Effect of Vinylidene Chloride Content on Film-Formation Property of Vinylidene Chloride-Methyl Acrylate Copolymer Latex

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ABSTRACT: Minimum film-formation temperature (MFFT) of vinylidene chloride (VDC)-methyl acrylate (MA) copolymer latexes prepared by batch emulsion polymerization with various compositions from 20 to 97 wt % of VDC were measured. For latexes with VDC content below 90 wt %, MFFT was similar to polymer T_g. As VDC content increased beyond 90 wt %, the MFFT curve plotted against VDC content rose sharply, in contrast with the T_g curve that descended smoothly. Measurements of infrared absorption of latexes in the dispersed state, and X-ray diffraction and infrared absorption of lyophilized polymers were conducted on 40 : 60, 80 : 20, and 95 : 5 VDC-MA specimens. These observations indicated that only 95 : 5 VDC-MA specimens were highly crystalline. It was therefore believed that film-formation property of latex with high VDC content was significantly affected by polymer crystallinity of particles in the dispersed state. Morphology and oxygen gas transmission rate of heat-treated and non-heat-treated coatings of 95 : 5 VDC-MA latex were investigated. Heat treatment of coatings beyond the temperature at which crystalline polymer began to melt induced effective particle coalescence, resulting in reduced oxygen gas transmission rate. This supported our belief that film-formation property of VDC-MA latex with high VDC content was significantly affected by polymer crystallinity. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 565–572, 1998

Key words: minimum film-formation temperature; coating morphology; polymer crystallinity; vinylidene chloride; methyl acrylate

INTRODUCTION

Vinylidene chloride (VDC) copolymer latex produced by emulsion polymerization is an excellent barrier material for coatings with low permeability to gases and moisture.[1] Plastic films and papers coated with VDC copolymer latex are widely used for packaging to preserve the quality of foods and drugs for extended periods of time. Barrier properties of packaging are determined by those of a thin coating of VDC copolymer latex. To attain excellent barrier properties, it is necessary to produce a continuous film-like coating with good latex particle coalescence.

In the process of film formation, polymer particles undergo packing and coalescence as water evaporates.[2–5] It is known that coalescence occurs simultaneously or consequently through mechanisms such as wet-sintering,[6] capillary pressure,[7] osmotic pressure,[8] dry-sintering,[9,10] and autodiffusion.[11,12] In any mechanism, the relationship between the deformative forces acting on particles and particle resistance to deformation is important.[13] Generally, film-formation characteristics of latex are determined by polymer properties such as T_g,[14,15] polarity[16] and hydrophilicity,[15]

and colloidal properties of the latex, such as particle size[6,17] and stability.

It is known that barrier properties of latex improve as VDC content in the polymer is increased. However, high VDC content latex is poor in film formation. Often, this cannot be explained by the factors mentioned previously and is thought to be due to polymer crystallinity. However, little has been published on the study of film-formation property of VDC copolymer latex.[17–20]

In the present work, the effect of VDC content on film-formation property of VDC-methyl acrylate (MA) copolymer latex was investigated. Focus was placed on polymer crystallinity.

EXPERIMENTAL

Latex Preparation

A series of copolymer latexes having different compositions of VDC and MA were prepared by the conventional batch process of emulsion polymerization in a 1000-mL pressure-resistant glass reactor with a stirrer in a closed system. The recipe for emulsion polymerization was:

- Deionized water: 400 mL
- Emulsifiers: sodium lauryl sulfate, 1.0 g/L of water; Dowfax 2A1, 3.0 g/L of water
- Initiator: potassium persulfate, 1.1 g/L of water
- Monomer mixture: 0.66 g/mL of water

VDC-MA monomer ratios were 20 : 80, 30 : 70, 40 : 60, 50 : 50, 60 : 40, 70 : 30, 80 : 20, 85 : 15, 90 : 10, 95 : 5, and 97 : 3 by weight. Water and emulsifiers were placed in the reactor, and air was replaced with nitrogen gas. Monomer mixture was loaded and followed by initiator. Reactions were conducted for 15 h at 50°C.

Measurements of minimum film-formation temperature (MFFT), relative crystallinity, and coating properties were conducted approximately 1 month after polymerization. The latexes were cleaned by conventional dialysis against deionized water overnight before measurements.

Latex Analysis

Nonvolatility of the obtained latexes were determined gravimetrically from sample weight after drying at 110°C for 1 h.

Particle diameter was measured with a JEOL JEM2000FX transmission electron microscope.

Latex diluted in water at about 1/1000 was placed on a collodion-coated carbon mesh and dried at room temperature. Chromium sputtering was performed before observation.

The polymer from each latex was analyzed for chlorine content by oxygen flask combustion.[21] Polymers were purified through precipitation from tetrahydrofuran solution by the addition of methanol before elemental analysis. Copolymer compositions were determined from chlorine content.

Measurement of MFFT

MFFT of latex samples was carefully measured by the temperature-gradient bar method described by Protzman and Brown[14] and Brodnyan and Konen.[15] Bar surface temperatures were stabilized before latex coating. Latex was coated on the bar with a 50 μm applicator and let stand to dry for 1 h. Care was taken to avoid exposure to direct air flow during the drying period. The minimum temperature at which a continuous film formed was determined to be the MFFT. All measurements were conducted in a room large enough to prevent deviation of humidity and temperature, which were maintained constant by a high-performance air conditioner.

Determination of Reactivity Ratios in VDC-MA Emulsion Copolymerization

The reactivity ratios of VDC and MA in emulsion copolymerization were determined by the Fineman−Ross[22] equation. Seven monomer mixtures with a range of compositions were polymerized using the same recipe and conditions as described previously. Polymerizations were stopped at low conversion. Chlorine content of purified and dried polymers were analyzed to determine copolymer compositions.

Measurement of X-ray Diffraction and Infrared Absorption

X-ray wide-angle diffraction measurement and Fourier transform infrared spectroscopy were used to determine the relative crystallinity of powder polymers from 40 : 60, 80 : 20, and 95 : 5 VDC-MA latexes. Samples were obtained by lyophilization of latexes, maintained at −40°C, well below T_g, until measurement. Samples were powderized before measurement. X-ray diffraction patterns were obtained by the reflection method using CuKα radiation with a graphite monochro-

mator on a Rigaku Rotaflex RU-200 X-ray generator. Infrared absorption was measured with a Japan Spectroscopic DP/S-3 Fourier transform infrared spectrometer using the KBr pellet method.

Infrared absorption of 40 : 60, 80 : 20, and 95 : 5 VDC-MA latexes in the dispersed state were measured using an arsenic selenide liquid cell with a light-path length of 25 μm.

Observation of Surface Structure of Latex Coatings

Surface structures of heat-treated and nontreated coatings of 95 : 5 VDC-MA latex were observed with a JEOL JSM T-300 scanning electron microscope (SEM). Latex samples were coated on 12-μm polyester film and dried by blowing 100°C air for 15 s, similar to industrial practice. Coating thickness was 3 μm when dried. Heat treatment was performed for 15 s at 190°C. Specimens were aged at 40°C for 48 h. Chromium sputtering was conducted before observation.

Measurement of Crystalline Melting Temperature

The crystalline melting temperature of polymer from 95 : 5 VDC-MA latex was determined using a Shimazu DSC-50 differential scanning calorimeter (DSC) with a heating rate of 20°C min^{-1}. Specimen was prepared by coating the latex on a glass panel and drying in the same manner as described previously. Coating thickness was 3 μm when dried. The coating was removed from the glass before measurement.

Measurement of Oxygen Gas Transmission Rate

Oxygen gas transmission rates of heat-treated and non-heat-treated latex coatings were measured at 20°C and 80% relative humidity by the ASTM D 3958 constant pressure method. Latex coatings were prepared in the same manner as described for surface structure observation. Coating thickness was 3 μm when dried. Heat treatment was carried for 15 s at 100, 120, 130, 140, 160, 180, and 190°C. All specimens were aged at 40°C for 48 h before measurement to allow the polymer of coatings to crystallize.

RESULTS AND DISCUSSION

Emulsion Polymerization

All emulsion polymerizations of VDC and MA monomer mixtures with 20 to 97 wt % VDC by the

Table I   Results of VDC-MA Emulsion Polymerization

VDC in Monomer (wt %)	Nonvolatility (%)	Particle Size (nm)	Chlorine in Polymer (wt %)	VDC in Polymer (wt %)
20.0	40.1	130	14.7	20.1
30.0	39.8	126	21.8	29.8
40.0	40.2	131	29.4	40.2
50.0	39.9	127	36.4	49.8
60.0	39.8	129	43.8	59.9
70.0	40.0	135	51.3	70.1
80.0	39.9	142	58.6	80.1
85.0	39.8	137	62.3	85.2
90.0	40.2	132	66.0	90.2
95.0	40.1	124	69.4	94.9
97.0	39.9	129	70.8	96.8

batch process resulted in stable latexes of nearly 100% conversion with negligible coagulum. Polymer compositions of the latexes were found to agree closely with monomer feed compositions (as shown in Table I). Particle diameters of the latexes were 124–142 nm. No relationship between composition and particle diameter was found.

MFFT

In this study, relative humidity was found to have significant effect on MFFT of 95 : 5 VDC-MA latex (as shown in Fig. 1). Measurements to establish the relationship between polymer composition and MFFT were therefore conducted under constant conditions, 20 ± 0.5°C and 55 ± 3% relative humidity.

Figure 2 shows the MFFT of VDC-MA latexes plotted against VDC wt % of monomer compositions, together with T_g of polymers as described by Wessling and colleagues.[23] In the region below 90 wt % VDC, the shapes of the MFFT and T_g curves were similar, rising smoothly to a local maximum at around 55 wt % VDC before sloping smoothly downward. MFFT of most latexes were a few degrees higher than the T_g of each polymer in this region. The MFFT curve rose sharply as VDC content increased beyond 90 wt %, in stark contrast with the T_g curve that continued its smooth descent in this region. It was thus apparent that MFFT in this high VDC wt % region was not significantly influenced by the T_g of the polymer.

The difference between MFFT and T_g was not as great as that reported by Powell and colleagues.[20] One factor in this difference is that the
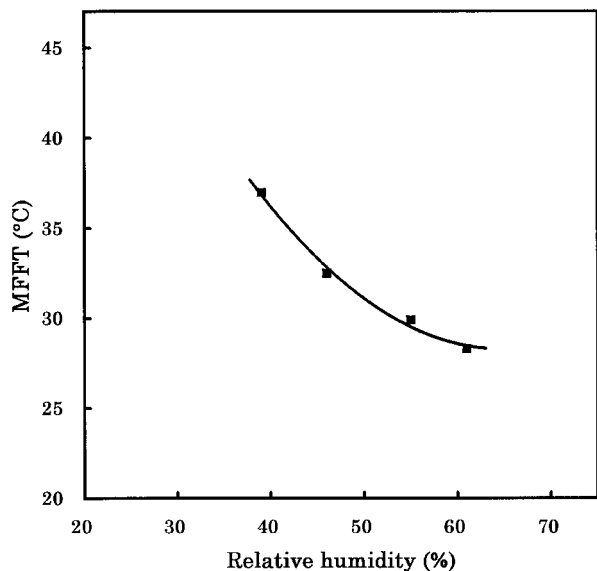
Figure 1 Effect of relative humidity on MFFT of 95 : 5 VDC-MA latex.

T_g data used in this study (as reported by Wessling and colleagues[23]) is believed to be more reliable than that used by Powell and colleagues. The differences between the MFFT data obtained by Powell and colleagues and that obtained in this study may be attributable to some extent to the fact that Powell and colleagues used different emulsifiers in their work.

Copolymer Composition Drift

The reactivity ratios in the VDC-MA emulsion copolymerization under the conditions of this
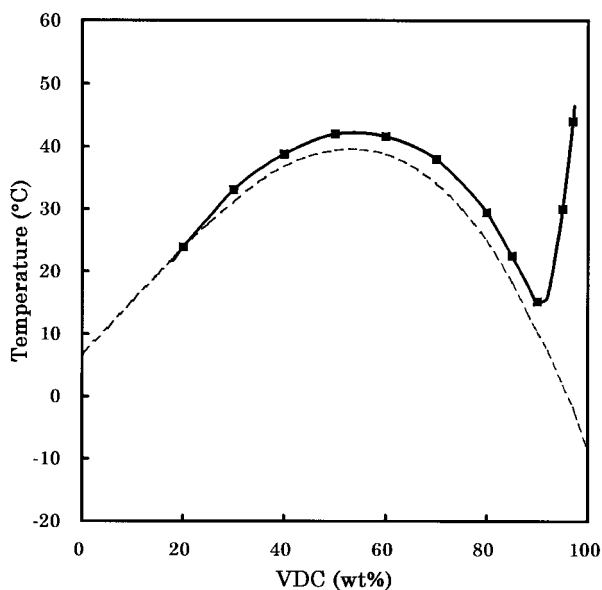
Figure 2 MFFT of VDC-MA latexes and T_g of VDC-MA polymers.[20] Solid line, MFFT; dashed line, T_g.

Table II Results of Low Conversion Polymerization of VDC and MA

VDC in Monomer		Conversion (%)	Chlorine in Polymer (wt %)	VDC in Polymer	
Wt %	Mol %			Wt %	Mol %
20.0	18.2	9.6	17.0	23.2	21.2
30.0	27.5	8.2	24.2	33.1	30.5
40.0	37.2	6.8	30.9	42.2	39.4
50.0	47.0	9.9	38.8	53.1	50.1
60.0	57.1	9.8	45.3	61.9	59.1
70.0	67.4	8.2	52.7	72.1	69.6
80.0	78.0	9.8	59.3	81.1	79.2

work were determined to estimate the copolymer composition drift in the batch process. The experimental results of low conversion batch emulsion polymerization of VDC and MA are shown in Table II. The reactivity ratios in this work, determined by the Fineman–Ross[22] equation, were $r_1 = 1.04$ and $r_2 = 0.83$ (as shown in Fig. 3). Figure 4 shows the instantaneous copolymer composition formed in any monomer mixture of VDC and MA calculated from r_1 and r_2 by the Mayo–Lewis[24] equation. Instanta-
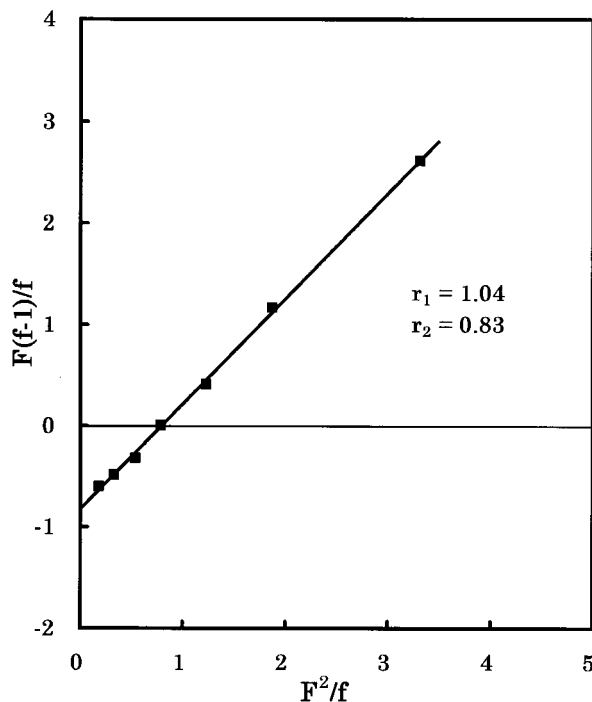

Figure 3 Reactivity ratios in VDC-MA emulsion copolymerization determined by the Fineman–Ross equation. F, VDC mole ratio in monomer mixture; f, VDC mole ratio in the copolymer.
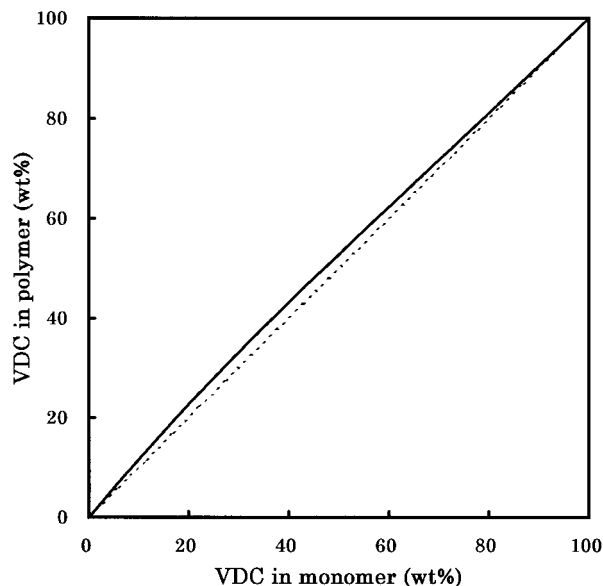
Figure 4 Instantaneous copolymer composition calculated by Mayo–Lewis equation. Solid line, calculated from the reactivity ratio of the VDC-MA system in this work; dashed line, $r_1 = r_2 = 1$.

neous copolymer composition was very near monomer composition, indicating that composition drift in the VDC-MA batch polymerization of this work was slight. Copolymer composition drift therefore is not believed to have significantly affected MFFT results in this work.

Relative Crystallinity of Powder Polymer

To estimate relative crystallinity of the polymer of particles in the latex, powder polymers obtained by lyophilization of latexes were investi-
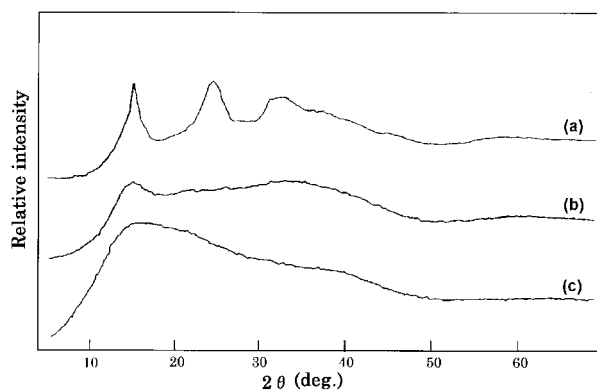

Figure 5 X-ray diffraction patterns of lyophilized VDC-MA latexes. (a) 95 : 5 VDC-MA, (b) 80 : 20 VDC-MA, and (c) 40 : 60 VDC-MA.
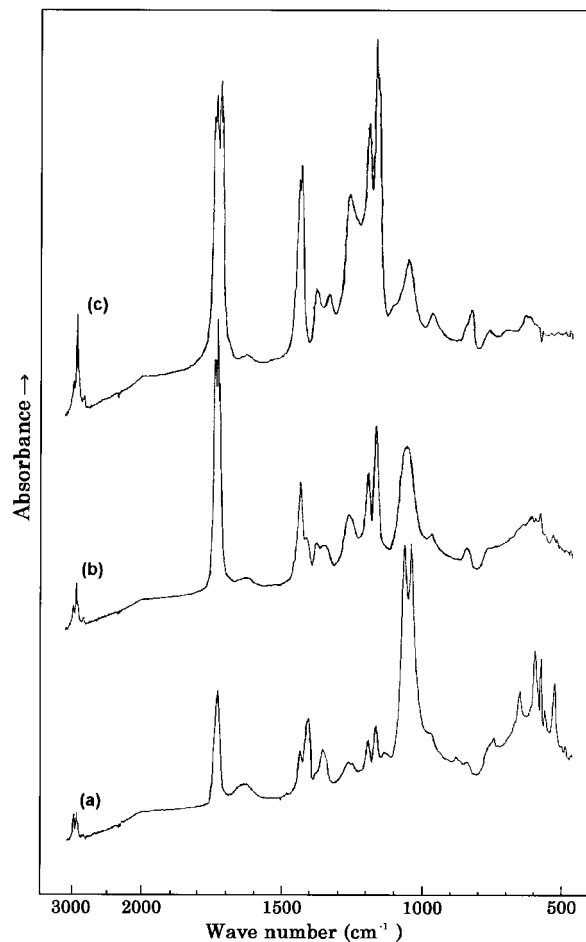

Figure 6 Infrared absorption spectra of lyophilized VDC-MA latexes. (a) 95 : 5 VDC-MA, (b) 80 : 20 VDC-MA, and (c) 40 : 60 VDC-MA.

gated by X-ray diffraction[25] and infrared absorption.[26–30]

Figure 5 shows the X-ray diffraction patterns of three polymers from 40 : 60, 80 : 20, and 95 : 5 VDC-MA latexes. The polymer from 95 : 5 VDC-MA latex exhibited three definitive peaks at 2θ of 15°, 25°, and 33°–38°. The diffraction patterns of 40 : 60 and 80 : 20 VDC-MA latexes showed no significant peak.

Figure 6 shows infrared absorption spectra of the same polymers. The polymer from 95 : 5 VDC-MA latex exhibited a strong doublet at 1048 and 1070 cm^{-1}, which is characteristic of crystalline poly-VDC (PVDC).[27,28,30] Absorption spectra of polymers from 40 : 60 and 80 : 20 VDC-MA did not exhibit the characteristic doublet.

The results of both X-ray diffraction and infrared absorption indicated that the polymer from 95 : 5 VDC-MA latex was highly crystalline, and

the polymers from 40 : 60 and 80 : 20 VDC-MA latexes were amorphous.

Relative Crystallinity of Particle Polymer in the Dispersed State

Direct measurement of infrared absorption of latex by the liquid cell method was used to estimate relative crystallinity of polymer of particles in the dispersed state. Figure 7 shows the spectra of 95 : 5 VDC-MA latex, ultracentrifuged serum of the latex, and the vacant cell. No significant interfering absorption from the serum or cell was observed in the range between about 1000 and 1500 cm^{-1}, an important region for the determination of the relative crystallinity of PVDC.

Figure 8 shows the infrared absorption spectra of 40 : 60, 80 : 20, and 95 : 5 VDC-MA latexes in the dispersed state. The results agreed with those of lyophilized polymer measurements. The strong doublet at 1048 and 1070 cm^{-1} observed in the 95 : 5 VDC-MA latex absorption spectrum indicates that the polymer of particles in the latex was highly crystalline in the dispersed state. It is
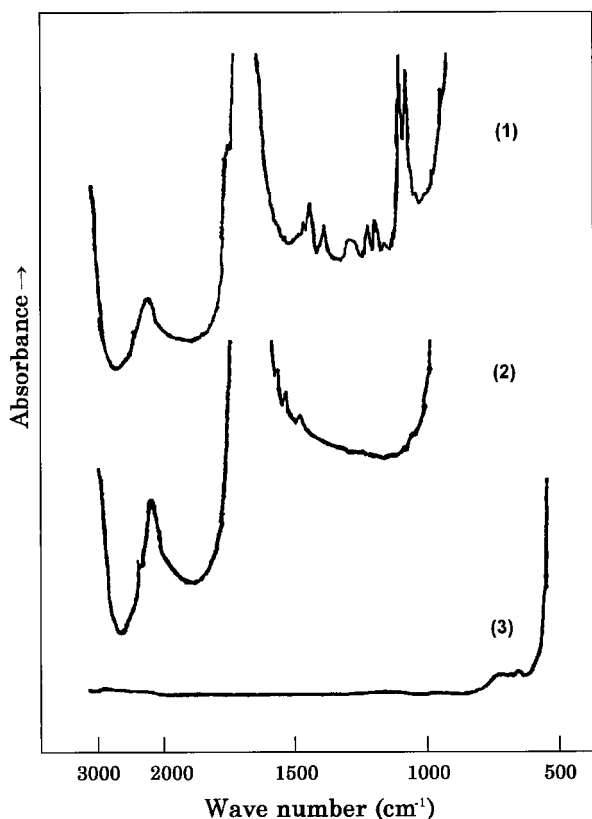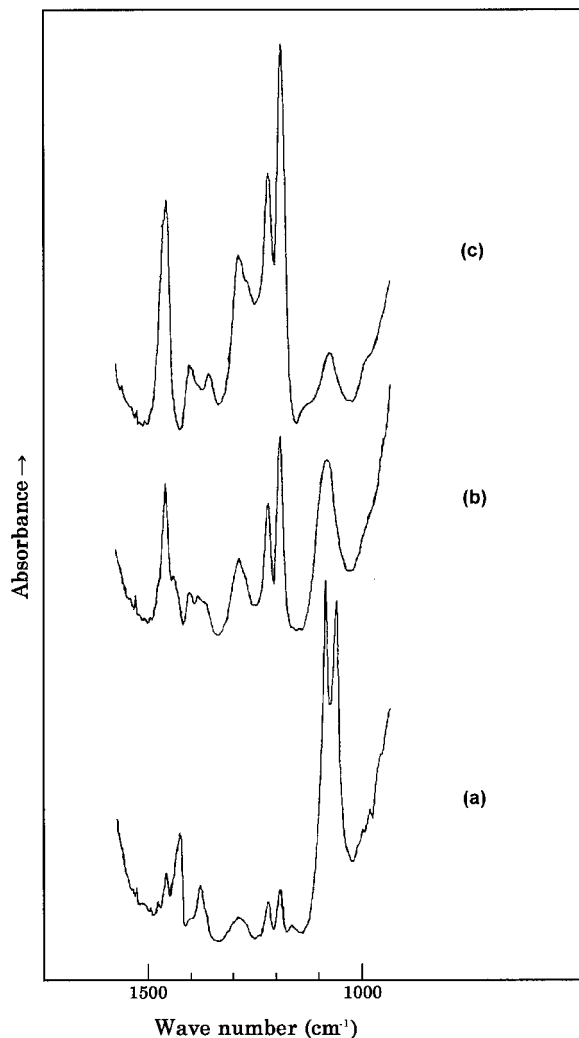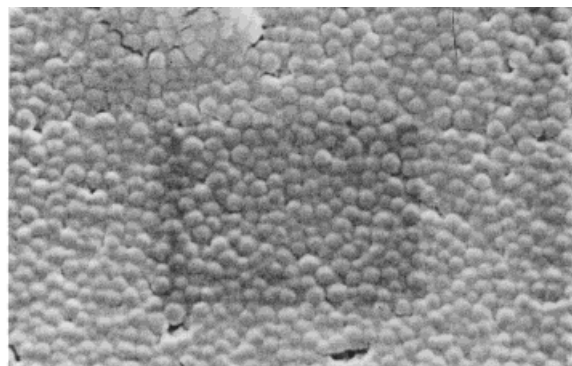
Figure 8 Infrared absorption spectra of VDC-MA latexes in the dispersed state. (a) 95 : 5 VDC-MA, (b) 80 : 20 VDC-MA, and (c) 40 : 60 VDC-MA.
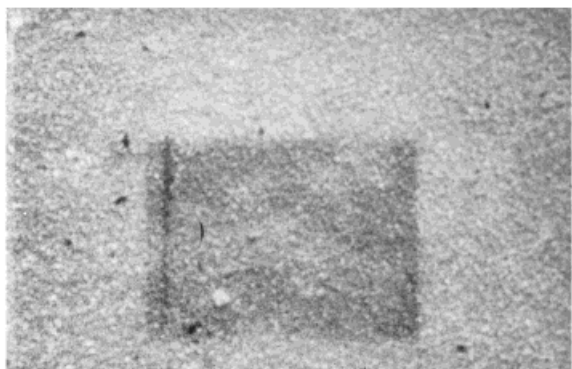
therefore believed that the MFFT of 95 : 5 VDC-MA latex was considerably higher than the T_g of the polymer due to the crystallinity of the polymer of particles. Because 80 : 20 and 40 : 60 VDC-MA latexes did not exhibit the absorption pattern characteristic of crystalline PVDC, it is believed that the MFFT approximated T_g because of the amorphous state of the particle polymer.

Coatings of Latex

Coating of 95 : 5 VDC-MA latex (30°C MFFT) on polyester film at conventional conditions gave a opaque coating. Figure 9(1) shows an SEM photograph of this coating. Individual particles and gaps in the surface of the coating can be clearly seen. Heat treatment at 190°C, well above the

Figure 7 Infrared absorption measurement by the liquid cell method. (1) 95 : 5 wt % VDC-MA latex, (2) latex serum, and (3) vacant cell.

(1) Non heat-treated

(2) Heat-treated at 190 °C for 15 sec.

500nm

Figure 9 SEM photographs of VDC-MA latex coatings. (1) non-heat-treated and (2) heat-treated at 190°C for 15 s.

melting point of crystalline polymer measured by DSC shown in Figure 10, made the coating transparent. As shown in the SEM photograph in Fig-
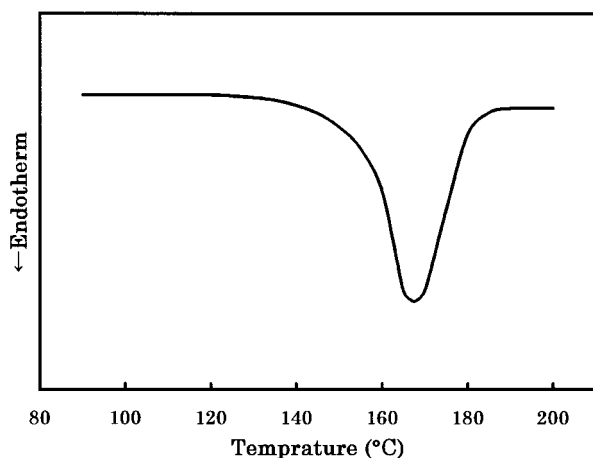

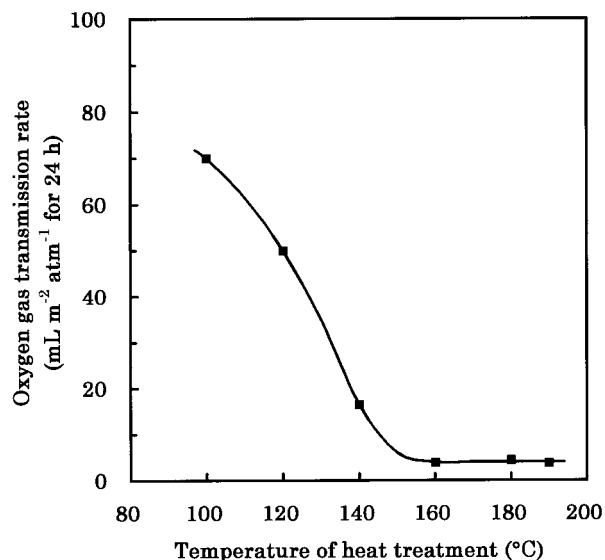**Figure 10** DSC curve of 95 : 5 VDC-MA latex coating.

Figure 11 Effect of heat treatment temperature on the oxygen gas transmission rate of 95 : 5 VDC-MA latex coating.

ure 9(2), individual particles could no longer be distinguished, and the gaps in the surface of the coating were no longer apparent, indicating that heat treatment caused effective coalescence of the particles.

The oxygen gas transmission rate of the non-heat-treated film, in which particle coalescence was incomplete, was 80 mL m^{-2} atm^{-1} for 24 h. Heat treatment at 190°C to induce particle coalescence reduced the transmission rate to 4 mL m^{-2} atm^{-1} for 24 h. Figure 11 shows the effect of heat treatment temperature on oxygen gas transmission rates of coated films. Oxygen gas transmission rate improved steadily as heat treatment temperature increased up to about 150°C, the temperature at which crystalline polymer began to melt according to DSC measurement. Heat treatment at higher temperatures did not cause notable improvement in oxygen gas transmission rate, indicating that heat treatment at 150°C or higher apparently caused effective particle coalescence.

CONCLUSIONS

Measurements of infrared absorption of latexes and X-ray diffraction and infrared absorption of lyophilized polymers from latexes indicated that the polymer of VDC-MA copolymer latex with VDC content of 95 wt % were highly crystalline in the dispersed state, whereas those with a VDC

content of 80 wt % and 40 wt % were amorphous. It was, therefore, believed that the sharp rise in MFFT curve plotted against VDC content in the region beyond 90 wt % VDC was caused by the crystallinity of polymer of particles in the dispersed state. Furthermore, heat treatment of coatings of VDC-MA latex with VDC content of 95 wt % beyond the temperature at which crystalline polymer began to melt effectively induced particle coalescence, resulting in greatly reduced oxygen gas transmission rate and improved morphology. It was, therefore, concluded that the film-formation property of VDC-MA latex with high VDC content was significantly affected by polymer crystallinity.

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