Water Vapor and CO₂ Permeabilities of Acrylic Latex Coatings

Jun-Woo Kim, Sang-Min Lee, Jong-Kyu Hong, Jong-Choo Lim, Byung-Sik Kim, Sangkwon Park†
Seung Min Hong*, Hyun Ki Lee*, and Jong Myung Park*

Department of Chemical Engineering, Dongguk University, Seoul 100-715, Korea
*Central Research Institute, Kumgang Korea Chemical Co. (KCC), Ltd., Kyunggi-do 449-910, Korea

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Abstract: Water vapor permeability (WVP) and CO₂ permeability (CDP) are important properties of modern architectural coatings for the protection of building materials such as concrete. A cup method and a high vacuum method were employed to measure the WVP and the CDP, respectively, for three sets of acrylic latex films which were prepared by either single-stage or two-stage emulsion polymerization. For a set of model latex films comprising different combinations of main and auxiliary monomers, it was found that the monomer composition significantly affected the WVP and the CDP. The WVP and the CDP results were explained in terms of the stiffness of polymer chain segments, the crystallinity, and the polarity of the latex films. Compared with the model latex films of a simple core structure containing butylacrylate as a main monomer, the control film of core/shell structure of similar composition showed desirable permeability properties of higher WVP and lower CDP. There was a rough trend of trade-off between the WVP and the CDP of the latex films. Among the model latex films, those containing ethylacrylate monomer showed relatively better behaviors for both the WVP and the CDP. For the other two sets of hard and soft latex films, the WVP for both sets significantly increased with increasing content of hydrophilic microgel particles. As the amount of microgel increased, the CDP for soft latex films was reduced, whereas that for hard latex films slightly increased.

Keywords: protective coatings, water vapor permeability, CO₂ permeability, acrylic latex films

Introduction

Recently, water-borne coatings have drawn much attention in the paint industry as they are practical and effective solutions for the reduction of volatile organic compounds (VOC). For the same reason, there has been increasing demand on water-borne products in the field of architectural paint that has the largest market among various application areas of coatings [1]. Of binder materials for water-borne paint, acrylic latex has been widely used due to its resistance to photodegradation, hydrolysis and saponification, low water absorption, and low dirt pick-up [2-4].

Modern exterior coatings for architecture are utilized for the protection of building materials against weathering as well as for the purpose of decoration. The degradation of building materials such as concrete is caused mainly by the penetration of water and CO₂ [5-8]. In particular, liquid water needs to be kept from migrating into because it carries aggressive ions and also causes deterioration by freeze/thaw cycles [8]. Bare concrete easily allows liquid water to penetrate inside through fine flaws or cracks which are formed as drying proceeds after construction [5,7]. One of the main protection functions of exterior coatings is to reduce such penetration of liquid water. However, even with barrier films liquid water may penetrate into the concrete in two ways. One way is seepage through fine defects on the hard coatings which are formed by expansion and/or retraction of the cracks on the concrete due to temperature fluctuation. The other way is a capillary absorption through the coating matrix [7]. The former is primarily to be prevented since it is relatively faster than the latter. Water penetration cannot be somewhat avoided even with barrier coatings and thus fast evaporation of

† To whom all correspondence should be addressed. (e-mail: parksk@dongguk.edu)
water is important to prevent deterioration. Besides, CO₂ also needs to be kept from permeating into because it decreases concrete alkalinity and thus accelerates the deterioration process of concrete. As such, desirable requirements of protective coatings therefore include low water absorption, high water vapor permeability, and low CO₂ permeability. Since these properties primarily depend on the nature of binder materials of the coatings, the effects of chemical composition and structure on such protective functions of architectural coatings need to be understood in order to design advanced binder materials of high performance for architectural coatings.

In this study, three sets of acrylic latex films, i.e., a set of model latex films comprising different combinations of main and auxiliary monomers, a set of the films formed from hard latex and microgel mixture solutions, and a set of the films from soft latex and microgel mixture solutions are used to measure the water vapor permeability and the CO₂ permeability. With the first set of films, the effects of monomer composition on the gas permeability are investigated. With the second and the third sets of films, which are of similar structure to commercial binder systems, the influences of the amount of relatively hydrophilic microgel particles on the gas permeability are examined.

**Experimental**

**Preparation of Model Latexes**

Nine acrylic latex solutions of different composition, named as E-A, B-A, 2-A, E-M, B-M, 2-M, E-S, B-S, and 2-S, were prepared by a single-stage emulsion polymerization using a main monomer (73.7 wt%), an auxiliary monomer (23.5 wt%), and methacrylic acid (MAA) (2.8 wt%). The main monomers were ethylacrylate (EA), butylacrylate (BA), and 2-ethylhexylacrylate (2-EHA). The auxiliary monomers were acrylonitrile (AN), methylmethacrylate (MMA), and styrene. As an anion emulsifier and an initiator, CO-436 (ammonium salt of sulfated alkylphenol ethoxylate, Alcolac Chemical Co.) and sodium persulfate were used, respectively. All the chemicals except CO-436 were purchased from Aldrich Chemical Co. and used without any further purification. A semicontinuous polymerization method, similar to that stated in the literature [9,10], was employed. For example, the detailed emulsion polymerization procedure for the B-M latex solution sample was as follows: an initial charge was composed of 111.3 g of monomer mixture of BA (73.7 wt%), MMA (23.5 wt%), MAA (2.8 wt%), 7.1 g of CO-436, and 807.0 g of deionized water. The initial charge was stirred at 150 rpm and 80 °C in a reaction flask (5 L) and the aqueous solution of initiator (1.5 wt%) was then added. Seeds were formed by maintaining the reaction temperature at about 86 °C for 40 min. A preemulsion was prepared by dissolving 1932.5 g of the monomer mixture of the same composition as the initial charge in the aqueous solution (929.2 g) of the emulsifier (5.9 wt%) and the initiator (1.7 wt%) and the preemulsion was fed to the seed solution by a pump. The polymerization reaction was allowed to proceed at the constant temperature of 86 °C for 1 h. The product solution was neutralized to pH 8.5 with the aqueous solution of ammonia (24.2 wt%) for 30 min, cooled down to 40 °C and filtered using 400 mesh Nylon filter. The solid content measured after drying the latex at 150 °C indicated the yield of 99.7%. The particle size measured by a laser light scattering method (Particle Size Analyzer, Brookheaven Instrument CO., 90 Plus) was 128.4 nm, of which size distribution was monodispersed, and the Tₘ measured by a differential scanning calorimeter (TA instrument Co., 2910) was 25.5 °C. Table 1 shows the detailed compositions, the particle sizes and the Tₘ values of the model latexes.

As a reference, a control sample, named as E-C, was prepared by the same procedure as above using only EA (97.2 wt%) and MAA (2.8 wt%). In addition, a control sample of core/shell morphology, named as B-CS, was prepared by a two-stage emulsion polymerization using BA (80 wt%), AN (10.2 wt%), MAA (2.7 wt%) and styrene (7.0 wt%). For both the control samples, the type and the amount of initiator and emulsifier were same as above.

**Preparation of Hard Latex, Soft Latex and Microgel**

A hard latex solution of core/shell structure was prepared by a two-stage emulsion polymerization of the semicontinuous type [9,10]. The first stage was a typical seeded emulsion polymerization using monomers of styrene (44.0 wt%), 2-EHA (42.0 wt%), and MAA (14.0 wt%), and the type of initiator and emulsifier was same as before. As a result, an acid-rich emulsion was prepared and it was then disintegrated by neutralization to pH 6~7 with sodium hydroxide solution. At the

<table>
<thead>
<tr>
<th>Model latex</th>
<th>Main monomer (73.7 wt%)</th>
<th>Auxiliary monomer (23.5 wt%)</th>
<th>Particle size (nm)</th>
<th>Tₘ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-A</td>
<td>EA</td>
<td>AN</td>
<td>141.5</td>
<td>-1.5</td>
</tr>
<tr>
<td>B-A</td>
<td>BA</td>
<td>AN</td>
<td>123.2</td>
<td>-26.0</td>
</tr>
<tr>
<td>2-A</td>
<td>2-EHA</td>
<td>AN</td>
<td>124.7</td>
<td>-32.6</td>
</tr>
<tr>
<td>E-M</td>
<td>EA</td>
<td>MMA</td>
<td>150.5</td>
<td>-0.9</td>
</tr>
<tr>
<td>B-M</td>
<td>BA</td>
<td>MMA</td>
<td>128.4</td>
<td>-25.5</td>
</tr>
<tr>
<td>2-M</td>
<td>2-EHA</td>
<td>MMA</td>
<td>128.6</td>
<td>-32.6</td>
</tr>
<tr>
<td>E-S</td>
<td>EA</td>
<td>Styrene</td>
<td>118.9</td>
<td>-2.1</td>
</tr>
<tr>
<td>B-S</td>
<td>BA</td>
<td>Styrene</td>
<td>118.7</td>
<td>-26.6</td>
</tr>
<tr>
<td>2-S</td>
<td>2-EHA</td>
<td>Styrene</td>
<td>119.6</td>
<td>-33.1</td>
</tr>
</tbody>
</table>
second stage, where the disintegrated polymers served as surfactants, a surfactant-free emulsion polymerization was conducted to prepare the core structure using the monomer composition of styrene (37.0 wt%), 2-EHA (33.0 wt%), MMA (27.0 wt%), and MAA (3.0 wt%). The resulting latex was of an inverted core/shell structure. The ratio of the total amount of monomers in the first stage to that in the second stage, i.e., the stage ratio was 1:13.7. A soft latex solution of core/shell structure was prepared by the similar procedures to those of the hard latex except the monomer composition and the stage ratio. Table 2 summarizes the total compositions, the measured particle sizes and the morphologies of the hard and the soft latexes. As seen in Table 2, the shell in the soft latex was not acid-rich as much as in the hard latex and it is much thicker than that in the hard one because of its different stage ratio. The Tg values of the hard and the soft latex films are 35.0 and 27.7 °C, respectively. Microgel particles having a complete core/shell structure were prepared by a typical two-stage emulsion polymerization of the semicontinuous type [9,10]. As shown in Table 2, at the first stage a cross-linked core was polymerized using monomers of styrene and 2-EHA, and at the second stage a hydrophilic shell structure was then prepared using 2-hydroxyethylacrylate (2-HEA, Aldrich Chemical Co.) and MAA of high concentration. The stage ratio was 1:0.31 and the Tg of microgel film was 0.3 °C, which is between those of the hard and the soft latexes.

**Film Formation**

A film-forming vessel was assembled by placing a glass cylinder of 8 cm diameter over a glass plate of 10 cm diameter and by sealing the outside of contact region with a silicon grease. A latex film was cast by drying the corresponding latex solution in the film-forming vessel at 25 °C and 50% relative humidity (RH) for 2 days. The dried film was carefully detached from the glass plate by soaking it in warm double-distilled water for few minutes and re-dried under vacuum at 25 °C for 2 days. The detached film did not turn hazy, which indicated that the amount of water absorption was not significant, and no significant change in the weight of latex film (usually less than 0.5 wt%) was observed after drying under vacuum, which indicated that the latex films was fully dried.

**Water Vapor Permeability**

Water vapor permeability (WVP) was measured by employing the cup method (ASTM E96-66). In this method, a weighing dish half-filled with double-distilled water was gas-tightly sealed by the latex film using molten wax. The weighing dish was placed on a digital balance and the water vapor was allowed to permeate through the latex film at 25 °C and 50% RH. The weight change for the dish was recorded on-line. The WVP, P_{H₂O}, was then calculated by the following equation:

$$ P_{H_{2}O} = \frac{24 \times W}{p_{vap} \times L \times (RH_{in} - RH_{out})} $$  \hspace{1cm} (1)

where \( W \), \( p_{vap} \), \( t \), \( t \), \( RH_{in} \), \( RH_{out} \) represent the amount of water loss (g), the vapor pressure of water at 25 °C (mmHg), the film thickness (cm), the exposure time (h), the exposure area (m²), the RH inside the dish, and the RH outside the dish, respectively.

In addition, water vapor diffusion coefficient (WVD) was calculated from a measured time lag to reach a steady state where evaporative rate is constant. According to Barrer [11], the following equation describes the relationship between the volume of permeated gas, \( Q \) and time, \( t \):

$$ Q = \frac{DC_{i}}{L} \left( t - \frac{L^2}{6D} \right) \hspace{1cm} (2) $$

where \( D \) and \( C_{i} \) denote the diffusion coefficient and the concentration of diffusing gas in the higher side. Here, the time lag is expressed as \( \theta = \frac{L^2}{6D} \) and thus \( D \) is readily calculated from an experimental \( \theta \). The water vapor solubility (WVS), \( S \) was calculated by the relationship of \( P_{H_{2}O} = \frac{S}{DS} \) [12,13].

**Table 2. Monomer Compositions, Particle Sizes and Tg of the Hard Latex, the Soft Latex and the Microgel**

<table>
<thead>
<tr>
<th>Latex</th>
<th>Monomer composition (wt%)</th>
<th>Tg (°C)</th>
<th>Particle size (nm)</th>
<th>Morphology (Stage ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Styrene</td>
<td>BA</td>
<td>2-EHA</td>
<td>MMA</td>
</tr>
<tr>
<td>Hard latex</td>
<td>37.5</td>
<td>-</td>
<td>33.6</td>
<td>25.2</td>
</tr>
<tr>
<td>Soft latex</td>
<td>4.2</td>
<td>46.1</td>
<td>30.6</td>
<td>17.6</td>
</tr>
<tr>
<td>Microgel</td>
<td>37.3</td>
<td>13.1</td>
<td>40.8</td>
<td>-</td>
</tr>
</tbody>
</table>
CO₂ Permeability

The CO₂ (carbon dioxide) permeability (CDP) was measured by employing a high vacuum method. Figure 1 shows the high vacuum apparatus used in this study. The apparatus basically consists of a CO₂ bomb, a permeation cell, automatic valves, a pressure transducer (MKS type 626A13TBE and type 626A10TBE), a power supply and a readout unit (MKS type PR4000AP2VIN), gas reservoir bottles, and a vacuum pump. The CO₂ permeability experiments were conducted according to the following procedures. The latex film was mounted in the permeation cell and the downstream line was then evacuated to less than 0.01 mmHg by a vacuum pump. In the upstream line, CO₂ gas of 1 atm was then allowed to flow through the permeation cell. The pressure increase in the downstream was detected by the pressure transducer. The data was finally collected and processed for further analysis using a personal computer. Figure 2 shows a typical permeation curve obtained by the current method. From the experimental permeation curve, the pressure increase per unit time, ΔP/Δt was determined and the CO₂ permeability, P_{CO₂} at standard temperature and pressure was calculated by the Equation (3).

\[
P_{CO₂} = \left( \frac{273}{760} \right) \left( \frac{V}{T} \right) \left( \frac{\Delta P}{\Delta t} \right) \left( \frac{L}{p₁} \right)
\] (3)

Figure 1. A high vacuum apparatus used for CO₂ permeability measurement.

Figure 2. A typical permeation curve by the high vacuum method.

Results and Discussion

Model Latex Films

Since the water vapor permeability (WVP), measured by the “cup method”, may be varied by the film thickness [14], a “true” permeability was determined by an extrapolation of the plot of 1/P_{H₂O} versus 1/L at infinite thickness. Figure 3 shows a representative plot of 1/P_{H₂O} versus 1/L. Figure 4(a) shows the WVP results for nine model latex films. For the latex films commonly containing AN, which are referred to as the AN series from now on in this paper, the WVP was in the order of BAEAB-EHA. For the MMA and the styrene series (which are of the same meaning as above), however the order was 2-EHA-MA>EA>BA and in particular the WVP of the films containing 2-EHA was more than twice as large as the others, which partly agrees with the results of Morgan’s work [15]. Morgan has reported that the longer was the alkyl chain of poly(alkylmethacrylate) homopolymers the higher was the WVP value. For the EA series, the WVP was almost same regardless of the type of auxiliary monomers. For the BA series, the WVP in the film containing MMA was slightly larger than the others, whereas for the 2-EHA series it was in the order of styrene>MMA>AN.

Figures 4(b) and 4(c) show the WVD and the WVS for the model latex films. Comparing Figure 4(a) with Figures 4(b) and 4(c), for the AN and the MMA series the WVP trends were similar to those of the WVD, whereas for the styrene series the WVP and the WVS were similar. These results indicate that the WVP
behaviors for the AN and the MMA series were dominated by the diffusion of water molecules, whereas those for the styrene series were governed by the solubilization. For the AN and the styrene series, the WVD was in the order of BA>EA>2-EHA, whereas for MMA series that was in the order of 2-EHA>EA>BA. Since the diffusion process involves the random migration of the diffusing molecule through polymeric matrix by elbowing its way between polymer chains, the larger are the diffusion coefficients [15,16]. The chain flexibility increases in the order of 2-EHA>BA>EA. In Figure 4(b), the WVD trends of 2-EHA>BA or 2-EHA>EA or BA>EA may be therefore explained in terms of the chain flexibility. However, there seems to be no systematic trend in the WVD of the EA, the BA, and the 2-EHA series. In general, the polymers with higher crystallinity and higher polarity have lower diffusion coefficient because the crystalline segments are impermeable to diffusing species and the segments of polar polymers attract one another so that they do not easily allow diffusing species to penetrate. Therefore, no systematic trend in such series suggests that those factors do not significantly affect the WVD of model latex films.

For the AN series, the WVS was at an almost same level irrespective of the type of main monomer and it was slightly lower than the MMA and the styrene series. For the MMA series the WVS was 2-EHA>BA>EA and for the styrene series 2-EHA>EA>BA. The WVS results for the AN series may be interpreted in terms of crystallinity or chain stiffness. It appears that three AN series films have almost same crystallinity or chain stiffness which is higher than those of the MMA and the styrene series, thus, yielding almost same WVS value which is slightly lower than that of the MMA and the styrene series. Meanwhile, the difference in the flexibility of polymer chain rather than the crystallinity seems to be main cause for the WVS results of the MMA series. The 2-EHA series showed the WVS order of styrene>MMA>AN. These results may be explained in terms of the polymer crystallinity or chain stiffness. It is known that the crystallinity of polystyrene is very low whereas that of polyacrylonitrile is moderate [16,17]. Similarly, styrene and MMA has no crystallinity whereas AN has, if any, a little crystallinity. Since solute molecules are not easily soluble in the polymer phase of crystalline or stiff chains, the solubility is reduced with those polymers. The EA and the BA series gave the WVS order of MMA>AN>styrene, which was not clearly understood.

Table 3 summarizes the WVP, the WVD, and the WVS results for the control samples of E-C and B-CS. The WVP of E-C was 1.6 – 1.8 times higher than those of the EA series whereas the E-C showed lower WVD and much higher WVS than them. Thus, the higher WVP of the EC film was found to be mainly due to a higher solubility. These results suggest that the addition of auxiliary monomers such as AN, MMA, and styrene to the main monomer EA caused a smaller increase in the WVD and a larger decrease in WVS, and thus a net decrease in the WVP. The B-CS film showed slightly higher WVP and WVD than the BA series, which are similar to it in composition, and it showed almost same WVS as those of the BA series. These results suggest that the introduction of the core/shell structure enhanced
Table 3. The Measured WVP, WVD, and WVS for the Control Latex Films

<table>
<thead>
<tr>
<th>Latex</th>
<th>WVP ((10^2 \text{ g cm}^{-2} \text{ cm} \cdot \text{mmHg}))</th>
<th>WVD ((10^{-6} \text{ cm}^3 \text{s}^{-1}))</th>
<th>WVS ((10^2 \text{ g cm}^{-2} \text{ cm} \cdot \text{mmHg}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-C</td>
<td>6.1</td>
<td>2.3</td>
<td>3.2</td>
</tr>
<tr>
<td>B-CS</td>
<td>4.6</td>
<td>8.2</td>
<td>0.65</td>
</tr>
</tbody>
</table>

the WVD and thus the WVP.

The carbon dioxide permeability (CDP), the diffusion coefficient (CDD), and the solubility (CDS) results are given in Figures 5(a), 5(b), and 5(c) respectively. For all the types of auxiliary monomers, the CDD was in the order of 2-EHA>BA>EA and the values of the films containing EA were significantly smaller than those of BA and 2-EHA. For example, the CDP of E-A film was just 12% of 2-A. For the EA series, the CDD gradually increased in the order styrene>MMA>AN, which is presumably because the polarity of auxiliary monomer is in the reverse order, i.e., AN>MMA>styrene. These results are consistent with the results of Salame's works [18,19]. He has found that the CDP of homopolymers is in the order of poly(styrene)>

poly(acrylonitrile)>

poly(methylmethacrylate), which was explained by his numerical analysis of relationship between the film structure and the CDP. For the BA and the 2-EHA series, however, it was difficult to distinguish a clear trend.

For the AN and the MMA series, the CDD was in the order of 2-EHA>BA>EA. These trends are well explained by an increase in the flexibility of polymer chain as discussed before and thus, decrease in \(T_g\) in the same order. To support this analysis, the CDD and \(T_g\) were correlated in Figure 6. The diffusion coefficient linearly increased as \(T_g\) decreased. Linear regressions showed that the CDD values for the AN, the MMA, and the styrene series increase \(8.2 \times 10^{-10}\), \(5.7 \times 10^{-10}\), and \(4.0 \times 10^{-10}\) cm$^3$/s, respectively, as their \(T_g\) increase 1 °C. Regardless of the types of auxiliary monomers, the CDS values of the films containing BA and 2-EHA were higher than those containing EA, which indicates that BA and 2-EHA are less polar and increase the CDS due to the low polarity. The CDP, the CDD, and the CDS results for the control samples of E-C and B-CS were given in Table 4. The CDP and the CDD of E-C were 3. 2 ~ 7.0 times and 3.3 ~ 5.5 times larger than those of the EA series, respectively whereas its CDS remained at about the same level as those of the EA series. These results indicate that the addition of auxiliary monomers such as AN, MMA, and styrene to the main monomer EA significantly lowered the CDP by the much reduction of the CDD. The B-CS showed much higher CDD and lower CDS, and thus slightly higher CDP than those of BA series that are similar in composition. These results indicate that the introduction of the core/shell structure lower the CDD and thus the CDP.

Finally, the WVP and the CDP behaviors of the model latex films were summarized in Table 5. For the WVP, the measured values in the range of \(2 \sim 5 \times 10^{-2}\) g cm$^2$/24 hnm$^2$ mmHg were estimated as good, those above the range were excellent, and those below the range were fair. Similarly, for the CDP, the values in the range of 20 ~ 50 \(\times 10^{-10}\) cm$^3$ (STP) cm$^{-2}$ s cmHg (=Barrer) were
Figure 6. The correlation between the CDD and the $T_g$ of the model latex films.

Table 4. The Measured CDP, CDD and CDS for the Control Latex Films

<table>
<thead>
<tr>
<th>Latex</th>
<th>CDP ($10^{-10}$ cm$^2$ (STP) cm$^3$ s cmHg)</th>
<th>CDD ($10^6$ cm$^2$/s)</th>
<th>CDS ($10^{-2}$ g/cm$^2$ cmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-C</td>
<td>92.6</td>
<td>13.8</td>
<td>0.067</td>
</tr>
<tr>
<td>B-CS</td>
<td>99.2</td>
<td>10.3</td>
<td>0.096</td>
</tr>
</tbody>
</table>

evaluated as good, those below the range were excellent, those in the range of 50–100 Barrer were fair, and those above 100 Barrer were poor. As seen in Table 5, there is a rough trend of trade-off between the WVP and the CDP. For example, E-A was excellent in the CDP but just good in the WVP, whereas 2-M and 2-S were excellent in the WVP but poor in the CDP. Based on these results, it appears that tentative candidates as desirable model binder system for protective coatings are EA series such as E-A, E-M, and E-S, which are more than good for both categories.

**Hard Latex/Microgel and Soft Latex/Microgel Films**

As discussed earlier, the control sample B-CS of core/shell structure showed higher WVP and lower CDP than those of the model latex films of simple core structure. Therefore, hard and soft latex films of the core/shell structure, of which compositions are close to those of commercial binders, were employed to measure the WVP and the CDP as a function of the amount of hydrophilic and internally cross-linked microgel particles. The results were shown in Figures 7(a), 7(b), and 7(c). As shown in Figure 7(a), the WVP for both the hard and the soft latex films significantly increased when the amount of microgel was more than 30 wt%.

The WVD remained at constant value without any monotonic increase or decrease. As the content of microgel increases, the core percolating pathways are formed [5], thus increasing the WVD, however the polarity and the content of cross-linking of the films increase, thus decreasing the WVD. This compensation effect appears to keep the WVD at a constant level. The WVD of the hard latex/microgel film was slightly higher than that of the soft latex/microgel. These results may be explained in terms of the difference in crystallinity. As seen in Table 2, the hard latex and microgel contain more content of styrene, of which homopolymer has very low crystallinity [16,17], than the soft latex. Therefore, it appears that the hard latex/microgel films are more permeable than the soft latex/microgel films. As seen in Figure 7(c), the more microgel is included in the latex films, the more water molecules dissolve in the films. This trend is attributed to the hydrophilic monomers such as MAA and 2-HEA contained in the microgel, which allow hydrogen bonding with water molecules. Consequently, the significant increase in the WVP at higher content of microgel resulted from the increase in the WVS.

Figures 8(a), 8(b), and 8(c) show the CDP, the CDD and the CDS results as a function of the amount of microgel (wt%), respectively. With increasing microgel content, the CDP for the soft latex/microgel films decreased whereas that for the hard latex/microgel films slightly increased. The CDP for the former was larger than that for the latter. The CDD for both systems commonly decreased with increasing microgel content. As the content of polar and cross-linked microgel increase the polarity and the cross-linking of the films increase and thus the CO$_2$ molecules become difficult to migrate through strongly-bound polymer segments. On the other hand the microgel particles seemingly do not provide pathways for nonpolar CO$_2$ molecules. Therefore, there is no compensation effect as described in the WVD thus giving rise to monotonous decrease in the CDD. Similar to the WVD, the CDD of the hard latex/microgel films was slightly higher than that of the soft latex/microgel presumably for the same reason as discussed previously. As the microgel content increased, for the soft latex/microgel films there was no clear CDS trend.

Table 5. Summary of the WVP and the CDP Results of the Model Latex Films

<table>
<thead>
<tr>
<th>Latex</th>
<th>High WVP (WVP value)</th>
<th>Low CDP (CDP value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-A</td>
<td>Good (3.9)</td>
<td>Excellent (13.2)</td>
</tr>
<tr>
<td>B-A</td>
<td>Good (4.0)</td>
<td>Fair (88.0)</td>
</tr>
<tr>
<td>2-A</td>
<td>Fair (1.7)</td>
<td>Poor (108.6)</td>
</tr>
<tr>
<td>E-M</td>
<td>Good (3.7)</td>
<td>Good (27.0)</td>
</tr>
<tr>
<td>B-M</td>
<td>Good (2.8)</td>
<td>Fair (98.3)</td>
</tr>
<tr>
<td>2-M</td>
<td>Excellent (8.2)</td>
<td>Poor (103.9)</td>
</tr>
<tr>
<td>E-S</td>
<td>Good (3.5)</td>
<td>Good (29.0)</td>
</tr>
<tr>
<td>B-S</td>
<td>Good (2.5)</td>
<td>Fair (87.4)</td>
</tr>
<tr>
<td>2-S</td>
<td>Excellent (8.8)</td>
<td>Poor (108.1)</td>
</tr>
</tbody>
</table>

aunit: $10^{-10}$ g cm$^2$/24 h m$^2$ mmHg.
bunit: $10^{-10}$ cm$^3$(STP) cm$^3$/s cmHg (=Barrer).
Figure 7. The measured (a) WVP, (b) WVD, and (c) WVS for the hard and the soft latex films as a function of the amount of the microgel particles (wt%).

whereas for the hard latex/microgel films the CDS slightly increased. The CDS values for the soft latex/microgel films were significantly higher than those of the hard latex/microgel films. Comparing Figure 7(a) with Figures 7(b) and 7(c), it is noted that for the soft latex/microgel films the gradual decrease in the CDP was influenced mainly by the CDD results whereas for the hard latex/microgel films the gradual increase in the CDP by the CDS results.

Figure 8. The measured (a) CDP, (b) CDD, and (c) CDS for the hard and the soft latex films as a function of the amount of the microgel particles (wt%).

Conclusions

The investigation on the effects of monomer compositions and microgel amount on the WVP and the CDP of the model acrylic latex films and the hard and the soft
latex films has lead to the following conclusions:
(1) The WVP and the CDP of the latex films were significantly influenced by their monomer compositions.
(2) The observed trends of the WVP and the CDP were explained in terms of the stiffness of polymer chain segments, the crystallinity or the chain stiffness, and the polarity of the latex films.
(3) The control sample of core/shell structure of similar composition to the BA series films showed desirable permeability properties of higher WVP and lower CDP whereas the addition of auxiliary monomers to the film comprising only EA resulted in decrease in both the WVP and the CDP.
(4) There was a rough trend of trade-off between the WVP and the CDP, and the possible candidates as desirable model binder systems for protective coatings were EA series, i.e., E-A, E-M, E-S yielding higher WVP and lower CDP to a extent.
(5) For both the hard and the soft latex films, the WVP significantly increased with increasing the content of the hydrophilic microgel particles, which was mainly caused by the increase in the WVS.
(6) As the amount of microgel increased, the CDP for the soft latex films was reduced primarily due to the decrease in the CDD, whereas that for the hard latex films slightly ascended by the combination of decrease in the CDD and increase in the CDS.

References