

# The influence of casting solvent composition on structure and permeability of acrylic-methacrylic ester copolymer films

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Decrease in the solvation of polymer by inclusion of ethanol in the acetone casting solution resulted in greater permeability to urea of cast acrylate-methacrylate film. The greater permeability was accompanied particularly by a decrease in pore size and increase in pore number, despite the absence of change in pore area. A decrease in cohesiveness in the film was suggested by the decrease in tortuosity of the pores as seen by scanning electron microscopy; also, water uptake was increased when the film was cast from an ethanolic solution. The results support the view that, in practice, the composition of the solvent, by its effect on microstructure, can affect the function of the film cast from it.

Each casting solvent used in the formation of polymeric films has its own affinity for the dissolved polymer and the strength of the resultant interaction may be expected to be reflected in the microstructure of the film formed. Thus, cellulose acetate film cast from solution in ethyl acetate assumes a dense crystalline structure but when the casting solvent is chloroform it has a fine grain (Kolonits, 1968). For any polymer the structure of the film formed may differ or the film may have different permeability when it is cast from a different solvent. But results in the literature do not always appear to bear out this expectation. For example, hydroxypropyl cellulose films have been found to show (Kildsig, Nedich & Banker, 1970) and not to show (Lindberg, 1971) permeability differences for water vapour when cast from different solvents. In the former instance water was compared with organic solvent for casting films of methylhydroxypropyl ethers of cellulose; in the latter instance hydroxypropyl cellulose films made from different organic solvents showed no significant permeability differences. In another report (Pickard, Elworthy & Sucker, 1975), aqueous and organic solvent films of hydroxypropylmethyl cellulose were stated to have similar water vapour permeability, but water cast films were 2-3 times as permeable as organic solvent-cast mixed film for hydroxypropylmethyl cellulose and ethyl cellulose.

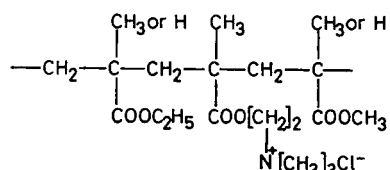
During film formation by casting on a substrate there is an upper (exposed to atmosphere) and a lower (in contact with substrate) surface. Overall

film permeability may vary for certain polymeric films depending on which of these surfaces of the film is first caused to accept the permeating substance (Abdel-Aziz, Anderson & Armstrong, 1975) termed by us the surfaces difference phenomenon. The ratio of differing permeabilities thereby obtained may vary with the structure of the film.

Despite the existence of alternative casting solvents that a formulator must consider, there is little in the literature about the effects of change of solvent used for casting polymeric film on permeability. We have therefore determined whether a pattern of solvent effect exists. The work described relates to the effect of solvent on film permeability and extends a preliminary report (Abdel-Aziz, Armstrong & Anderson, 1974).

## MATERIALS AND METHODS

Two polymers of acrylic and methacrylic esters differing in content of quaternary ammonium groups were studied and are referred to as AMAE(L) and AMAE(S). In AMAE(L), the more hydrophilic, the ratio of quaternary ammonium groups to polymer is 1:20, while in AMAE(S) it is 1:40. The unit of polymer is:



AMAE(L) and AMAE(S) were obtained from Röhm, Pharma, Darmstadt, W. Germany under

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the names Eudragit RL 100 and RS 100 respectively. The polymers have an average molecular weight of about 150 000 and differ in capacity for water uptake although both are insoluble in water at 20° over the pH range 2–8. One part of each is soluble respectively at 20° in 3.60, 3.36 parts acetone; 4.04, 4.55 parts methanol; 5.99, 10.98 parts ethanol.

Urea acetone and ethanol were Analar grade; glycerol triacetate was laboratory reagent grade.

Swelling in water was determined (Ratner & Miller, 1972) after the cast films had been dried in a desiccator to constant weight, immersed in water for 24 h at 37°, blotted dry and weighed. Re-weighing after drying (70°) to constant weight allowed determination of water uptake which was used as an index of swelling.

#### *Film casting*

Films were cast from 2.5% w/w solutions of the polymer in acetone containing 0.5% w/w glycerol triacetate as plasticizer; and also from acetone solutions containing 1, 2, 5, 7.5, and 10% w/w ethanol, using the following casting technique. The solution was filtered through sintered glass (porosity 3) and 5 cm<sup>3</sup> of the clear filtrate was poured into a dust free circular PTFE mould (diameter 7.30 cm; depth 1.0 mm). The mould was covered with an inverted funnel (stem orifice diameter 5.7 mm) to control solvent evaporation and placed on a level surface in a laminar flow hood (Microflow laminar air flow station), with an air speed of 0.5 ms<sup>-1</sup> and a relative humidity of about 50%. Solvent was permitted to evaporate for 24 h at ambient temperature before transfer of the formed film to a desiccator containing silica gel, where it was stored for a further 24 h before use. Residual acetone and ethanol could not be detected (g.l.c.) in the film after the 24 h evaporation period.

Film thickness was measured at ten random points using a digital micrometer and the mean film thickness calculated ( $21 \pm 0.3 \mu\text{m}$ ). Inclusion of ethanol in the casting solvent did not alter the mean thickness.

#### *Film evaluation*

A permeability cell was constructed in Perspex after Gonzales, Nematollahi & others (1967). It consisted of two compartments separated by the film. That in which the solution of permeant (urea, 10% w/v) was placed was designated donor; the other (acceptor) compartment contained deionized water. The rate of appearance of urea in the acceptor compartment was determined and taken as the rate

of permeation through the film. The permeation experiment was carried out at  $36.95^\circ \pm 0.015^\circ$ , and both compartments were stirred with magnetic stirrers (300 rev min<sup>-1</sup>, determined stroboscopically). Upper and lower film surfaces were exposed to the donor compartment using a fresh film for each exposure and results from at least four samples of film were obtained in each experiment.

#### *Scanning electron microscopy*

Before examination using the electron microscope, the films were kept for not more than 7 days in a desiccator containing dry silica gel after use in permeation experiments. Circular film specimens (1 cm diameter) were mounted on aluminium studs of the same size, using double-sided pressure sensitive adhesive tape and were vacuum-coated with gold/palladium mixture to give coat thickness 0.05  $\mu\text{m}$  before examination in the magnification range 200–2000 $\times$ , according to the specimen structure. The magnification used for any specimen was that best suited to reveal the structure of the specimen under investigation. To reveal internal structure cross sections of fresh unused film were made manually using a new scalpel blade.

*Pore size determination.* The micrographs of the film surfaces were further enlarged (36 times) and pore size distribution determined by measuring the diameters of all pores appearing in the field (200–1000 pores). The mean pore size (arithmetic mean diameter) was calculated from the pore size distribution in each micrograph.

## RESULTS AND DISCUSSION

Permeability characteristics of the cast film may be determined by the surface (upper or lower) which is exposed to the permeant (Anderson, Armstrong & Abdel-Aziz, 1973; Abdel-Aziz & others, 1975). Also, the effect of other solvents in the casting solution may be seen in changes in the permeability characteristics of either film surface to permeant. Fig. 1 shows the effect of addition of ethanol to the acetone casting solution on film urea permeation rate. The fourfold difference in the scales in Fig. 1 highlights the difference between the more permeable more hydrophilic AMAE(L), and less permeable less hydrophilic AMAE(S) polymer. Addition of ethanol also resulted in an increase in permeation rate for films of both polymers. This was so when either the less permeable upper or the more permeable lower surfaces of films of both polymers were exposed to the permeant. But, the change was greater for the less permeable upper

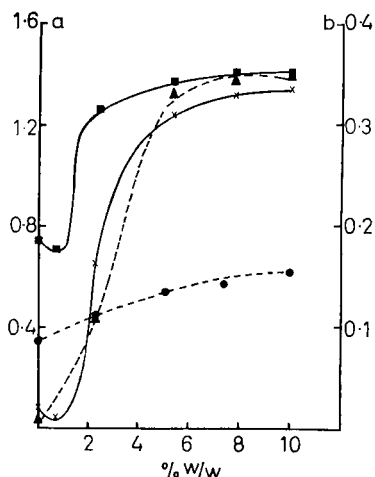


FIG. 1. The effect of ethanol concentration in the casting solution (% w/w) on the rate of permeation of urea ( $\text{g h}^{-1}$ ) through a—AMAE(L) (more hydrophilic) and b—AMAE(S) films.

× ■ ——— upper and lower surfaces respectively of AMAE(L) exposed to the permeant solution.  
 ▲ ● - - - - upper and lower surfaces respectively of AMAE(S) exposed to the permeant solution.

surface in both cases. Addition of 10% ethanol to the casting solution eliminated the permeability difference between the upper and lower surfaces in the more hydrophilic AMAE(L) film and actually reversed the extent of permeability in the less hydrophilic AMAE(S) film. Whilst the films of the two polymers differed markedly in permeation rate, the nature of the change caused by including ethanol in the casting solution followed a similar trend in both cases; the ratio (lower/upper surfaces) of permeation rate approached unity as the ethanol concentration in the casting solution increased (Fig. 2), and for the less hydrophilic AMAE(S) it fell below unity as the permeability alters. Inclusion of ethanol in the casting solution resulted in the development of large numbers of smaller sized pores on both

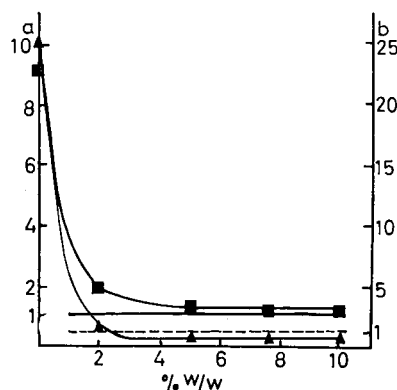


FIG. 2. The effect of ethanol concentration in the casting solution (% w/w) on the extent of surface-difference (permeability ratio) in a—AMAE(L) ■, and b—AMAE(S) ▲, film using urea as permeant. Note. The lines at 1 on each scale represent regions at which surface difference does not exist in AMAE(L) (unbroken line) and AMAE(S) (broken line).

film surfaces (after 3 h urea permeation; lower film surface exposed to permeant), compared with acetone casting solvent. Although pore size decreased a large increase in pore number occurred (Table 1). For this to be accepted as the cause of increased permeability of the film when ethanol is added to the acetone casting solution, some explanation of the reasonably constant value for pore area (Table 1) is required.

The effect of ethanol in the casting solution on the AMAE(S) films is seen in the cross sections of the film (Fig. 3). The upper surface of the film cast from acetone comprised a dense layer with few pores, but this layer was replaced by a layer containing large pores when 5% ethanol was included in the casting solvent. With 10% ethanol the upper surface dense layer disappeared and the porous structure became more regular and continuous between the two surfaces with a marked diminution of non-porous polymer matrix. The change in the

Table 1. Effect of ethanol concentration (in the casting solution) on the apparent porosity of AMAE(L) film surfaces (after 3 h urea permeation). The lower film surface was exposed to permeant solution.

Ethanol in casting solution % w/w	Pore number, $\text{mm}^{-2}$		Pore size $\pm$ s.d. ( $\mu\text{m}$ ) surface		Total pore area $\mu\text{m}^2 \text{mm}^{-2}$	
	lower	upper	lower	upper	lower	upper
0	40	38	$3.57 \pm 1.1$	$2.57 \pm 1.1$	400.19	197.02
1	477	45	$0.96 \pm 0.2$	$2.39 \pm 0.9$	345.08	201.78
5	885	315	$0.72 \pm 0.3$	$0.9 \pm 0.3$	360.11	200.28
10	2345	410	$0.45 \pm 0.1$	$0.81 \pm 0.2$	340.03	211.26

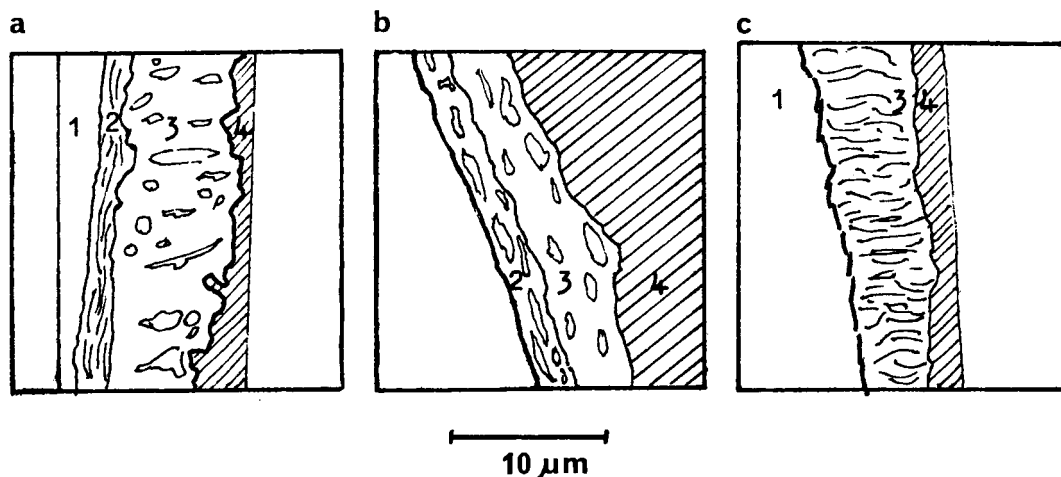


FIG. 3. Cross section of AMAE(S) film cast from acetone, a; acetone with 5% w/w ethanol, b; and acetone with 10% w/w ethanol, c. 1. upper surface. 2. upper surface layer. 3. film core. 4. lower surface.

tortuosity of the internal structure doubtless contributed to the markedly increased film permeability (Fig. 1) especially when the upper surface was used as the permeant entry surface. Fig. 4 shows the effect on the internal structure of AMAE(L) film when 10% w/w ethanol was in the acetone casting solution. As with AMAE(S), the internal sponge-like structure with apparently discontinuous pores gave way to a less tortuous channelled structure connecting the two surfaces of the film. This is in accord with the fact that the development of a large number of smaller sized pores on the film surfaces was associated with greater permeability even though mean pore size was decreased. Obviously a larger number of smaller, but more nearly continuous, pores would facilitate pore permeation to a greater extent than a smaller number of larger but apparently less continuous pores, despite the relatively unchanged pore area. A relation between structural and permeability changes is also indicated by the swelling (water uptake) data (Table 2) which show that the more permeable more hydrophilic AMAE(L) had its capacity further increased when 10% ethanol

was included in the casting solvent. AMAE(S), being less hydrophilic and with meagre permeability and uptake capacity, changed five-fold when 10% ethanol was included in the casting solvent. Thus, the structural change induced by using an ethanolic solvent was more pronounced for AMAE(S) and, although the total water uptake and equilibrium value was less than for the more hydrophilic AMAE(L), the change in capacity caused by ethanol was greater.

At least part of the reason for the effect of ethanol may be found in the vaporization rate of the casting solvent during desolvation. Ethanol and also mixtures of ethanol and acetone, have higher boiling points and lower vapour pressures than acetone. Addition of ethanol to the casting solution would be expected to decrease the vaporization rate of the solvent during film formation. Accordingly the temperature of the polymer solution will be lowered to a lesser extent than when acetone, with its high vaporization rate, is used alone as the casting solvent. Higher temperatures within the polymer solution tend to promote supermolecular de-aggregation of the polymer in solution, which according to Kunst & Sourirajan (1970a,b) and Pageau & Sourirajan (1972) tends to produce a larger number of smaller sized pores on film surfaces, a result which has been clearly obtained.

In the conditions encountered in the present work, addition of ethanol to the casting solution for both AMAE(L) and AMAE(S) films may have also affected the cohesion within the resulting film. Generally, a maximum polymer solvation in the casting solution is believed to produce films showing

Table 2. Water uptake (swelling) by films cast from solutions in different solvents.

Solvent	Mean uptake at 24 h at 37° (g water per 100 g film)	
	AMAE(L)	AMAE(S)
Acetone	59	6.7
Acetone + 10% w/w ethanol	74	33

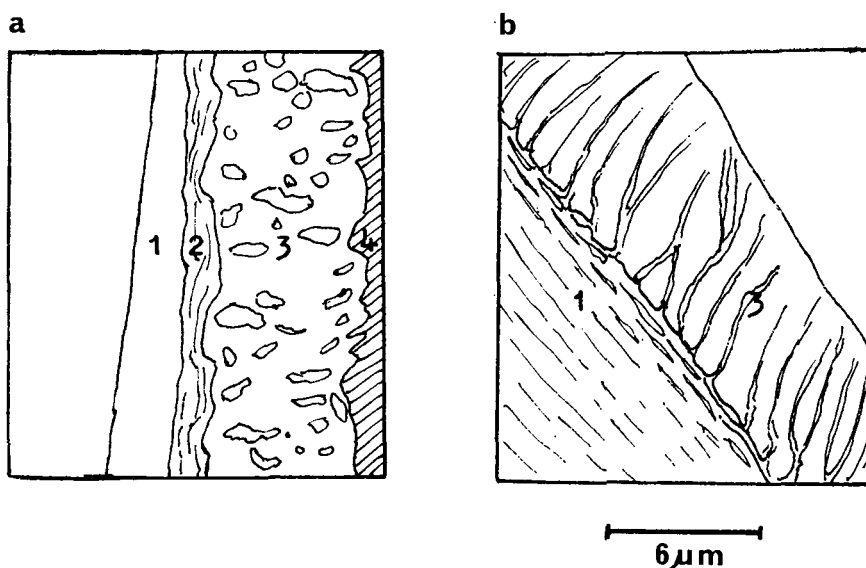


FIG. 4. Cross section of AMAE(L) film cast from acetone, a; and acetone with 10% w/w ethanol, b. 1. upper surface. 2. upper surface layer. 3. film core. 4. lower surface.

the greatest combined strength and cohesiveness. As the polymers are less soluble in ethanol than in acetone, addition of ethanol, with consequent decrease in polymer solvation and molecular dispersion, will tend to result in a generalized decrease in film cohesive strength and be associated with the more nearly continuous channels between the two surfaces of the film and higher film permeability.

Thus, decrease in polymer solvation by alteration of the composition of the casting solvent has resulted

in substantial change in porous structure and a consequent increase in film permeability. In practice, therefore, solvent composition should not be varied without assessing the effect on the properties of the film.

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