

Mechanically strong films produced from cellulose acetate latexes

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Mechanically strong films, comparable with those obtained from organic solutions, can be produced from cellulose acetate latexes, a new type of dispersion, both by casting and spraying. The prerequisite conditions for high strength, which include choice of water-soluble plasticizers possessing some degree of volatility, are discussed.

The handling of aqueous latex coating entails extensive trial and error before films of reasonable strength can be prepared. This is particularly true for dispersions of cellulosic derivatives produced by direct emulsification of the polymer (Banker 1980, 1982; Heinz 1982), such as Aquacoat and Aquateric (FMC Corp.), which are, respectively, an ethyl cellulose and a cellulose acetophthalate latex. Due to the high glass transition temperature of this kind of polymer, these latexes require incorporation of a plasticizer to yield continuous films (Bindschaedler et al 1983).

We encountered difficulties when we tried to prepare water-permeable membranes from cellulose acetate latexes (Bindschaedler et al, unpublished observations) and, subsequently, coatings for osmotic pumps (Bindschaedler et al 1986). These were probably due to the high temperature range of second-order transitions of cellulose acetate (Mandelkern & Flory 1951; Russel & Van Kerpel 1957) and the viscous character of its solutions (Johnston & Sourirajan 1974). The amounts of plasticizer (10–40%) ordinarily added were found to be inefficient in plasticizing cellulose acetate dispersions, so much larger amounts of plasticizer had to be admixed. In addition, the use of more hydrophobic conventional plasticizers such as dimethyl phthalate, which although they are able to dissolve CA, produce weak membranes, that crack or crumble in contact with water. To circumvent this difficulty, we tested some hundred plasticizing agents before our attention turned toward a promising set of water-miscible additives.

The aim of this paper is to show that cellulose acetate latexes can yield coatings or cast films nearly as resistant as those obtained from organic solutions, providing skilful choice is made of plasticizers and processing conditions.

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MATERIALS AND METHODS

Materials

Latexes were prepared from cellulose acetate with a degree of acetylation of 39.8% (CA 398-10, Eastman Kodak, Rochester, NY, USA) according to a procedure described elsewhere (Bindschaedler et al 1983, 1985). The surfactant stabilizing the latexes was analytical grade sodium dodecyl sulphate (Fluka, Buchs, Switzerland).

The plasticizers (diacetin, diethyl tartrate, ethylene glycol diacetate, ethylene glycol monoacetate, triacetin, triethyl and trimethyl phosphates) were supplied by Fluka. Their degree of purity was at least 97%, except diacetin and ethylene glycol monoacetate which were technical grade chemicals containing a high proportion of the fully acetylated components, triacetin and ethylene glycol diacetate, respectively. Gas chromatography of ethylene glycol monoacetate showed the following composition: ethylene glycol monoacetate (50%), ethylene glycol diacetate (46%), ethylene glycol (4%).

Film preparation

(a) *Cast films with different plasticizers.* The CA latex used had a mean particle size of 340 nm and a polydispersity index of 4, as measured with the Coulter Nano-Sizer (Coulter Electronics Ltd, Harpendon, UK). Its sodium dodecyl sulphate content was 1.9% by weight of CA. The casting blends contained 160% plasticizer by weight of CA, except those with ethylene glycol monoacetate (320%). The percentage of CA in the blends was 6.0%. To avoid coagulation, a predetermined amount of water was first added to the water-soluble plasticizer and the concentrated latex (usually 30–40% solids) was then slowly poured into the plasticizer solution while stirring. Each sample contained 0.5 g CA which corresponded to 8.33 g total mixture. The blends were cast on glass plates to which siliconized glass

rings of 13.2 cm inner diameter were fitted. The drying was performed during 54 h in an air-stream oven (Salvis TSW 270-E, Lucerne, Switzerland) at 60 °C.

(b) *Films prepared by spraying a cellulose acetate latex onto potassium chloride discs.* Hard potassium chloride discs of approximately 2 g weight were manufactured by direct compression (flat punches of 20 mm diameter fitted into an eccentric tableting machine Korsch EK-O, Korsch Maschinenfabrik, Berlin, FRG) of potassium chloride crystals (Siegfried, Zofingue, Switzerland) without any further additive. Their crushing strength, as measured with a Heberlein tester 124 (Schleuniger, Zurich, Switzerland) exceeded 100 N. The discs (80 g) were mixed with 190 g tablets (8 mm diameter) of microcrystalline cellulose (Avicel PH-101, FMC, Philadelphia) in a fluidized bed column (Aeromatic Ktre-1, Muttentz, Switzerland). Owing to these Avicel tablets being much lighter, the heavy discs were maintained in suspension. The flow rate of air was 130 m³ h⁻¹ and the air pressure at the nozzle was fixed to 1.5 kg cm⁻² (rate of supply of coating liquid: 2.7 to 32.0 mL min⁻¹). The spraying blends contained 30 g CA and were prepared, like the casting mixtures, from the above mentioned latex with 1.9% sodium dodecyl sulphate. The percentage of CA was 7.14% with triethyl phosphate as a plasticizer, 7.35% with ethylene glycol monoacetate and 8.33% with diethyl tartrate. For some batches with 320% ethylene glycol monoacetate, the amount of surfactant was varied (0.5, 2.6 and 5.0% by weight of CA, respectively) by adding sodium dodecyl sulphate to a latex containing initially 0.5% of this additive (mean particle size: 334 nm). This was done to investigate the effect of this factor on the mechanical properties of the films.

Assessment of mechanical properties

Cast samples were submitted to tensile trials using an Instron tester model 1114 (Instron, High Wycombe, Bucks, UK). The films were cut in rectangles (length 70–76 mm, width 20–26 mm, thickness 30–150 μm), the distance between the grips was 50 mm and the elongation rate was 0.5 mm min⁻¹. For each sample, the thickness was taken as the mean of 15 to 20 random measurements.

Membranes prepared by spraying a CA latex onto potassium chloride discs (films of section b) were detached from their substrate and cut out in micro-test pieces after insertion in a brass template shown in Fig. 1. The micro-test pieces were tested with an Instron 1122, the elongation rate, V_t , being

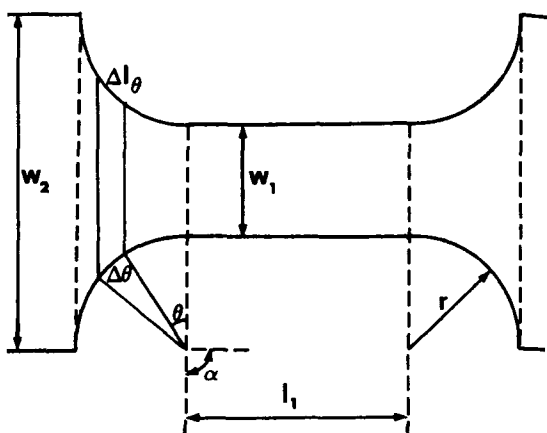


FIG. 1. Template of micro-test pieces. $l_1 = 5$ mm, $w_1 = 5$ mm, $w_2 = 10$ mm, $r = 2.5$ mm.

0.5 mm min⁻¹. Since the length l_1 of the central part of the micro-test pieces was short (5 mm), a correction was required to calculate the elasticity modulus. Thus, the elongation rate of the central part, V_1 , was determined from:

$$V_t = l_1 \dot{\epsilon}_1 + 2rw_1 \dot{\epsilon}_1 \int_0^{\alpha = \pi/2} \frac{\cos \theta d\theta}{w_1 + 2r(1 - \cos \theta)} \quad (1)$$

where V_t is the total elongation and the product $l_1 \dot{\epsilon}_1$ is equal to V_1 , $\dot{\epsilon}_1$ being the strain rate. By numerical integration, $\dot{\epsilon}_1 = 0.0541$ min⁻¹, $V_1 = 0.2706$ mm min⁻¹ and the modulus of elasticity was deduced from

$$E = \frac{\sigma}{\epsilon} = \frac{F l_1}{S \Delta l_1} = \frac{F l_1 V_t}{S \Delta l_1 V_1} \quad (2)$$

where σ is the tensile strength, ϵ the strain, F the force, S the cross-sectional area of the central segment of the test pieces and Δl_1 and Δl_t the central part and total elongation, respectively. All values of the elasticity modulus were calculated from the linear part of the traction curves. Both for cast and sprayed formulations, 3 to 4 samples were assessed for each batch.

RESULTS AND DISCUSSION

Table 1 lists the mechanical properties of films cast from CA latexes containing plasticizers miscible with water (see Materials and methods, section (a)) together with the plasticizers' boiling points. Values are also given for a reference sample produced from an 5% acetic solution, dried at room temperature (20 °C) before being placed in an oven at 60 °C. In this series of films, samples plasticized with ethylene glycol monoacetate were nearly as strong as those resulting from evaporation of an acetic solution. More generally, very volatile additives such as

Table 1. Influence of the plasticizer on mechanical properties of cast cellulose acetate films.

Plasticizer	% Plasticizer by wt of CA in the latex	Plasticizer characteristics		Film properties	
		Boiling point (°C)	Solubility in water at 22 °C (% w/w)	$\sigma_u^a \pm s.d.$ (MPa)	$E^b \pm s.d.$ (MPa)
Diacetin	160	259	∞	24.6 ± 1.4	1865 ± 331
Diethyl tartrate	160	280	∞	37.6 ± 3.2	2260 ± 192
Ethylene glycol diacetate	160	190	15.8	49.0 ± 5.0	2802 ± 238
Ethylene glycol monoacetate	320	182	∞	51.3 ± 2.1	2852 ± 133
Trimethyl phosphate	160	193	∞	43.0 ± 2.8	2359 ± 103
5% Acetonic solution of CA	—	—	—	50.4 ± 9.1	2962 ± 173

^a Ultimate tensile strength.

^b Elasticity modulus.

ethylene glycol monoacetate and ethylene glycol diacetate yield films of high ultimate tensile strength and elasticity modulus ($\sigma_u > 47$ MPa; $E > 2600$ MPa). This may appear surprising when one remembers the initial plasticizer load in the latex which is as high as 320% of CA weight. At 60 °C however, the major part of the plasticizer evaporates from the incipient film. Hence, through careful selection of volatile plasticizers, we have a means of fulfilling two apparently contradictory requirements: high mechanical strength of films and extra high initial amounts of plasticizer. Yet, it should be emphasized that the activity of the plasticizer must be low enough to permit enrichment of the solvent mixture in plasticizer and not in water.

High boiling point additives such as diethyl tartrate and diacetin, give weaker membranes because these plasticizers are retained to a larger extent than very volatile ones. Yet, even in the latter case, the final plasticizer concentration is much lower than the initial one.

Table 2 shows the mechanical characteristics of membranes obtained by spraying a CA latex onto potassium chloride discs (see Materials and methods, section (b)) together with the conditions for coating. A comparison is also made with samples produced either by casting or spraying an organic solution of CA. The weight loss of leachable materials (essentially plasticizer and sodium dodecyl sulphate), shown in the last column of Table 2, was determined by immersing the membranes in pure water at 25 °C for 20 h and by weighing the dry samples before and after soaking (% weight loss = $100X$ (dry weight before - dry weight after)/(dry weight before)). In most instances, this parameter agrees within 5% or less with the nominal residual amount of plasticizer in the membranes, as assessed by gas chromatography or by testing membranes of known plasticizer content.

Examination of the values of tensile strength and elasticity modulus reveals the same trend as for cast samples. Ethylene glycol monoacetate is only weakly retained and thereby yields strong coatings. Films containing triethyl phosphate, a more permanent additive, are less resistant. Finally, formulations with diethyl tartrate exhibit still weaker properties. Note also that the residual amount of diethyl tartrate can easily be modulated by changing the processing conditions.

Although the plasticizer content of the membranes is the foremost factor in controlling film strength, other parameters are also involved. For example, the impact of the initial proportion of plasticizer in the spraying liquid becomes obvious when one considers the respective maximal tensile strength (34.9 and 53.0 MPa) of samples stemming from latex systems with 160 and 320% ethylene glycol monoacetate by weight of CA. A too low amount of plasticizer probably results in an inefficient welding of the particles. Similarly, a minimum alteration of rate of supply of coating liquid can induce considerable changes in the mechanical strength (compare batches with diethyl tartrate, spraying rates: 3.5 and 4.0 mL min⁻¹).

Table 2 also gives the values of tensile strength and elasticity modulus for micro-test pieces cut from films obtained by spraying or casting an organic solution of CA devoid of plasticizer. These values are not considerably higher than those relevant to latex films plasticized with ethylene glycol monoacetate, a clue to the high quality of the latter class of membranes. Furthermore, diethyl tartrate-containing latex and organic solvent formulations possess approximately the same strength at comparable loss of leachable materials.

For similar organic solvent formulations, values of elasticity modulus appear considerably lower for micro-test pieces (Table 2) than for rectangular

Table 2. Mechanical properties of membranes obtained by spraying a cellulose acetate latex onto potassium chloride discs and comparison with reference samples.

Plasticizer ^a	Conditions for coating				Properties of films			
	% Plasticizer by weight of CA in the coating liquid	% Sodium dodecyl sulphate by weight of CA	Exhaust air temp. (°C)	Rate of supply of coating liquid (mL min ⁻¹)	Thickness range (µm)	$\sigma_{\max}^b \pm s.d.$ (MPa)	$E^c \pm s.d.$ (MPa)	% Weight loss of leachable materials in water at 25 °C
Spraying a latex								
EGM	160	1.9	60	32.0	160–180	34.9 ± 0.3	1536 ± 34	14.25
EGM	320	1.9	60	6.0	220–260	53.0 ± 1.7	1673 ± 71	14.67
EGM	320	0.5	65	6.0	215–225	52.4 ± 1.4	2021 ± 124	14.12
EGM	320	2.6	65	6.0	230–280	55.2 ± 3.4	1975 ± 78	16.47
EGM	320	5.0	65	6.0	270–300	43.4 ± 2.0	1581 ± 37	20.37
TEP	160	1.9	65	9.0	240–270	23.0 ± 0.4	1149 ± 64	24.00
DET	160	1.9	60	3.5	310–360	15.3 ± 1.3	700 ± 45	31.45
DET	160	1.9	60	4.0	200–230	20.3 ± 2.1	765 ± 55	31.83
DET	120	1.9	50	2.7	330–350	7.2 ± 0.1	279 ± 8	38.95
Spraying of a 5% organic solution ((dichloromethane–ethyl acetate–methanol 60:25:15) w/w)								
—	—	—	30	15	225–285	64.7 ± 5.5	1948 ± 48	6.92
DET	42.85	—	30	15	253–380	23.0 ± 1.2	876 ± 74	30.36
DET	53.85	—	30	15	270–290	16.3 ± 0.4	707 ± 25	33.56
DET	66.66	—	30	10	291–383	6.9 ± 0.4	192 ± 16	39.08
Casting of a 5% acetic solution								
—	—	—	—	—	16–26	55.9 ± 6.9	2289 ± 211	—
—	—	—	—	—	270–370	70.7 ± 16.4	1811 ± 138	—

^a DET = diethyl tartrate; EGM = ethylene glycol monoacetate; TEP = triethyl phosphate.

^b Maximal tensile strength.

^c Elasticity modulus.

samples (Table 1). At the same time, tensile strength values fall within the same range for both testing methods. No reasonable explanation for this discrepancy could be found, but comparisons between latex and organic solvent formulations are not impaired.

Conclusions

Provided that a suitable choice is made of plasticizers and film-forming conditions, cellulose acetate latexes yield strong membranes. Samples cast from latexes plasticized with ethylene glycol monoacetate, a very volatile additive, are nearly as resistant as films obtained from organic solutions. With polar cellulosic derivatives, our results suggest at least two means of reducing the quality gap between films produced from organic solutions and from latexes.

Firstly, it is advantageous to incorporate very high loads of volatile plasticizers instead of smaller amounts of very permanent additives into the latexes. This holds true as long as the relatively high temperature (50–70 °C) needed to facilitate plasticizer evaporation is not damaging to the drugs in the core tablets; and secondly, development of a new latex system should be accompanied by a systematic testing effort to select appropriate plasticizers. Here,

the various water-soluble additives have high efficiency.

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