffusion path for oxygen through the composite film. One side effect of increasing clay concentration is the degradation of polymer transparency. In the absence of clay, PVOH has a % transmission around 100 and haze is $< 1\%$, but with 10 wt % clay these values become approximately 73 and 80%, respectively. Other techniques to reduce PVOH water susceptibility without affecting transparency, such as crosslinking, would not be capable of simultaneously reducing oxygen permeability. It is possible that crosslinking clay-filled PVOH may decrease permeability at 90% RH, where clay alone shows no benefit.

The authors thank the Avery Dennison Corporation for financial support of this work. Appreciation is also extended to Alicia Thompson and John Currulli, of the Center for Electron Microscopy (CEMMA) at the University of Southern California, for assistance with TEM sample preparation and imaging. A special thanks is paid to Melissa Grunlan, of the Loker Hydrocarbon Institute at the University of Southern California, for performing DSC measurements.

References

- Marten, F. L. in *Encyclopedia of Polymer Science and Engineering*; Kroschwitz, J. I., Ed., Wiley: New York, 1989; Vol. 17, pp. 167–198.
- Zhang, Z.; Britt, I. J.; Tung, M. A. *J Appl Polym Sci* 2001, 82, 1866.
- Tsai, B. C.; Jenkins, B. J. *J Plast Film Sheet* 1988, 4, 63.
- Iwanami, T.; Hirai, Y. *Tappi J* 1983, 66, 85.
- Kollen, W.; Gray, D. *J Plast Film Sheet* 1991, 7, 103.
- Hopfenberg, H. B.; Apicella, A.; Saleeby, D. E. *J Membrane Sci* 1981, 8, 273.
- Salame, M. *J Polym Sci* 1973, 41, 1.
- DeLassus, P. T. *J Vinyl Technol* 1979, 1, 14.
- Bansleben, D. A.; Huynh-Tran, T.-C.; Blanski, R. L.; Hughes, P. A.; Roberts, W. P.; Grubbs, R. H.; Hatfield, G. R. U.S. Patent 6203923 B1, 2001.
- Lagaron, J. M.; Gimenez, E.; Catala, R.; Gavara, R. *Macromol Chem Phys* 2003, 204, 704.
- Koros, W. J. in *Barrier Polymers and Structures*; Koros, W. J., Ed.; American Chemical Society: Washington, DC, 1990; Chapt. 1.

12. Burrows, P. E.; Graff, G. L.; Gross, M. E.; Martin, P. M.; Shi, M. K.; Hall, M.; Mast, E.; Bonham, C.; Bennett, W.; Sullivan, M. B. *Displays* 2001, 22, 65.
13. Zhang, Z. B.; Britt, I. J.; Tung, M. A. *J Plast Film Sheet* 1998, 14, 287.
14. Alger, M. M.; Stanley, T. J.; Day, J. in *Barrier Polymers and Structures*; Koros, W. J., Ed.; American Chemical Society: Washington, DC, 1990; Chapt. 10.
15. Schaper, E. *Modern Plastics* 1989, 66, 94.
16. Kollen, W.; Gray, D. *J Plast Film Sheet* 1991, 7, 103.
17. Yeo, J. H.; Lee, C. H.; Park, C. S.; Lee, K. J.; Nam, J. D.; Kim, S. W. *Adv Polym Technol* 2001, 20, 191.
18. Lohfink, G. W.; Kamal, M. R. *Polym Eng Sci* 1993, 33, 1404.
19. Lee, S. Y.; Kim, S. C. *Polym Eng Sci* 1997, 37, 463.
20. Vieth, W. R. *Diffusion in and through Polymers*; Oxford University Press: New York, 1991; Chapt. 4.
21. Hu, Y. S.; Liu, R. Y. F.; Rogunova, M.; Schiraldi, D. A.; Nazarenko, S.; Hiltner, A.; Baer, E. *J Polym Sci B Polym Phys* 2002, 40, 2489.
22. Xu, P. in *Polymer Data Handbook*; Oxford University Press: New York, 1999; p. 117.
23. Sundararajan, P. R. in *Polymer Data Handbook*; Oxford University Press: New York, 1999; pp. 890–909.
24. Alexandre, M.; Dubois, P. *Mater Sci Eng* 2000, R28, 1.
25. *Polymer-Clay Nanocomposites*; Pinnavaia, T. J., Beall, G. W., Eds.; J Wiley S: Chichester, 2000.
26. Bharadwaj, R. K.; Mehrabi, A. R.; Hamilton, C.; Trujillo, C.; Murga, M.; Fan, R.; Chavira, A.; Thompson, A. K. *Polymer* 2002, 43, 3699.
27. Krook, M.; Albertsson, A.-C.; Gedde, U. W.; Hedenqvist, M. S. *Polym Eng Sci* 2002, 42, 1238.
28. Chang, J.-H.; Park, K. M.; Cho, D.; Yang, H. S.; Ihn, K. J. *Polym Eng Sci* 2001, 41, 1514.
29. Sekelik, D. J.; Stepanov, E. V.; Nazarenko, S.; Schiraldi, D.; Hiltner, A.; Baer, E. *J Polym Sci B Polym Phys* 1999, 37, 847.
30. Bissot, T. C. in *Barrier Polymers and Structures*; Koros, W. J., Ed.; American Chemical Society: Washington, DC, 1990; Chapt. 11.
31. Cussler, E. L.; Hughes, S. E.; Ward, W. J.; Aris, R. J. *Membrane Sci* 1988, 38, 161.
32. Neilson, L. E. *J Macromol Sci Chem* 1967, A1, 929.
33. Koo, C. M.; Ham, H. T.; Choi, M. H.; Kim, S. O.; Chung, I. J. *Polymer* 2003, 44, 681.
34. Chang, S. H.; Gupta, R. K.; Ryan, M. E. *J Rheol* 1992, 36, 273.
35. Chang, S.-H.; Ryan, M. E.; Gupta, R. K.; Swiatkiewicz, B. *Coll Surf* 1991, 59, 59.
36. Host-Guest Hybridization of Photofunctional Organics with Layered Host Materials (www.apchem.nagoya-u.ac.jp/ketuzai/english/study-e.html).
37. Bharadwaj, R. K. *Macromolecules* 2001, 34, 9189.
38. Carrado, K. A.; Xu, L.; Seifert, S.; Csencsits, R.; Bloomquist, C. A. A. in *Polymer-Clay Nanocomposites*; Pinnavaia, T. J., Beall, G. W., Eds.; J Wiley: Chichester, 2000; Chapt. 3.
39. Tsagaropoulos, G.; Eisenberg, A. *Macromolecules* 1995, 28, 6067.
40. Bassner, S. L.; Klingenberg, E. H.; *Am Ceram Soc Bull* 1998, 77, 71.
41. Davidson, R. L.; Sittig, M. *Water-Soluble Resins*; Reinhold: New York, 1968; 2nd ed.,
42. Zosel, A. *Colloid Polym Sci* 1993, 271, 680.
43. Toyoshima, K. in *Polyvinyl Alcohol: Properties and Applications*; Finch, C. A., Ed.; Wiley: New York, 1973; Chapt. 2.