

Effect of Storage on Film-Formation Property of Vinylidene Chloride-Acrylonitrile-Methyl Acrylate Terpolymer Latex

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ABSTRACT: Latex prepared from 91 : 5 : 4 wt % vinylidene chloride-acrylonitrile-methyl acrylate monomer mixture by seeded semicontinuous emulsion polymerization was investigated for a change in minimum film-formation temperature (MFFT) during storage, with focus placed on polymer crystallinity in the dispersed state. MFFT rose from 20°C to 32°C, with storage at 20°C for 49 weeks. Infrared absorption of fresh and stored latexes in the dispersed state indicated an increase in absorbance at 1048 cm⁻¹, which is characteristic of a crystalline vinylidene chloride polymer, that correlated with the MFFT rise with storage. This suggested that the MFFT rise with storage was caused by increasing crystallinity of the polymer in the dispersed state. X-ray wide-angle diffraction and infrared absorption of powder polymers obtained by lyophilization of fresh and stored latexes also indicated increasing crystallinity with latex storage. Oxygen gas permeabilities of films coated with fresh and stored latexes were measured. Latex stored for long periods exhibited poor barrier property, indicating that such latex is unsuitable as an industrial barrier coating material for films and papers. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 573–579, 1998

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

INTRODUCTION

Vinylidene chloride (VDC) copolymer latex prepared 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. It is known that barrier

properties of latex improve as VDC content in the polymer increases. However, high VDC content latex is poor in film formation.² Often minimum film-formation temperature (MFFT) of high barrier latex with high VDC content in the polymer rises during storage. MFFT rise with storage is a serious industrial concern in terms of latex shelf life. If MFFT of latex is too high, insufficient coalescence of latex particles will occur during film formation with industrial coating processes and permeability of the film to gases and moisture will be unacceptably high. Knowledge of the mechanism for MFFT rise during storage is therefore industrially significant. However, little has been published on the study of film-formation property, including MFFT rise, of VDC copolymer latex.^{2–5}

In the present work, the MFFT rise of latex prepared from a 91 : 5 : 4 wt % VDC-acrylonitrile

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(AN)-methyl acrylate (MA) monomer mixture by seeded semicontinuous emulsion polymerization was investigated by observing the physical and mechanical properties of fresh and stored latexes, placing focus on polymer crystallinity.

EXPERIMENTAL

Latex Preparation

Terpolymer latex of VDC-AN-MA was prepared by seeded semicontinuous emulsion polymerization in a 10-L, pressure-resistant, glass-lined reactor in a closed system. The recipe for emulsion polymerization was:

For seed formation:

- Deionized water: 4500 mL
- Emulsifier: 25% sodium dodecyl benzene sulfonate, 27 g
- Initiator: potassium persulfate, 6.8 g
- Monomer mixture: 91 : 5 : 4 wt % VDC-AN-MA, 450 g

For semicontinuous polymerization:

- Emulsifier: 25% sodium dodecyl benzene sulfonate, 90 g
- Monomer mixture: 91 : 5 : 4 wt % VDC-AN-MA, 4050 g

For seed formation, water and emulsifier were placed in the reactor, and air was replaced with nitrogen gas. Monomer mixture was loaded, and temperature was controlled at 55°C. Initiator was then loaded into the reactor. Reaction was conducted for 90 min. Just after seed formation, semicontinuous polymerization was conducted at 55°C. Emulsifier was loaded into the reactor containing the seed latex, and the monomer mixture was fed in at a constant feed rate over 10 h. Reaction was performed for 2 h, after monomer mixture feed was completed.

After polymerization, surface tension of latex was adjusted to 41 mN m⁻¹ by addition of emulsifier. Latex was then cleaned by conventional dialysis against deionized water overnight.

Latex Analysis

Nonvolatility of the obtained latex before surface tension adjusting was determined gravimetrically

from sample weight after drying at 110°C for 1 h. Conversion of emulsion polymerization was calculated from nonvolatility of latex.

Particle diameter was measured with a JEOL JEM2000FX transmission electron microscope. A small amount of latex diluted in water at about 1/1000 was sprayed onto a collodion-coated carbon mesh and dried at room temperature. Chromium sputtering was conducted before observation. To calibrate magnification of the electron microscope, a micrograph of a standard carbon grating was taken at the same setting as that used for the latex particles. Diameters of at least 100 particles were measured, and their average value was reported.

Polymer from latex was analyzed for chlorine content by oxygen flask combustion⁶ and nitrogen content with CHN analyzer. Polymer was purified through precipitation from tetrahydrofuran solution by the addition of methanol before element analysis.

Measurement of MFFT

MFFT of the latex sample was carefully measured by the temperature-gradient bar method described by Protzman and Brown⁷ and Brodnyan and Konen.⁸ 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 at 20 ± 0.5°C and 55 ± 3% relative humidity by a high-performance air conditioner.

Measurement of Infrared Absorption and X-ray Diffraction

Fourier transform infrared spectroscopy was used to determine the relative crystallinity of polymer in both dispersed and powder states with a Japan Spectroscopic DP/S-3 Fourier transform infrared spectrometer. Direct infrared absorption measurements of fresh and stored latexes in the dispersed state were conducted using an arsenic selenide liquid cell with a light-path length of 25 μm. 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 VDC polymer. In the powder state, lyophilized polymers from fresh and stored latexes were measured using the KBr pellet method. To prevent alteration of the crystallinity of the latex state, lyophilized polymer specimens were maintained at temperatures under 0°C, well below T_g of the polymer, during drying, and until measurement.

X-ray wide-angle diffraction patterns of the lyophilized powder polymers from fresh and stored latexes were obtained by the reflection method using $\text{CuK}\alpha$ radiation with a graphite monochromator on a Rigaku Rotaflex RU-200 X-ray generator. Samples were powderized before measurement.

Measurement of Tensile Property of Latex Film

Tensile measurements of aged and nonaged cast film prepared from fresh latex were conducted with Orientec Tensilon UTM-III-500 at 20°C. Crosshead speed was 40 mm min^{-1} . The specimen was prepared by casting the latex on aluminum foil with a coating rod and drying at 70°C for 2 min. The cast film was removed from the foil and was cut into 15 × 80 mm specimens. Film thickness was 20 μm when dried. Aging was conducted at 40°C for 48 h. Five specimens were measured, and their average values were reported.

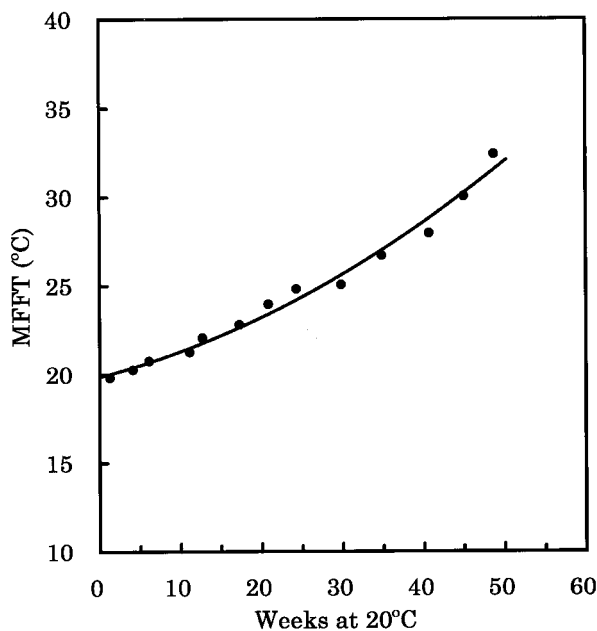


Figure 1 Effect of storage on MFFT of 91 : 5 : 4 VDC-AN-MA terpolymer latex.

Table I Particle Diameter of Fresh and Stored 91 : 5 : 4 VDC-AN-MA Terpolymer Latexes

| Storage Period (weeks) | Particle Diameter (nm) |
|------------------------|------------------------|
| 0 | 144 |
| 21 | 142 |
| 41 | 141 |
| 49 | 145 |

Measurement of Oxygen Gas Transmission Rate

Oxygen gas transmission rates of polyester films coated with fresh and stored latexes were measured at 20°C and 80% relative humidity by the ASTM D 3958 constant pressure method. Latex samples were coated on 12 μm polyester film with a coating rod and dried for 15 s with blown air. Temperatures of air for drying were 80, 90, 100, 110, and 120°C. Coating thickness was 3 μm when dried. 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

Emulsion polymerization of 91 : 5 : 4 wt % VDC-AN-MA monomer mixture by seeded semicontinuous process resulted in a stable latex with negligible coagulum. Polymerization conversion calculated from nonvolatility of latex, 49.7%, was nearly 100%. Chlorine and nitrogen contents in the polymer by element analysis were 66.5% and 1.3%, respectively, indicating that polymer composition agreed closely with fed monomer mixture composition.

MFFT

Figure 1 shows the MFFT of latex prepared from 91 : 5 : 4 wt % VDC-AN-MA monomer mixture by seeded semicontinuous emulsion polymerization, plotted against period of storage at 20°C. The MFFT rose from 20°C to 32°C with storage for 49 weeks. Slope of the plots in the initial period of storage was smaller than that in the latter period: 0.15°C week^{-1} in the first 10 weeks, and 0.35°C week^{-1} in the last 10 weeks.

Particle diameter, pH, and electric conductance of fresh and stored VDC-AN-MA terpolymer latexes are shown in Table I and Figure 2. Particle

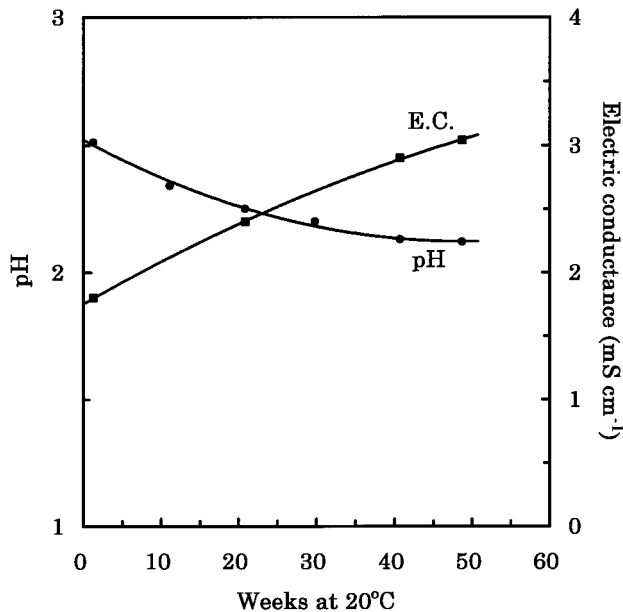


Figure 2 Effect of storage on pH and electric conductance of 91 : 5 : 4 VDC-AN-MA terpolymer latex.

diameter was 144 nm in fresh latex, and exhibited no change with storage, indicating that no significant particle coagulation occurred. The fall in pH and increase in electric conductance during storage was attributed to the well-known phenomenon of elimination of hydrogen chloride from polymer. Concentration of chloride anion in the latex measured by a chloride ion meter increased from 250 to 600 ppm, with storage at 20°C for 49 weeks, indicating that about 0.05% of chlorine in the polymer was eliminated, confirming that polymer composition was not significantly affected. It was believed that the elimination of hydrogen chloride would not significantly affect physical properties of polymer because the change in polymer composition was slight with storage at 20°C.⁹⁻¹¹

To estimate the effect of change of pH and electric conductance on MFFT, the stored latexes were cleaned by dialysis overnight against deionized water. As shown in Table II, MFFT of stored

Table II Properties of Stored 91 : 5 : 4 VDC-AN-MA Terpolymer Latexes after Redialysis

| Storage Period (weeks) | pH | Electric Conductance (mS cm ⁻¹) | MFFT (°C) |
|------------------------|-----|---|-----------|
| 21 | 2.7 | 1.2 | 23 |
| 41 | 2.7 | 1.3 | 27 |
| 49 | 2.9 | 0.9 | 34 |

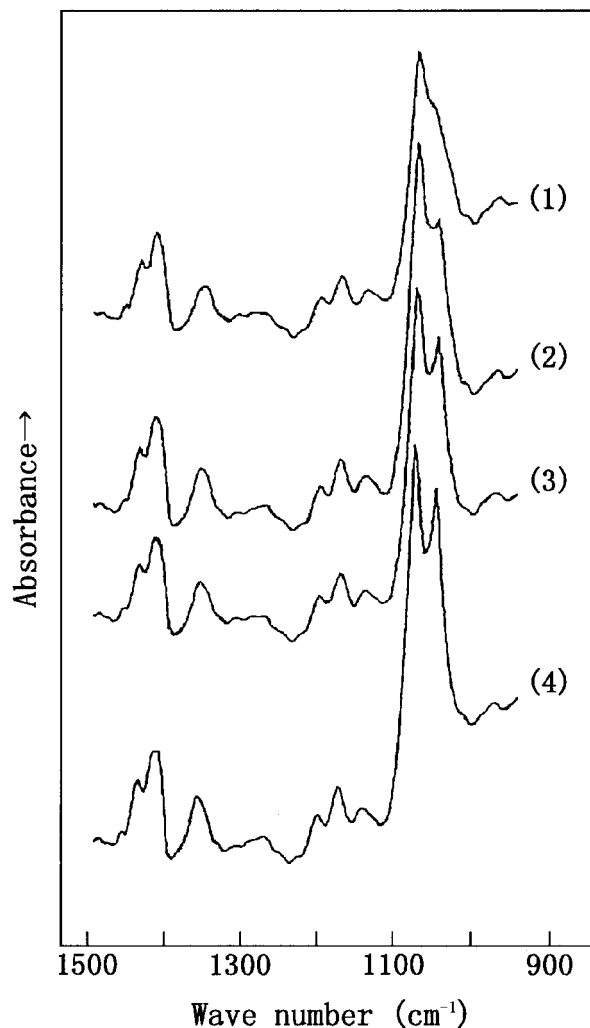


Figure 3 Infrared spectra of fresh and stored 91 : 5 : 4 VDC-AN-MA terpolymer latexes in the dispersed state: (1) fresh, (2) stored for 21 weeks, (3) stored for 41 weeks, and (4) stored for 49 weeks.

latexes exhibited no change with redialysis, although pH rose to above that of fresh latex and electric conductance decreased to below that of fresh latex. These results indicate that coagulation of latex particles and change of electric properties of latex aqueous phase are of little significance to the MFFT rise of VDC-AN-MA terpolymer latex during storage in this study.

Relative Crystallinity of Polymer

Figure 3 shows infrared absorption spectra of fresh 91 : 5 : 4 VDC-AN-MA terpolymer latex and those stored for 21, 41, and 49 weeks, in the dispersed state by the liquid cell method. An absorp-

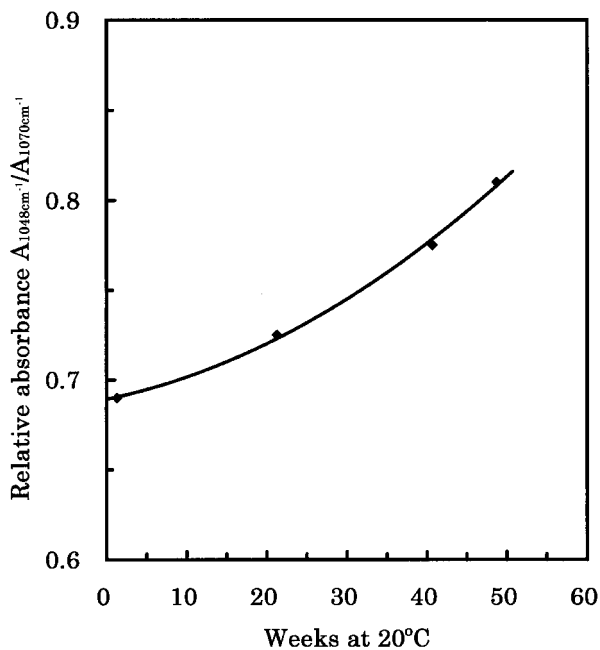


Figure 4 Effect of storage on relative infrared absorbance of 91 : 5 : 4 VDC-AN-MA terpolymer latex in the dispersed state.

tion peak at 1048 cm^{-1} , which is characteristic of crystalline VDC polymer,¹²⁻¹⁴ was observed in the spectra of the latexes stored for 21, 41, and 49 weeks, and the peak became more pronounced as

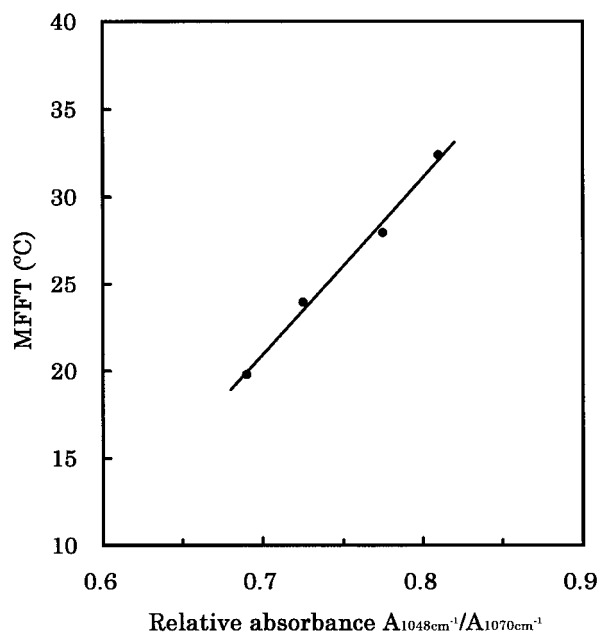


Figure 5 Relationship between relative infrared absorbance and MFFT of fresh and stored 91 : 5 : 4 VDC-AN-MA terpolymer latexes.

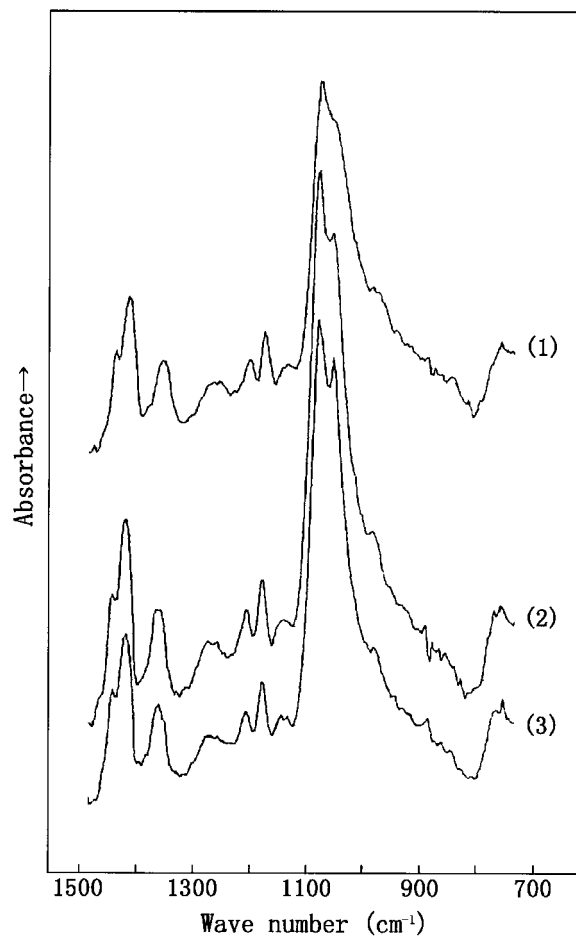


Figure 6 Infrared spectra of lyophilized polymer from fresh and stored 91 : 5 : 4 VDC-AN-MA terpolymer latexes: (1) fresh, (2) stored for 21 weeks, and (3) stored for 41 weeks.

storage periods increased. In the spectrum of the fresh latex, absorption at 1048 cm^{-1} appeared as a discernible shoulder to the side of the peak at 1070 cm^{-1} . In Figure 4, infrared absorbance at 1048 cm^{-1} in the dispersed state normalized with that at 1070 cm^{-1} , which is not associated with polymer crystallinity (relative absorbance: $A_{1048\text{ cm}^{-1}}/A_{1070\text{ cm}^{-1}}$) is plotted against storage period. Relative absorbance $A_{1048\text{ cm}^{-1}}/A_{1070\text{ cm}^{-1}}$ increased with storage, and its slope in the initial period was smaller than that in the last period, similar to the curve of MFFT plotted against storage period. The relationship between MFFT and relative infrared absorbance $A_{1048\text{ cm}^{-1}}/A_{1070\text{ cm}^{-1}}$ for fresh and stored latexes in the dispersed state was approximately linear (as shown in Fig. 5).

Powder polymers obtained by lyophilization of

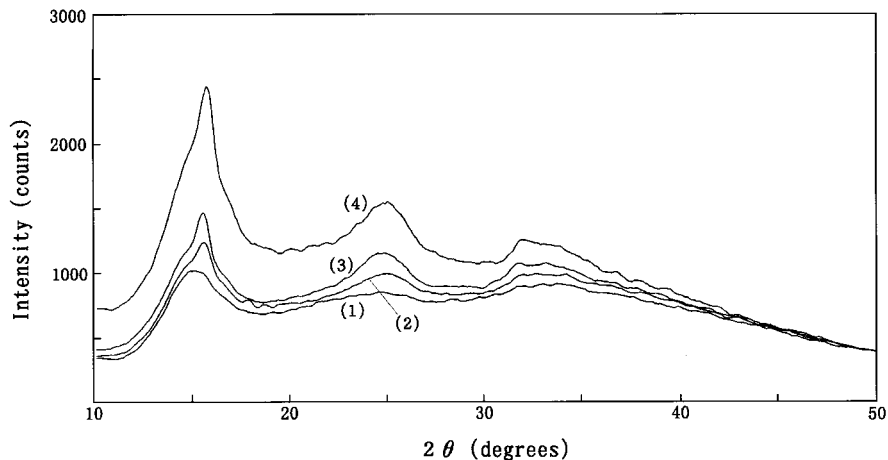


Figure 7 Wide-angle X-ray diffraction patterns of lyophilized powder polymer from fresh and stored 91 : 5 : 4 VDC-AN-MA terpolymer latexes: (1) fresh, (2) stored for 21 weeks, (3) stored for 41 weeks, and (4) stored for 49 weeks,

fresh and stored 91 : 5 : 4 VDC-AN-MA terpolymer latexes were investigated for relative crystallinity by infrared spectroscopy¹²⁻¹⁶ and X-ray diffraction measurement¹⁷ to indirectly estimate crystallinity of particle polymer in the dispersed state. Figure 6 shows the infrared spectra of lyophilized polymers from fresh VDC-AN-MA terpolymer latex and those stored for 21 and 41 weeks. Similar to results in the dispersed state, an absorption peak at 1048 cm^{-1} was observed in the spectra of polymer from the latexes stored for 21 and 41 weeks, and the peak became more pronounced as storage increased. In the spectrum of polymer from the fresh latex, absorption at 1048 cm^{-1} appeared as a discernible shoulder to the side of the peak at 1070 cm^{-1} . Figure 7 shows the wide-angle X-ray diffraction patterns of lyophilized polymers from fresh VDC-AN-MA terpolymer latex and those stored for 21, 41, and 49 weeks. All diffraction patterns exhibited three definitive peaks at 2θ of 15° , 25° , and 33° , to 38° . Diffraction peaks grew more pronounced with latex storage time; that of polymer from the latex stored for 49 weeks

being sharpest and that of polymer from fresh latex being most subtle.

Results of infrared absorption of latex and lyophilized polymer and X-ray diffraction of lyophilized polymer indicate that crystallization of polymer increased with storage in the dispersed state. The relationship between crystallinity and storage period correlated to that between MFFT and storage period in this study.

Properties of Latex Cast Film

Table III shows relative infrared absorbance $A_{1048\text{ cm}^{-1}}/A_{1070\text{ cm}^{-1}}$ and tensile properties of cast film from the fresh 91 : 5 : 4 VDC-AN-MA terpolymer latex before and after aging at 40°C for 48 h. Relative absorbance $A_{1048\text{ cm}^{-1}}/A_{1070\text{ cm}^{-1}}$ increased from 0.74 to 0.96 with aging, indicating that crystallinity of polymer of the film increased. Young's modulus increased by a factor of 6, from 0.3 to 1.8 kg cm^{-2} , and elongation decreased by a factor of 12, from 240% to 20%, with aging. The cast film thus became extremely hard as crys-

Table III Effect of Film Aging on Relative Infrared Absorbance and Tensile Properties of Cast Film from Fresh 91 : 5 : 4 VDC-AN-MA Terpolymer Latex

| Aging | Relative Infrared Absorbance ($A_{1048\text{cm}^{-1}}/A_{1070\text{cm}^{-1}}$) | Tensile Properties | |
|-----------------------------|---|--|-------------------|
| | | Young's Modulus (kg cm^{-2}) | Elongation (%) |
| None | 0.74 | 0.3 | 240 |
| 40°C for 48 h | 0.96 | 1.8 | 20 |

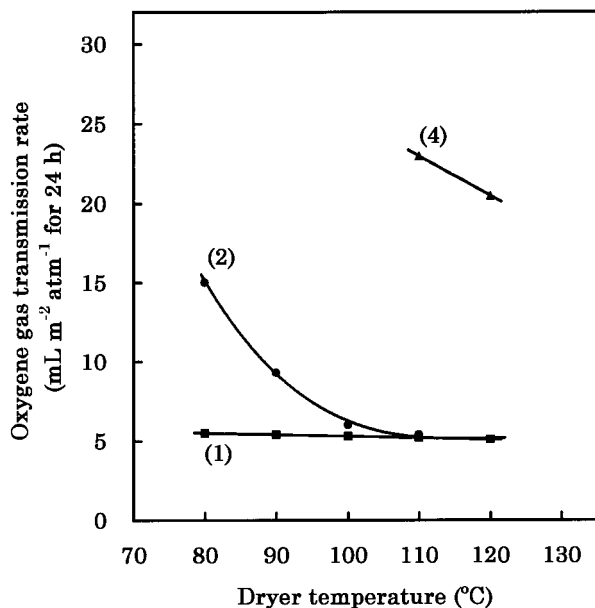


Figure 8 Effect of drying air temperature of coating machine on oxygen gas transmission rate of polyester film coated with fresh and stored 91 : 5 : 4 VDC-AN-MA terpolymer latexes: (1) fresh, (2) stored for 21 weeks, and (4) stored for 49 weeks.

tallinity of polymer increased with aging. These results suggest that the MFFT rise of 91 : 5 : 4 VDC-AN-MA terpolymer latex in this study was probably caused by increasing hardness of polymer particles as crystallinity of polymer in the dispersed state increased with storage.

Oxygen Gas Transmission Rate

Figure 8 shows oxygen gas transmission rates of polyester films coated with fresh 91 : 5 : 4 VDC-AN-MA terpolymer latex (20°C MFFT) and latexes stored for 21 weeks (24°C MFFT) and 49 weeks (32°C MFFT) against drying air temperature. Films coated with fresh latex exhibited excellent oxygen gas barrier properties over the range of drying air temperatures from 80 to 120°C, which are used industrially for high-barrier coatings. Latex stored for 21 weeks exhibited poor gas barrier properties when drying air temperatures were below 90°C, indicating that care must be taken during industrial coating using such latex. The gas barrier properties of latex stored for 49 weeks were extremely poor, making this material unsuitable for use as a barrier coating.

CONCLUSIONS

Direct measurement of infrared absorption of VDC-AN-MA terpolymer latex was useful for characterization of the polymer of latex particles in the dispersed state with respect to relative crystallinity. MFFT of 91 : 5 : 4 VDC-AN-MA terpolymer latex rose with storage at 20°C, and latex stored for long periods yielded coatings with insufficient barrier properties. Results of infrared absorption of latex and lyophilized polymer, and X-ray diffraction of lyophilized polymer suggested that the MFFT rise of the VDC-AN-MA terpolymer latex during storage was probably caused by a hardening of the particles of the latex due to increasing crystallinity of the polymer of particles in the latex state.

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