An Investigation into the Mechanical and Transport Properties of Aqueous Latex Films: A New Hypothesis for the Film-Forming Mechanism of Aqueous Dispersion System

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The effects of plasticizer, physical aging, and film-forming temperature on the mechanical and transport properties of films formed from aqueous dispersions of ethylcellulose latex were investigated. The water vapor permeability of latex films was found to decrease with diethyl phthalate to a minimum value and then to increase with diethyl phthalate at higher concentrations. Because of the decrease in free volume and the further coalescence of particles of latex polymer films in the physical aging range, the creep compliance of latex films decreased with physical aging time. Within 60 to 100°C, the film-forming temperature was found to have no effect on the mechanical and transport properties of Aquacoat films. However, since many pinholes formed in the latex films when the film-forming temperature was above 100°C, the water vapor permeability of latex films was higher than that of latex films formed between 60 and 100°C. The formation of films from aqueous latex dispersions is suggested to proceed gradually from the top to the bottom of the latex dispersion in this study.

INTRODUCTION

Aqueous film coating techniques are of current interest in the pharmaceutical industry. The aqueous, colloidal latex, and pseudolatex dispersions provide new coating capabilities for total water-based systems at a time when solvent coating has become unattractive from cost, environmental, and safety concerns (1). Aqueous latex dispersions of polymers are produced by emulsions polymerization and contain polymers in the form of spherical latex particles up to about 1 μm in diameter dispersed in water (2). For successful formation of an aqueous latex film, the minimum film-forming temperature (MFFT) must be determined, since this is the lowest temperature at which a polymer emulsion forms a continuous film. The methods and apparatus for determining the minimum film forming temperature of polymer emulsions have been studied by many investigators (3–7).

The effects of plasticizer and polymer ratio on the permeation of chlorpheniramine maleate through aqueous dispersion Eudragit RS30D and RL30D films was studied by Ho and Suryakusumn (8). They found that the increasing concentration of RS30D increased the film strength and decreased the permeation rate of chlorpheniramine maleate. Films containing 20% diethyl phthalate showed the slowest permeation rate of chlorpheniramine maleate, while films containing either 25 or 15% diethyl phthalate gave higher permeation rates. Wald *et al.* (9) found that the diffusion cell system appeared to be a convenient and efficient method for predicting the permeation rate of drugs through Aquacoat and Surelease membranes. The effect of additives on the properties of an aqueous film coating was studied by Porter (10), who found that the indiscriminate use of plasticizers was contraindicated, particularly when considering the mechanical properties of latex film. Osmotic water transport through cellulose acetate latex membranes was studied by Bindschaedler *et al.* (11). They found that the permeabilities of these films varied over a wide range that depended on the physicochemical properties of the plasticizer and its initial concentration in the polymer latex and on the conditions for coating (temperature, rate of spraying, and drying duration).

Guo and co-workers (12) have studied the effects of physical aging on the water permeation of cellulose acetate and ethylcellulose, the mechanical properties of ethylcellulose, and the dissolution property of hydroxypropyl methylcellulose phthalate. The water permeabilities of cellulose acetate and ethylcellulose and the dissolution rate of hydroxypropyl methylcellulose phthalate all were found to decrease with physical aging time after being quenched from above the glass transition temperatures to sub-T_g temperatures. The effect of physical aging on the morphological changes in latex films was studied by Bradford and Vanderhoff (13,14). Although the clarity of latex films is often considered evidence of the complete coalescence of the latex particles, since the further gradual coalescence continues with time, the physical properties of latex films usually appear to improve with physical aging.

In this study, we investigated the effects of plasticizer and physical aging on the mechanical and transport properties of aqueous based ethylcellulose membranes. The film-forming mechanism of aqueous latex dispersions and the effect of the film forming temperature on the properties of latex films were studied as well.

MATERIALS AND METHODS

Preparation of Free Films

Ethylcellulose (Sigma Chemical Company; Lot 104F-0689; ethoxy content, 48.5%; viscosity, 45 cps) and diethyl phthalate (Sigma Chemical Company; Lot 88F3507; FW 222.2; purity, 99%) were dissolved in 1:4 (v/v) acetone/methylene chloride mixtures at a concentration of 4% (w/v). Aquacoat (ethylcellulose aqueous dispersion NF; FMC Corporation; Lot J9461; moisture content, 70%; ethylcellulose ethoxy content, 48.3%) and diethyl phthalate were mixed together and put on the shaker for 2 days. The diethyl phthalate levels in the dry ethylcellulose and Aqua-

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coat films were varied from 0 to 40% (w/w). To form films, 2 mL of ethylcellulose solutions was poured into aluminum evaporating pans and covered with an inverted funnel to prevent solvent removal by convection at room temperature. Two milliliters of the mixture of Aquacoat and diethyl phthalate was poured into aluminum evaporating pans and placed into an oven. The temperature of the oven was set in the range of from 35 to 140°C. After drying, the ethylcellulose and Aquacoat free films were lifted off the pans and cut into 15 × 2-mm rectangular pieces and 1.5- or 2.0-cm diameter circular pieces. The film samples were stored in a desiccator for a minimum of 1 week. The micrographs of Aquacoat films were taken by a Diaphoat-TMD microscope (Nikon Inc., MI). The film-forming times for Aquacoat, the time for Aquacoat dispersion (plasticized by 40%, w/w, diethyl phthalate) to form a homogeneous polymer film, and the evaporation times of water (70%, same amount of Aquacoat used in film-forming time tests) were measured (the time for water totally evaporate) in an oven at different temperatures (from 32 to 140°C).

Permeability Measurements

Serum bottles (50 ml, 1.3-cm diameter) were used to test the water vapor transmission of Aquacoat films. The bottles contained 30 mL of supersaturated sodium chloride solution and excess sodium chloride, which gave an internal relative humidity of 75.28% at 25°C. The polymer films were placed over the opening of the bottles, and rubber rings were put over the films, then metal seals. The bottles were sealed by using a crimper, and the original weight of each bottle was measured. The bottles were put into a desiccator, which was placed into a constant 25°C water bath. Periodically, the weight of the bottles was measured, and the water vapor permeability coefficient was calculated from

$$P_{wv} = -\frac{dM}{dt}\left(\frac{h}{A \cdot \Delta p}\right) \tag{1}$$

where P_{wv} is the water vapor permeability coefficient, dM/dt is the rate of weight change of the serum bottles with time, h is the thickness of polymer film, A is the area of the opening of the serum bottle, and Δp is the vapor pressure gradient across the film.

The sucrose permeability tests of Aquacoat free films were performed in a standard diffusion cell system at 25°C. The system included a MGW Lauda M3 water circulator (Messgerate-Werk Lauda, Lauda-Konigsofen, West Germany) and 3 mL side-by-side diffusion cells (Crown Glass Co., Vineland, NJ). Before each permeability experiment was performed, the thickness of the film was measured. Two 3-mm Silastic gaskets were placed on each side of the circular film and placed between each half of a diffusion cell. The cells were then clamped to ensure no leakage. In the donor side of the system a saturated sucrose solution in the presence of excess sucrose was placed, while distilled water was added to the receiver side. In order to reduce boundary layer effects, stirring bars were added into both cells. The water in the donor side was monitored at 200 nm using a Masterflex pump drive (Cole Parmer Instruments, IL) in conjunction with a Lambda 3B UV/VIS spectrophotometer (Perkin

Elmer Instruments, Norwalk, CT). The sucrose permeability of Aquacoat films could be calculated from

$$P_s \cdot A \cdot \Delta C = \frac{dM}{dt} \tag{2}$$

where P_s is the sucrose permeability of the Aquacoat films, A is the surface area of the film that contacts with solution, ΔC is the sucrose concentration difference between the two diffusion cells, and dM/dt is the rate of weight change of sucrose with time in the receiver cell.

Mechanical Experiments

Creep compliance tests and the glass transition temperature measurement of ethylcellulose and Aquacoat film samples were performed and measured with a Mettler TMA40 thermomechanical analyzer (Mettler Instruments, Hightstown, NJ). Film samples were fixed between two stainless-steel clamps, with emery paper placed between the clamp and the sample to avoid slippage. Then the samples were placed in a dry nitrogen environment in the TMA40 and the creep compliance behavior was measured at 25°C. For the aging tests, the Aquacoat film samples were equilibrated at 5°C above the glass transition temperatures for 15 min. Following this, the samples were quenched to 25°C and annealed at this temperature for varying times. After elapsed times of 1, 3, 5, 10, 20, and 30 hr, the creep compliance behavior was measured, the creep compliance being the ratio of the relative creep extension to the applied stress. The glass transition temperatures of film samples were measured in the TMA40.

RESULTS AND DISCUSSION

The effects of diethyl phthalate on the glass transition temperatures of ethylcellulose and Aquacoat films are shown in Fig. 1. The glass transition temperatures of both the ethylcellulose and the Aquacoat films decrease with increasing diethyl phthalate weight ratio. Probably because of the presence of cetyl alcohol and sodium lauryl sulfate in the Aquacoat, the glass transition temperature of Aquacoat is lower than that of ethylcellulose at a low diethyl phthalate level. The glass transition temperatures of both the ethylcellulose and the Aquacoat are approaching the same value when the plasticizer reaches higher levels, since the effects of cetyl alcohol and sodium lauryl sulfate on the glass transition temperature of Aquacoat films become relatively insignificant.

The effect of physical aging on the 500-sec creep compliance of Aquacoat films (plasticized by 15%, w/w, diethyl phthalate) is shown in Fig. 2. The creep compliance was found to decrease with physical aging time. The gradual approach toward thermodynamic equilibrium during physical aging has been found to decrease the free volume of the polymer, and this decrease in free volume is accompanied by a decrease in the transport mobility, with concomitant changes in those properties of the polymer that depend on it (15–20). Many investigators have postulated that latex particles would never undergo complete coalescence because of the incompatibility of the surface groups with the particle interior, and the structure has been thought to be the result
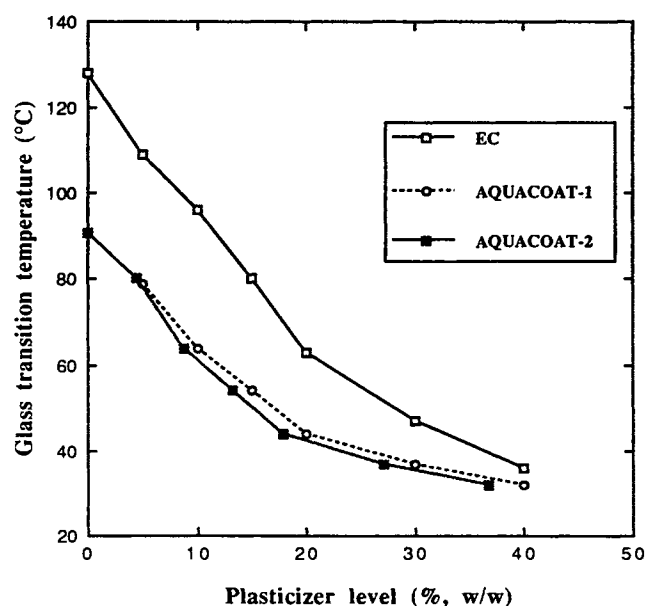
Fig. 1. The effect of diethyl phthalate on the glass transition temperature of ethylcellulose organic solvent films (□) and Aquacoat free film. Aquacoat-1 (○) represents the plasticizer level based on the total amount of Aquacoat, and Aquacoat-2 (■) represents the plasticizer level based on the solid content in Aquacoat.

of the original latex particles only partially coalescing during film formation (21,22). The degree of coalescence of latex particles is known to increase with aging time, and any degree of incomplete latex particle fusion will affect the properties of the film, such as mechanical strength and permeability characteristics (13,14,21,23,24). Therefore, the decrease in creep compliance of Aquacoat films could be caused by the decrease in free volume and the further gradual coalescence of latex particles in the latex films during physical aging range.

The effects of diethyl phthalate and the film-forming temperature on the water vapor permeability of Aquacoat
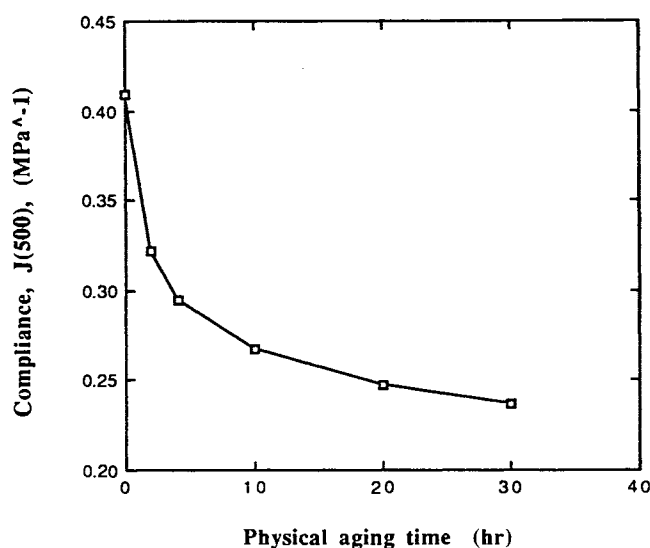
are presented in Fig. 3. The water vapor permeability of Aquacoat was found to decrease with increasing diethyl phthalate level to 20% diethyl phthalate and then increase with higher diethyl phthalate concentration. The water vapor permeability of Aquacoat formed at 140°C was higher than that formed at 100°C at all plasticizer levels. The influence of plasticizer content on the coalescence conditions of the ethylcellulose latex films was investigated by Arwidsson et al. (25). They found that film formation from an aqueous dispersion was totally different from that from an organic solution of the polymer, and to obtain complete coalescence, films from the aqueous dispersion must contain an adequate amount of plasticizer. For example, the fracture stress of Aquacoat ECD-30 (ethylcellulose aqueous latex) plasticized by 30% triethyl citrate was higher than that of Aquacoat ECD-30 plasticized by 12% triethyl citrate. In agreement with the result of Ho and Suryakusumn (8), 20% diethyl phthalate could be the adequate amount of plasticizer for obtaining complete coalescence of Aquacoat films. Higher amounts of plasticizer only dilute the latex film system and increase the water vapor permeability of Aquacoat films.

Micrographs of Aquacoat films formed at two different temperatures and containing different amounts of diethyl phthalate are shown in Fig. 4. Many small voids or pinholes were found in the Aquacoat films formed at 140°C, but not in those formed at 100°C. However, the plasticizer content had relatively little effect. The existence of these voids or pinholes is probably the factor that caused the water vapor permeability of Aquacoat films formed at 140°C to be higher than those of Aquacoat films formed at 100°C.

The effect of film-forming temperature (60 to 140°C) on the water vapor permeability, the 10-sec creep compliance, and the sucrose permeability of Aquacoat (plasticized by 40%, w/w, diethyl phthalate) are shown in Table I. No significant difference was found in the water vapor permeability, creep compliance, and sucrose permeability of Aquacoat films formed within the range of 60 to 100°C. Hence, the

Physical aging time (hr)

Fig. 2. The effect of physical aging on the 500-sec creep compliance of Aquacoat free films (plasticized by 15% diethyl phthalate).
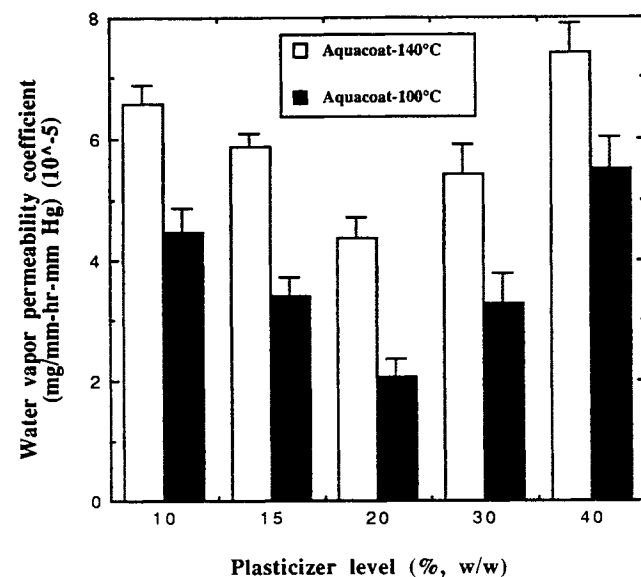

Plasticizer level (%, w/w)

Fig. 3. The effects of diethyl phthalate on the water vapor permeability of Aquacoat free films. (■): the Aquacoat films formed at 100°C; (□): the Aquacoat films formed at 140°C.
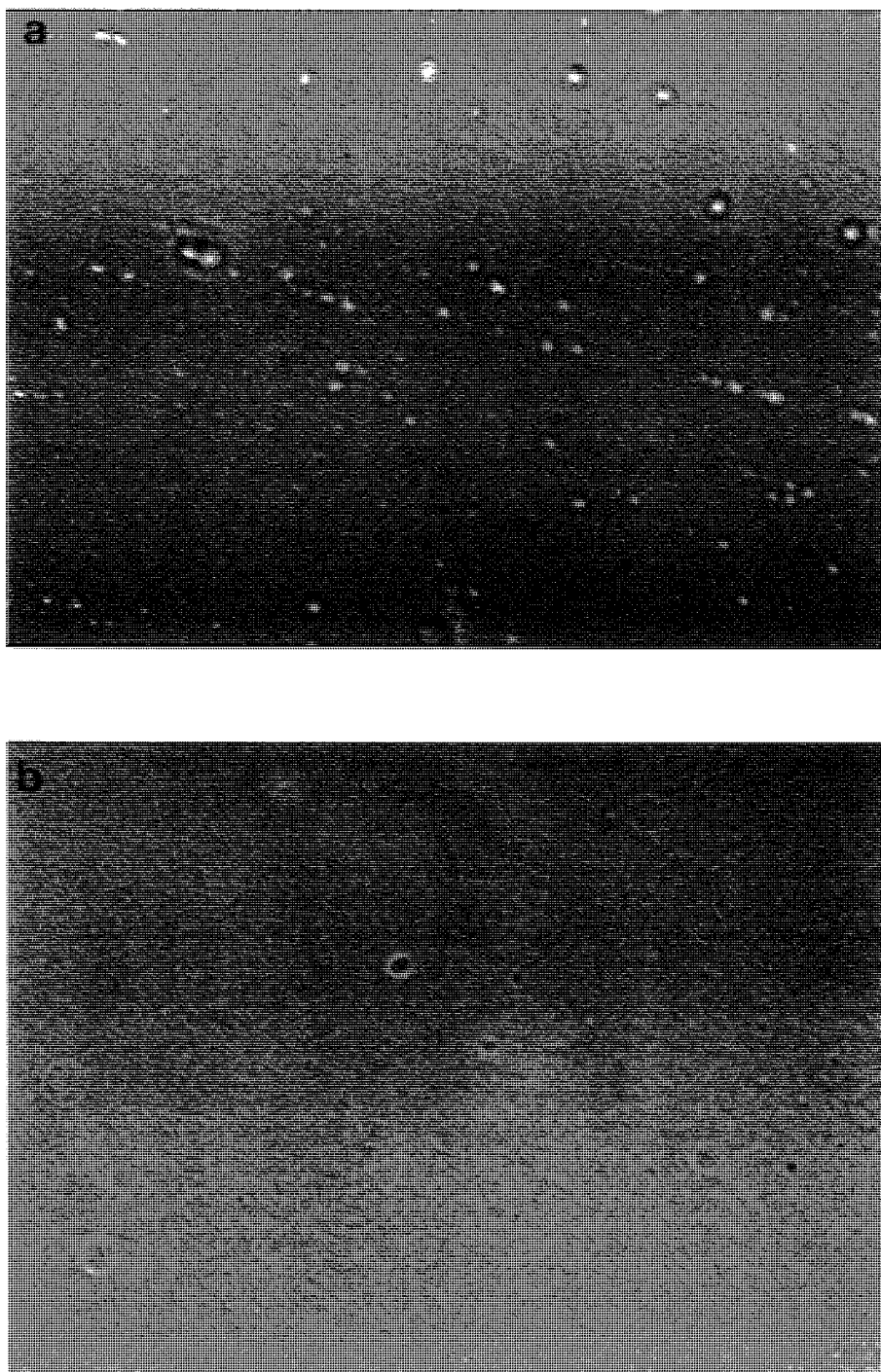
Fig. 4. The micrographs of Aquacoat free films. (a) Aquacoat film plasticized by 10% diethyl phthalate and formed at 140°C; (b) Aquacoat film plasticized by 10% diethyl phthalate and formed at 100°C.

film-forming temperature has no significant effect on the mechanical or transport properties of Aquacoat films within this range (at least for 40% plasticized Aquacoat films).

The effects of temperature on the time for water evaporation and for film-forming of Aquacoat (plasticized by 40%, w/w, diethyl phthalate) are presented in Fig. 5. The times for water evaporation and for forming a continuous Aquacoat film are almost the same at all film-forming tem-

peratures. Hence, the evaporation of water and the coalescence of latex particles can be assumed to occur simultaneously. A diagram for film formation from a latex at temperatures below 100°C is represented in Fig. 6. Since the evaporation of water and the coalescence of latex particles appear to occur at the same time, a totally coalesced film would seem to form on the top of the aqueous latex dispersion. The water beneath the film will continue to diffuse
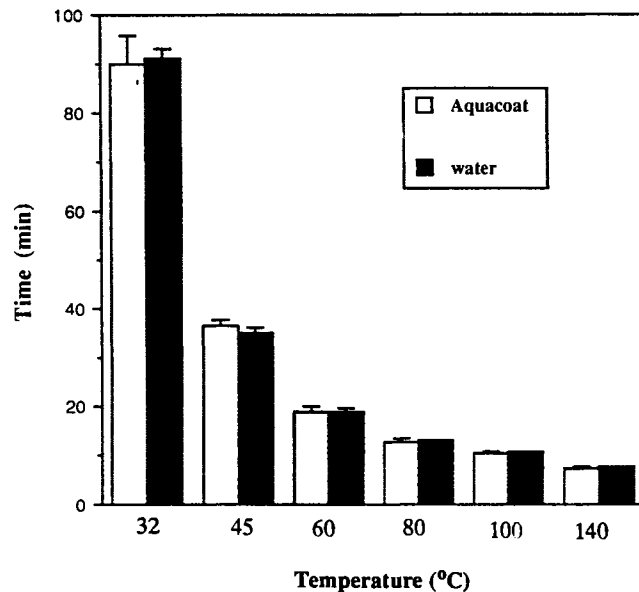
Table I. The Effects of Film-Forming Temperatures (°C) on the Water Vapor Permeability (WVP) (mg/mm-hr-mm Hg, 10^{-5}), Sucrose Permeability (SP) (cm/sec, 10^{-6}) and the 10-sec Creep Compliance (CC) (MPa^{-1}) of Aquacoat Free Films (Plasticized by 40% Diethyl Phthalate)

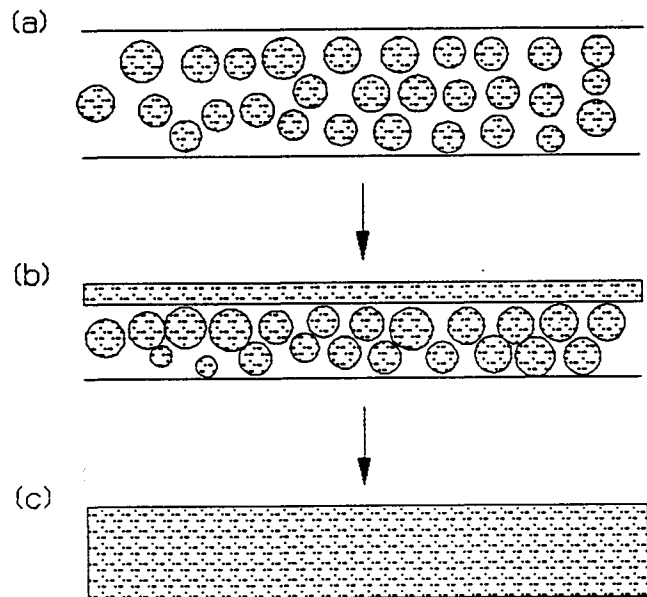| Temp.	WVP	SP	CC
60	5.67 ± 0.60	6.78 ± 0.60	0.637 ± 0.004
70	5.70 ± 0.80	6.67 ± 0.50	0.640 ± 0.003
80	5.50 ± 0.50	6.82 ± 0.60	0.635 ± 0.003
100	5.52 ± 0.50	6.62 ± 0.55	0.638 ± 0.004
140	7.40 ± 0.50		

through the top film, and the latex particles will gradually coalesce from the top to the bottom of the aqueous dispersion. A diagram for latex film formation at temperatures above 100°C is shown in Fig. 7. The vapor pressure and rate of evaporation water increase with film-forming temperature, and when the film-forming temperature is above 100°C, the water vapor pressure under the top film will exceed 1 atm and water vapor will burst through the top film and leave voids and pinholes. Therefore, many small voids and pinholes were found in the Aquacoat films formed at 140°C.

CONCLUSION

A hypothesis for latex film formation is that the upper surface of the latex film forms initially, with the film progressively drying from the top to the bottom. Since a decrease in free volume accompanies the further gradual coalescence of latex particles in the latex films because of physical aging, the creep compliance of Aquacoat films decreases with time. Because an adequate amount of plasticizer is necessary for obtaining a completely coalesced latex film, the water vapor permeability of latex films is found to
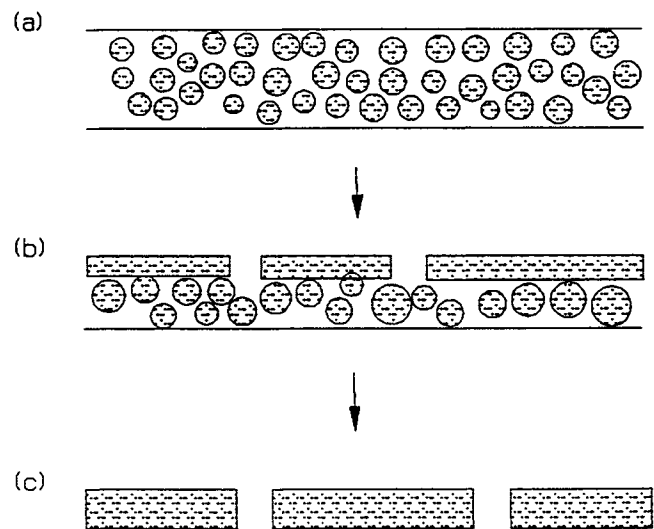

Fig. 6. The diagram for aqueous latex film forming at temperatures below 100°C. (a) Latex particles disperse in the aqueous phase; (b) a thin film is formed at the top of the dispersion system and water vapor continuously diffuses through the top film; (c) a continuous film is formed.

decrease with diethyl phthalate to a minimum. At a greater concentration of diethyl phthalate, the diethyl phthalate only dilutes the latex film system and increases the water vapor permeability of latex film. The film-forming temperature was found to have no effect on the mechanical and transport properties of Aquacoat films when the film-forming temperature was in the range of 60 to 100°C. For film-forming temperature above 100°C, the film may develop pinholes from the rapid escape of water vapor.

Fig. 5. The effect of temperature on the film-forming time of Aquacoat (plasticized by 40% diethyl phthalate) (□) and the evaporation time of water (■).

Fig. 7. The diagram for aqueous latex forming at temperatures above 100°C. (a) Latex particles disperse in the aqueous phase; (b) a thin film is formed at the top of the dispersion system and water vapor bursts out from the top film; (c) a continuous film containing many voids or pinholes is formed.

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