Preparation of Polymer Latex Films by a Flash Casting Technique

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Synopsis

Conventional film casting methods have proved unsuitable for the preparation of thin (10–100 μ) films from surfactant-free polymer latices. A flash casting technique has been devised and successfully employed to cast films from a wide range of surfactant-free homopolymer, copolymer and core-shell polymer latices. Essentially, the method involves spraying the latex at a specially designed hotplate, the surface of which is coated with a thin layer of PTFE. The hotplate is maintained at a temperature between 393 and 473 K. When sufficient thickness of film has been built up, the hotplate is switched off and allowed to cool to the temperature at which the film is to be removed. For homogeneous latex films, the optimum temperature range for removal lies in the region of the glass transition temperature of the polymer concerned. Where this is below ambient, the appropriate cooling mixture is placed in a slush bath, situated to the rear of the hotplate, thereby cooling the hotplate to the correct temperature. The film is removed by gently peeling it from the surface. The surfaces of the films appeared smooth to the naked eye, but the sprayed surfaces of freshly prepared poly(n-butyl methacrylate) films were rough when examined by scanning electron microscopy. The surfaces smoothed out on ageing, resembling those of solvent-cast films after one months storage.

INTRODUCTION

The physical and mechanical properties of thin polymer films are important from both academic and industrial points of view. These properties are affected not only by the nature of the polymer, but by the method of film preparation and conditioning.[1,2] In many cases, films are obtained from commercial sources, where they are manufactured by processes such as calendering or extrusion.[3] On a smaller scale, films have been prepared by solvent casting or compression molding.[1,4] All these techniques start with bulk polymer, and are therefore unsuitable for the direct preparation of films from latex dispersions. Paint and coatings technologists have long been interested in the preparation of free films from both aqueous and oil-based formulations, and have devised several methods for achieving this. These include: casting on photographic paper and removing the film by soaking in warm water to dissolve the gelatin[5]; casting on aluminum foil followed by amalgamation with mercury[6]; and casting on silanized plate glass[7] and in PTFE dishes,[8] in which cases the film is removed by gently peeling it from the substrate.

Several film preparation techniques have been evaluated during an investigation of the transmission properties of films formed from surfactant-free polymer latices.[9] The films were examined according to the following criteria:

i. Films having a thickness in the range 10–100 μm, constant over a circular area of ca. 15 cm^2 were required. This restriction was imposed by the sensitivity of apparatus used to measure film permeabilities.

ii. The surfaces of the films were required to be as smooth as possible, and the interior free from cracks, voids, and fissures which might contribute to the film permeability.

iii. It was necessary to avoid techniques which contaminated the films, especially since the latex precursors had been rigorously cleaned beforehand.

The techniques evaluated included casting on a mercury surface, on photographic paper,[5] on PTFE,[8] and silicone rubber dishes and on silanized glass[7]. After extensive trials, all were rejected, either because the substrate concerned contaminated the film, or the minimum thickness of film it was possible to cast was at least an order of magnitude greater than that required. The means of film preparation which was eventually adopted was developed from the flash coating method of tablet coating which is widely used by the pharmaceutical industry. The noncontaminating PTFE substrate was retained, but the aim was to form the polymer film so quickly that the liquid film could not disjoin.

APPARATUS

The hotplate comprised a smooth PTFE surface bonded to the front face of a copper block (220 × 120 × 25 mm), the body of which contained four thermostatically controlled heaters. The electrical components were enclosed to prevent the ingress of latex. Small holes were drilled parallel to the front face, and as close to it as possible, permitting easy measurement of the surface temperature. Provision for a slush bath was made so that the block could be cooled below room temperature. The hotplate is depicted in Figure 1.
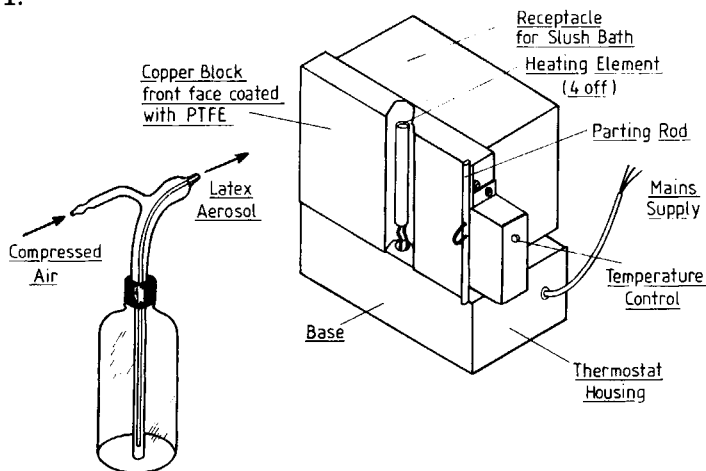

Fig. 1. Flash casting apparatus.

Several types of sprayer were evaluated and these included a chromatography spray powered by an aerosol propellant canister (Fisons Scientific Apparatus Ltd., Bishop Meadow Road, Loughborough, Leicestershire, UK), an electrically powered airless paint sprayer (Model 969; Burgess Power Tools, Sapcote, Leicestershire, UK), and an aerosol generator designed to produce an average droplet size of 2 μm ("Collison" spray[10]). The sprayers were tested to see if they could produce a sufficiently fine aerosol (maximum droplet diameter 20 μm) without blockage by latex polymer. The droplet size produced by the sprayers was estimated by spraying toluene into a vigorously stirred, dilute solution of sodium dodecyl sulfate, and measuring the size distribution of the resulting emulsion on a Coulter Counter. The sprayer selected was a pyrex glass unit (glass spray unit; Sigma Chemicals Ltd., Fancy Road, Poole, Dorset, UK) used with compressed air (Fig. 1), and is of the conventional atomizer type. The latex is drawn up a narrow bore glass tube to an orifice, which is surrounded by a larger concentric orifice: a rapid stream of air passes through the latter, atomizing the latex.

METHOD

The hotplate was switched on and left until the temperature oscillations settled down. The spray reservoir was filled with latex at the required solids content. The block was then sprayed slowly and evenly, at a distance of approximately 1 m. Depending on the thickness of film required some 20–50 passes were necessary, taking between 1 and 3 min. The initial and final bursts of spray tended to contain much coarser droplets, and so care was taken to ensure that the sprayer was started and stopped with the jet aimed to one side of the hotplate. Immediately after spraying, the hotplate was switched off and allowed to cool to the temperature at which the film was to be removed. If this was below room temperature, the appropriate cooling mixture was placed in the bath behind the block (Table 1[11]).

The film was removed from the surface by means of the parting rod, to which it adhered. With the block at the correct temperature, the grub screw securing the rod was slackened. The parting rod was then pulled away from the block slowly and evenly, thereby peeling the film away from the surface.

TABLE I
Cooling Mixtures[a]

Liquid	Temperature/K
Cyclohexane	279
Methyl salicylate	264
Carbon tetrachloride	250
o-Xylene	244
Pyridene	231
Ethyl malonate	223
n-Octane	217
Isopropyl ether	213

[a]The liquids were used in admixture with solid carbon dioxide to produce the temperatures shown.

Particular care was necessary to avoid small tears, which generally formed at the edges of the film, from spreading to the center.

Providing the hotplate was at the optimum temperature for film removal for the polymer concerned, the film could be peeled from the surface without unduly stressing it. In most cases, there was no detectable increase in the length of the film resulting from its removal from the hotplate. Even in the worst cases, the extension was only a few percent of the original length of the film.

Although it is difficult to extrapolate results obtained with polyethylene to the polymers studied in this work, the results of Poulos and Thomas,[12] on the effect on gas permeability of postdrawing polyethylene film, are relevant here. They found that, to produce a measurable drop in the oxygen permeability, the polyethylene film had to be stretched to beyond twice its original length. The reduction in permeability was caused by alignment of the crystallites. It is therefore likely that the amount by which the latex films were stretched during their preparation would not measurably affect their transmission properties, particularly since the polymers are entirely amorphous.

After the film had been removed the PTFE surface of the hotplate was cleaned by washing with a solvent mixture containing approximately equal proportions of acetone, butanone, and toluene.

RESULTS AND DISCUSSION

The apparatus was evaluated under a wide range of conditions (e.g., surface temperature, applied air pressure, latex solids content, distance between sprayer and hotplate, etc.) in order to determine the procedure which gave the best results. A poly(n-butyl methacrylate) latex ($T_g = 300$ K) was used for this initial work since it was readily removed from the PTFE substrate at room temperature and its films were amenable to scanning electron microscope examination.

Effect of Temperature

The surface temperature could be varied between 373 and 493 K. At temperatures below 393 K, the first burst of spray cooled the hotplate to below the boiling point of water, giving the aerosol droplets time to coalesce and form spots or runs on the film surface. The upper temperature limit was set by the melting point or decomposition temperature of the polymer concerned.[13,14] However, it was found that poly(n-butyl methacrylate) films left at 493 K for about 10 min became too brittle to remove from the surface. This effect was confirmed by heating a previously prepared free film in an oven at 493 K and leaving for 10 min.

Effect of Applied Pressure

The average droplet diameter at 20 psi was 12 μm, and the maximum size 17 μm. The droplet size fell slightly with increasing pressure, but below 20 psi the aerosol was visibly coarser. Any attempt to spray a latex at above 50 psi resulted in blockage of the orifice, presumably due to shear instability. With surfactant-containing latices higher pressures could be employed. The

pressure giving the optimum delivery of aerosol was found to be in the range 25–30 psi.

Effect of Solids Content

A film prepared from a latex of greater than 8% solids content usually had a visibly rough top surface. However, if the latex was too dilute, a large number of passes was necessary to obtain the required thickness, and this tended to produce a rougher top surface. Within these limits, there was no apparent difference between two films of similar thickness cast from latices of different solids content.

Effect of Latex Particle Size

Films were cast from latices with particle diameters in the range 100–900 nm. There was no discernible effect of particle size on the film properties or the ease of preparation.

Film Morphology

Sprayed Film Surface. A freshly cast poly(n-butyl methacrylate) film had a lumpy top surface (see Fig. 2), presumably arising from the last burst of spray during preparation. The largest of these lumps appeared to comprise 10–20 individual particles and extend about five particle diameters above the plateau (Fig. 3). On fully aged films, these lumps had disappeared, and the surface took on a rippled appearance, with depressions of a few μm deep and hundreds of μm across (Figs. 4 and 5). The debris scattered on the film surface depicted in Figure 4 is dust which accumulated during the 1-month storage period. It is conceivable that some dust is trapped in the interior of the film when the latex is sprayed. However, precautions were taken to avoid this, and none was ever observed in fracture
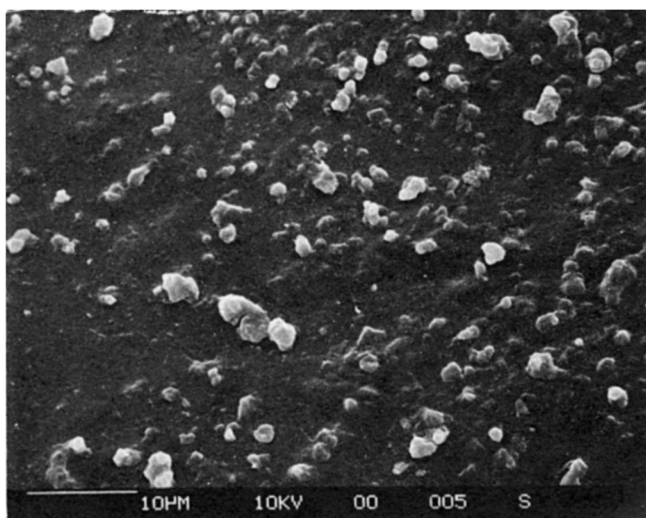

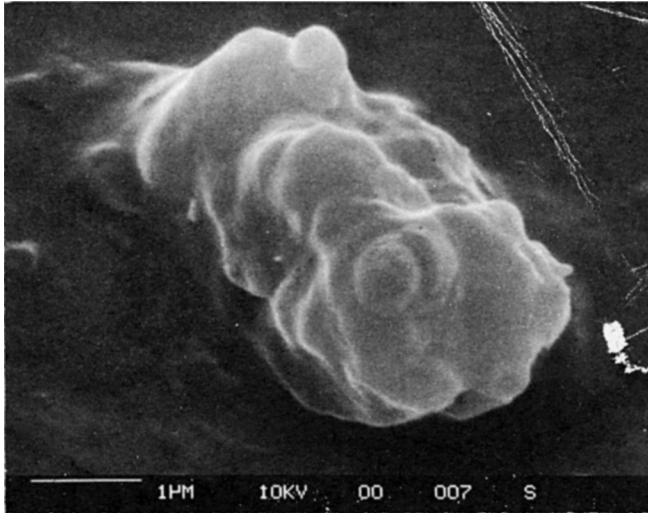Fig. 2. SEM of poly(n-butyl methacrylate) latex film. Sprayed surface immediately after casting. Magn. 2400×.

Fig. 3.　SEM of poly(n-butyl methacrylate) latex film. Sprayed surface immediately after casting. Magn. 24000×.

cross sections. Film thicknesses were measured with a dial gauge having a flat tip. This tip would be expected to bridge several lumps, giving a thickness 2–3 μm larger than the plateau thickness. The variation in thickness of any given film sample was around 10%, so that it was not possible to determine if the measured thickness altered on ageing.

Surface Coast against PTFE Substrate. The surface cast against the PTFE substrate was smooth, with no imperfections visible by scanning electron microscopy (Fig. 6).

Interior Morphology. Several cross-sections of films, prepared by fracturing at liquid nitrogen temperature, were examined by SEM. The fracture cross section of a freshly cast poly(n-butyl methacrylate) film is shown in
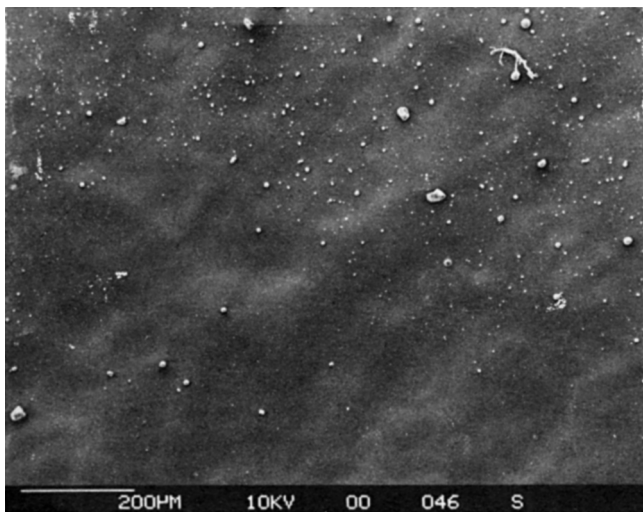

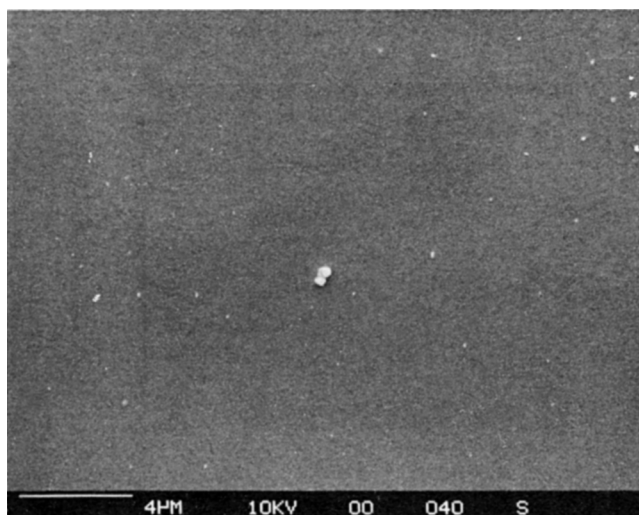Fig. 4.　SEM of poly(n-butyl methacrylate) latex film. Sprayed surface 1 month after casting. Magn. 125×.

Fig. 5. SEM of poly(*n*-butyl methacrylate) latex film. Sprayed surface one month after casting. Magn. 6250×.

Figure 7: This is typical of all such films examined, none of which appeared to alter on ageing. It can be seen that approximately equal numbers of small lumps and cavities are scattered around the surface of the cross-section: these are probably due to individual polymer chains having separated from, or removed to, the opposite surface, producing the lumps and cavities, respectively. If the film was allowed to warm up between fracturing and shadowing, these features disappeared—presumably due to polymer flow. The film shown in Figure 7 is approximately 20 μm thick, and its latex precursor had a particle diameter of 480 nm. If it is assumed that one third of the reduction in volume, which accompanies particle coalescence, occurs only along the thickness dimension, then the film will be 45
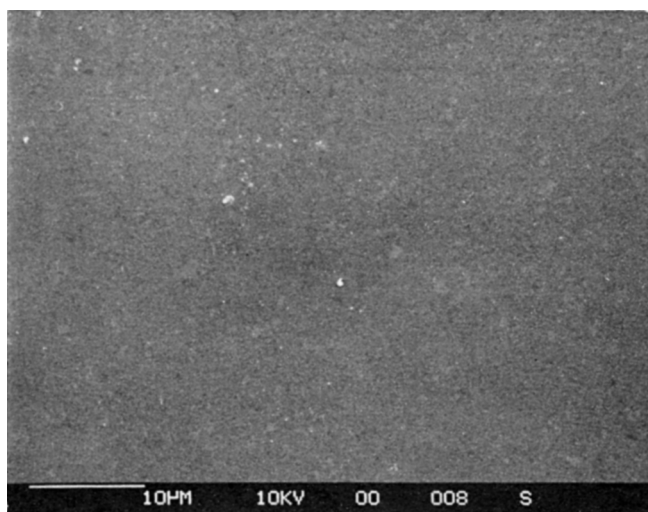

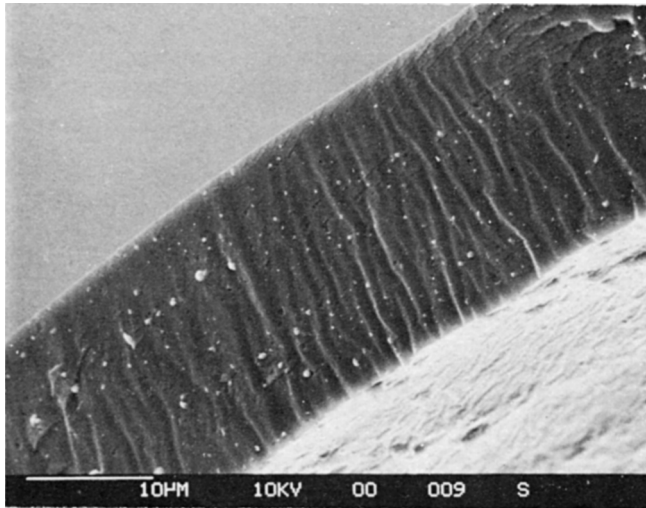Fig. 6. SEM of poly(*n*-butyl methacrylate) latex film. Surface cast against PTFE coated copper. Magn. 2500×.

Fig. 7.   SEM of poly(n-butyl methacrylate) latex film. Cross section fractured at 77K. Magn. 2500×.

particles thick. If a particle structure existed in the film then it would be visible in the SEM. No such structure was ever observed, even at high magnifications.

It is interesting to compare the apparently featureless fracture cross-section of a flash cast poly(n-butyl methacrylate) latex film (Fig. 7) with the corresponding solvent-cast polymer films (cast in a dish using butanone as solvent) (Fig. 8). This film displays the same rippled top surface as the fully-aged flash cast latex films. In addition there is a separate top layer, approximately 1 μm thick, which may be due to a skin forming on the surface of the film during the initial stage of drying. This surface layer contains a number of what appear to be air bubbles. These were found even when the polymer solution was degassed under vacuum prior to casting the
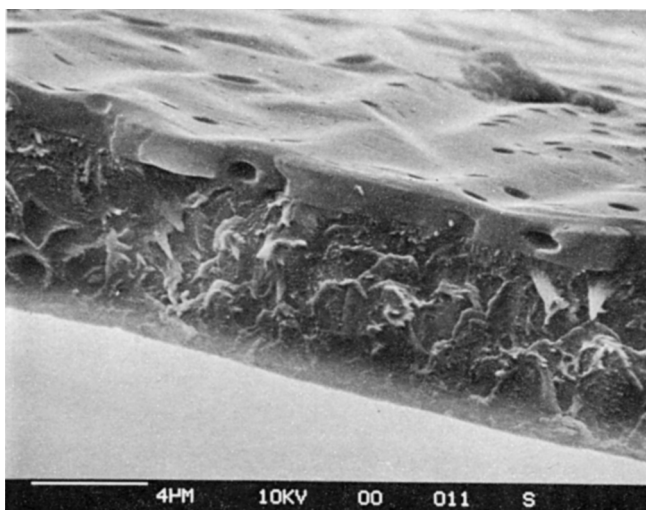

Fig. 8.   SEM of poly(n-butyl methacrylate) film cast from solution in butanone. Cross-section fractured at 77 K. Magn. 6250×.

film. A further difference between the fracture cross-sections (which were both done at liquid nitrogen temperature) is that the latex film is much smoother than the solvent cast film. It is tentatively suggested that this is due to the more complete mixing of polymer chains in the solution prior to casting, causing greater disruption of the structure on fracture. The latex film may simply have cleaved along a line of particle boundaries, presuming these to have been maintained.

The interior morphology of a core/shell latex film [poly(ethyl acrylate) coated polystyrene] is shown in Figure 9. The thickness of the coat was only just sufficient (50 nm) to give a coherent film. This was, however, very brittle and flaked off rather than peeled from the surface. The film was cast at 393 K, i.e., 20 K above the T_g of polystyrene. It is interesting to note that the polystyrene core particles are easily visible as spheres, and have not deformed into dodecahedra. A polystyrene latex of comparable particle size formed films (under comparable casting conditions) which were usually nonporous (as determined by its low permeability coefficient). Another feature of the film shown in Figure 9 is the high degree of order in the packing of the latex particles.

Uniformity of Film Thickness

The variation in thickness of sprayed films could usually by kept to less than 10% and, after practice, variations of as little as 5% could be achieved. As might be expected from the side-to-side spraying pattern, the variation across this dimension was less than from top to bottom. The optimum thickness for uniformity was in the range 30–70 μm. Films thinner than 30 μm were generally less uniform and more prone to pinholes. The thinnest nonporous film prepared was 16 μm. Films thicker than 70 μm could be prepared, but the top surface was often unacceptably rough, due to the high solids content or large number of passes required. One maladroit pass could
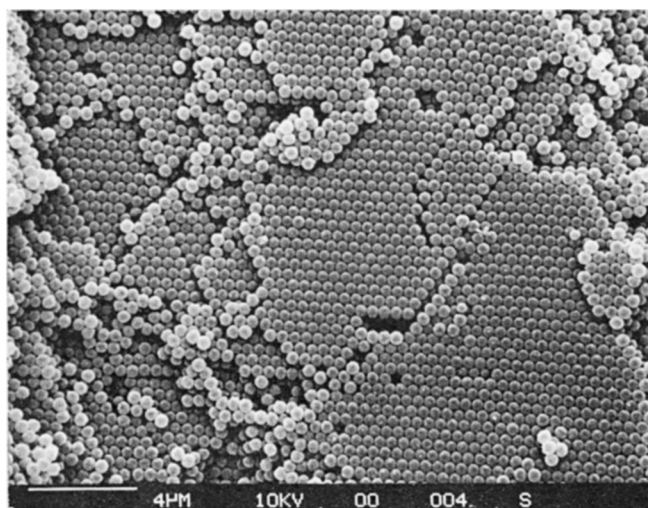

Fig. 9. SEM of poly(ethyl acrylate)-coated polystyrene core-shell latex film. Cross section fractured at room temperature. Magn. 6000×.

ruin a film which had already taken upwards of 80 passes, so that thick films were only attempted when strictly necessary.

Optimum Temperature for Film Removal

When attempting to cast films other than from poly(n-butyl methacrylate) latexes, it became apparent that the optimum temperature range for removal of the films varied according to the polymer type. It was necessary to maintain the block at a temperature within a few degrees of the T_g of the polymer concerned. If the temperature was too high, the film adhered to the surface too strongly and stretched on removal. If too low, the film was quite often brittle and disintegrated. The optimum removal temperature for films cast from core-shell latexes was higher than that of the coating polymer. The extent increased with decreasing coating polymer thickness and was greatest (around 40 K) where the coating thickness was only just enough to impart adequate strength to the film.

Range of Latex Films Available

A wide range of thin homopolymer, copolymer, and core-shell latex films were prepared by means of the flash casting technique. The limits of its applicability were set by the temperature at which the film was removed. Where the difference between this temperature and ambient was too great, hard and soft polymer films became respectively too brittle or too elastic, once stripped from the surface, to withstand the remainder of the removal process undamaged. For this reason, no poly(methyl methacrylate) or poly (n-butyl acrylate) films could be prepared. This limitation might possibly be overcome by housing the hotplate in a chamber such that the surroundings could be maintained at a suitable temperature for complete film removal. This solution would, however, hinder manual removal of the film, and hence poses considerable practical difficulties.

A few polystyrene films were prepared, with great difficulty, on the prototype hotplate, where the PTFE was stretched over the substrate, rather than directly bonded to it. The surface of the PTFE on this hotplate was sightly pliant, and probably stretched slightly during film removal. This would have reduced the tension on the brittle polystyrene film enabling it to be removed.

Copolymer and core-shell latex films were also prepared by the flash casting technique. There were no special problems associated with these films (even with polystyrene core contents as high as 68%, which is close to the theoretical maximum). However, films cast from blends (i.e., mixtures of two latexes) could not always be successfully prepared. In particular blends containing more than 20% polystyrene, in combination with any acrylate or methacrylate polymer latex, could not be removed from the hotplate, although the films appeared to be continuous. Min et al.[15] found that a film cast from a mixture containing 50% each of polystyrene and poly(n-butyl acrylate), by drying at room temperature, formed an opaque, cracked film. In contrast, core-shell latexes of the same composition, prepared by seeded emulsion polymerization, formed clear, continuous films.

Some workers have, however, reported the preparation of continuous films from blends of hard and soft latexes. Hughes and Brown[16] were able

to prepare films from a mixture containing equal proportions of polystyrene and poly(methyl acrylate). Peterson[17] prepared films containing 28% polystyrene, poly(vinylidene chloride) or poly(methacrylate) dispersed in poly(vinyl acetate). To prevent agglomeration of the disperse phase latex on mixing, it was necessary to dilute it beforehand. Samples of the films were examined by scanning electron microscopy. This showed that the polystyrene particles were deformed, and Peterson attributed this to powerful compressive forces generated by the continuous phase poly(vinyl acetate) particles on drying. This explanation seems unlikely here since spherical polystyrene particles have been observed in fracture cross-sections of core-shell latex films prepared by the flash casting technique (Fig. 9). It is not certain why these particles remain undeformed, although they are above the T_g of polystyrene.

Appearance of Latex Films

The clarity, flexibility and tackiness of different types of latex film are listed in Table II and some typical tension–extension curves are shown in Figure 10. In appearance the latex films were rarely transparent, although films prepared from freeze-dried latex polymer dissolved in, and cast from,

TABLE II
Visual Properties of Latex Films

|		
Homopolymers		
Polystyrene		Translucent, brittle, nontacky
Poly(ethyl methacrylate)		Translucent, brittle, nontacky
Poly(n-butyl methacry late)		Translucent, flexible, nontacky
Poly(methyl acrylate)		Translucent, flexible, nontacky
Poly(ethyl acrylate)		Transparent, flexible, tacky
Copolymers		
Ethyl acrylate–methyl methacrylate	67/33	Transparent, flexible, tacky
	20/80	Translucent, flexible, nontacky
Ethyl acrylate–	40/60	Transparent, flexible, tacky
n-butyl methacrylate	60/40	Transparent, flexible, tacky
	80/20	Transparent, flexible, tacky
Blends		
Polystyrene/poly(n-butyl methacrylate)	20/80	Translucent, brittle, nontacky
Polystyrene/poly(ethyl acrylate)	20/80	Translucent, brittle, nontacky
Poly(ethyl acrylate)	40/60	Transparent, flexible, nontacky
Poly(n-butyl methacrylate)	60/40	Transparent, flexible, tacky
	80/20	Transparent, flexible, tacky
Core-shell		
	19.7/80.3	Translucent, flexible, nontacky
Polystyrene/poly	26.7/73.3	Translucent, flexible, nontacky
(n-butyl methacrylate)	42.2/57.8	Translucent, flexible, nontacky
	60.6/39.4	Translucent, brittle, nonptacky
	68.6/31.4	Translucent, brittle, nontacky
Polystyrene/poly	20.3/79.7	Translucent, brittle, nontacky
(n-butyl acrylate)	32.8/67.2	Translucent, flexible, nontacky
Poly(n-butyl methacrylate) poly(ethyl acrylate)	60/40	Translucent, flexible, nontacky
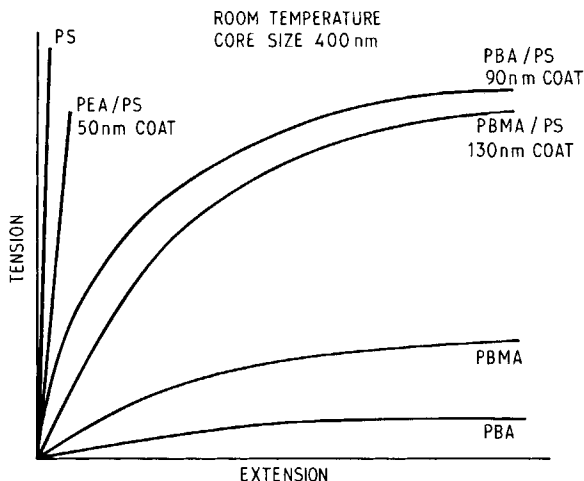
Fig. 10.   Graph showing tension – Extension curves for some homopolymer and core shell latex films.

solution often were. In terms of tackiness and flexibility, the behavior of both latex and solvent cast films usually resembled each other quite closely. The exceptions were films cast from either core-shell latexes or blends, which contained a high proportion of a hard core polymer (usually polystyrene). These films were extremely brittle. The corresponding solvent cast films were similar to a copolymer film containing the two components in the same proportions. The brittleness of the core-shell and blend latex films is probably due to the influence of hard, undeformable polystyrene particles which are sufficiently close together as to resist any motion relative to one another. The blend films were more brittle than core-shell films of the same composition and this may indicate aggregation of the dispersed polystyrene particles, in a manner similar to that observed by Peterson.[17] Solvent cast films prepared from the same precursors behave differently, presumably because the components are more intimately mixed.

The tension–extension curves shown in Figure 10 show the expected rigidity of polystyrene and elasticity of poly(n-butyl acrylate) and poly (n-butyl methacrylate). The core-shell latex films behave in the manner expected of filled polymer films,[18] combining the rigidity of the dispersed polystyrene particles with the elasticity of the continuous acrylate polymer phase.

CONCLUSIONS

The preparation of free polymer films, free of contamination, from surfactant-free polymer latexes could not be achieved by any previously reported technique. The flash casting technique reported in this paper has been successfully employed to cast films from homopolymer, copolymer, and core-shell polymer latices which are uniform over at least 15 cm², are smooth, pinhole-free, and homogeneous, and are in the thickness range 10– 100 μm.

The main limitation of the technique is that films of polymers having

glass transition temperatures too far removed from ambient (less than 248 K and greater than 373 K) could not be removed from the PTFE substrate intact.

The flash casting technique was mainly used with surfactant-free latexes, and no problems with thermal decomposition were encountered. However, due caution should be exercised if using latexes containing surfactant or other additives, since these may decompose during film preparation. The resulting film might have a more porous or open structure.

The surfaces of the films prepared by flash casting appeared smooth to the naked eye, but the sprayed surfaces of freshly prepared poly(n-butyl methacrylate) latex films were rough when viewed by scanning electron microscopy. The surfaces smoothed out on aging, and after 1 month's storage resembled the surface of a solvent cast film. This would appear to suggest that surface tension forces are operative during the final stages of film formation, and act to reduce the film surface area. Current theories of film formation[19,20] consider only capillary forces, and shold therefore be extended to take account of this.

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