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# An overview of polymer latex film formation and properties

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**Abstract**

The literature on polymer latex film formation has grown enormously in recent times — driven by the need to find alternatives for solvent-based systems with their adverse environmental impacts. Although greater insight has been shown by the use of modern instrumental techniques such as small angle neutron scattering, direct non-radiative energy transfer and atomic force microscopy, the actual mechanisms involved in deforming spherical particles into void-free films are still the subject of controversy and debate. Surfactant-free homopolymer model colloid latices, favoured in academic studies, together with latices containing surfactants whose redistribution can influence film properties, and the more complex copolymer, blended, core-shell and pigmented systems needed to satisfy a full range of film properties are all considered. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Polymer latex; Drying; Film formation; Morphology; Surfactants; Plasticisers; Pigment volume fraction

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## 1. Introduction

This paper surveys the literature covering scientific research into the field of polymer latex film formation and properties. This is an important area of research since a large proportion of the commercially produced latex polymers will typically be utilised by being cast into films or acting as binders. The area is one that has developed greatly in recent years with new advances in instrumental techniques [1,2], such as Small Angle Neutron Scattering (SANS), Environmental Scanning Electron Microscopy (ESEM), Atomic Force Microscopy (AFM) and Direct non-radiative Energy Transfer (DET), allowing the monitoring of latex particle coalescence and polymer chain interdiffusion in greater and greater detail. Such fundamental understanding of film formation provides a positive feedback allowing modification to polymerisation reactions/coating recipes and methods of film formation and the development of better quality films. This is illustrated in the paint industry where the traditional solvent-based paints are seen as environmentally unfriendly and the increasingly good quality finish of waterborne coatings is allowing solvent-based coatings to be substituted.

It may be anticipated that the range of applications of latex polymers will continue to increase into the next millennium, beyond their current uses in paints, adhesives, binders, paper coatings, textile finishes, pharmaceuticals (including sustained and controlled release formulations), floor polishes, printing inks, etc. because of the reduced volatile organic compound (VOC) emissions afforded by these water-based systems.

The physical and mechanical properties of thin polymer films are important from both an academic and an industrial point of view. These properties are affected not only by the nature of the polymer(s), but also by the method of both: (i) polymer; and (ii) film preparation and conditioning. As an example, emulsion polymers typically contain surfactant, which may not be uniformly dispersed throughout the full thickness of the film [3] or, due to incompatibilities, may exude from the polymer [4]. Films may be amorphous homopolymers or heterogeneous depending



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on whether they are prepared from a single polymer type or from blended polymers or core-shell-type latex particles. Such heterogeneity may provide uniquely tailored properties, e.g. the dispersion of a softer, lower glass transition temperature ($T_g$) latex, or soft particle core, into a matrix of harder polymer can act [5] to prevent crack propagation through the system (i.e. act as an impact modifier).

Although polymer latices are the primary focus of this review it should be recognised that water-soluble and water dispersible polymers may also be used in water-based coating systems [6]. Polyurethanes, polyesters, alkyds and epoxies, of low-to-moderate molecular weights prepared by step growth polymerisation and then dispersed in water, can have advantages of toughness in relation to film formation temperature as compared with emulsion polymers. Pseudo-latex dispersions of polyurethanes, for example, can be prepared without surfactant addition, at sizes as low as 20–100 nm and offer low film formation temperatures as a consequence of their water-swollen and plasticised nature [7]. There are also, however, disadvantages in using waterborne systems, in general, since extra formulation components are often needed [6]. The high latent heat of evaporation of water leads to long drying times such that, commercially volatile co-solvents have been used to reduce this problem and to aid plasticisation of high $T_g$ polymers. Current pressures are to choose environmentally more acceptable co-solvents or to eliminate them altogether. When lower $T_g$ polymers are chosen at the outset, their film surfaces tend to be tacky. Composite low $T_g$ and high $T_g$ formulations can overcome this problem especially when core-shell morphologies are employed. The high surface tension of water leads to wetting problems which could potentially be overcome by the use of co-solvents (albeit with the aforementioned disadvantages) or by the use of surfactants with the disadvantages of foam stabilisation and possible entrapment of air bubbles into films. The high freezing point of water when compared to organic solvents, means that, commercially, anti-freeze may need to be added or the problem overcome by the use of strong steric stabilisation. The growth of micro-organisms in aqueous systems [8] means that preservatives are often used.

This review of polymer latex film tries to provide a general overview of the trends that need to be considered, without providing case specific values of variables or quantities which may be a function of a polymer's molecular weight, composition or functionality. The authors were prompted to compile this overview from the vast literature on the subject of polymer latex films as a result of a large number of enquiries to the web site of one of us about the availability of just such a publication.

## 2. Preparation of polymer latex films

### *2.1. The casting substrate*

Paint and coating technologists have long been interested in the preparation of films from aqueous-based and oil-based formulations. For the coatings tech-



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nologist, mechanical strength and adhesion to (and in the case of waterborne coatings, wetting of) the substrate, will be the main requirements [9]. Such surfaces, as required for film formation from an academic point of view, are far removed from the typical everyday surfaces that the developed end-coatings will typically be used on. In contrast to commercial polymer coatings, the academic study of films often requires that they are free of any substrate, and ease of removal of the film from its casting substrate is, thus, one of the main requirements. (It has been shown [10,11] that when a film is stretched, the underlying residual particulate structure can be displaced or be deformed — in a manner dependent on the nature of the original latex particles. Such deformation can affect the diffusion or mechanical properties of the film.) Latex films often contain surfactant that is residual from the polymerisation and this too can affect a film's adhesion to a substrate. Kientz et al. [12–14] have studied the adhesion of latex films containing various types of surfactant, to glass, by measuring 'peel energy' (peel rate) as a function of surfactant concentration. Resultant data plots showed various shapes (e.g. minima, maxima, plateaux, etc.) dependent on surfactant type, whilst the locus of adhesion failure was found to be independent of peel rate or surfactant concentration and occurred at the top of the surfactant layer located between the substrate and polymer.

Several methods of ameliorating the problem of removal of a film from its substrate have been devised. These include: casting onto photographic paper and removing the film by soaking in warm water to dissolve the gelatine; casting onto aluminium foil followed by amalgamation of the aluminium with memory; and casting onto silanised plate glass or into PTFE dishes, in which case the film is removed by gently peeling it from the substrate.

Chainey et al. [15,16] evaluated these film preparation techniques during an investigation of the transmission properties of films formed from surfactant-free polymer latices. After extensive trials, all were rejected on the grounds that either the substrate concerned contaminated the film, or that the films were too thick compared to the required specification. The method of film preparation eventually adopted was developed from the flash coating method, which is widely used for tablet coating in the pharmaceutical industry. The aim was to form the film so quickly that it could not disjoin, and this was achieved by spraying the latex onto a heated block, coated with PTFE, at temperatures exceeding 393 K. Multiple (20–50) passes of the spray gun were employed and the film was allowed to return to room temperature before it was removed from the block, and in some cases was cooled to near the polymer's $T_g$ using an appropriate solid–$CO_2$ slush bath. Spitael and Kinget [17], however, found that sprayed solvent-cast films exhibited a higher degree of porosity than similar dish-cast solvent-based films, due to their droplet-like nature, created during spraying, which remained apparent in the final film structure.

Roulstone [18] cast poly(*n*-butyl methacrylate) (PBMA) films onto Pyrex glass plates, from which they could be removed by soaking in hot water, or in the case of additive-present films, cast onto nylon plates from which the films could be removed without soaking. Such nylon plates did, however, have a tendency to warp



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after prolonged use, and there were concerns about possible leaching of additives from the plate into the film.

Yaseen and Raju [19] have reviewed the full range of film preparation techniques, finding pros and cons for each depending on the intended application of the film. It should also be noted, however, that film casting can be achieved by methods other than evaporation of the latices aqueous phase at temperatures above the polymer's $T_g$. Sosnowski et al. [20] for example, have prepared films by freeze-drying surfactant-free polystyrene and poly(methyl methacrylate) latices and then using a press to compress the latex 'powder' until a transparent film was achieved. Sosnowski compared the structures of these films to those of films cast by slow evaporation of the water at 313 K using the techniques of scanning electron microscopy (SEM) and freeze-fracture transmission electron microscopy (FFTEM). Freeze drying led to less ordered films, but gentle compression yielded body centred cubic (BCC) packing in addition to the more usual face centred cubic (FCC) packing.

### *2.2. Latex film formation*

The formation of a latex film arises from the 'coalescence' (i.e. compaction, deformation, cohesion and polymer chain interdiffusion) of the individual latex particles — which are normally held apart by stabilising forces (electrostatic and/or steric) resulting from the charged polymer chain endgroups or adsorbed surfactant/polymer. These forces (and others resisting particle deformation) can be overcome upon evaporation of the continuous phase (water).

The formation of a continuous film (i.e. transparent and crack-free) is then dependent on the minimum film formation temperature (MFFT) of the polymer, as judged visually on a bar having a temperature gradient [21], which in turn is dependent on the elastic modulus (resistance to particle deformation), and to a lesser extent, the viscosity of the polymer. If the film is cast above its MFFT, then deformation and cohesion of the latex particles can occur. However, if casting takes place below the MFFT, then a friable discontinuous film or powder compact may form, which is typically opaque due to the presence of voids capable of scattering light. The more desirable outcome (in the context of this study) of film-formation is something of a compromise since the tendency of the spheres to flow and fuse into a continuous film can, in the extreme, also result in a permanently tacky film that is more suited to adhesive applications [22]. [Note, however, that high $T_g$ latices dried from non-aqueous dispersions and compressed to transparent films, have been used by Canpolat and Pekcan [23–33] to study thermal annealing using the technique of a steady-state fluorescence transfer combined with direct non-radiative energy transfer (see later in review): the use of such 'powders' providing a valid technique allowing the authors to show repeatedly the occurrence of polymer chain interdiffusion during annealing.]

The formation of films at temperatures slightly lower than the MFFT, has been studied using an ultrasonic impedance technique by Myers and Schultz [34]. The results, with respect to the formation of a continuous film, were found to be



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dependent on the rate of drying and, hence, the rate of relief of stresses within the film. At temperatures within 6 K below the MFFT, and with a sufficiently slow drying rate, a certain amount of creep occurred permitting the formation of a film due to the stresses being at a level insufficient to fracture the film. As the rate of drying was increased, the creep mechanism was not fast enough to relieve the stress such that initially the films became crazed, and at the highest drying rates, cracked.

The MFFT, although tending to be close to the $T_g$ of a given polymer, where the shear modulus of the polymer resisting particle deformation would change markedly, has been reported, for various polymers, to be above or below the $T_g$ [35,36]. Both the MFFT and $T_g$ are influenced by the same molecular features (e.g. the inclusion of a softer (co-)polymer will lower both the $T_g$ and MFFT). Ellgood [37] showed, for a series of vinylidene chloride (VDC)/ethyl acrylate copolymers, that both the $T_g$ and MFFT peaked with increasing VDC content, but not at the same composition. Below 55% VDC content, the $T_g$ was found to be greater than the MFFT. A difference of 15 K was found between the $T_g$ and MFFT at the extremes, and different surfactants were also found to alter the MFFT and its relationship to the $T_g$ of the copolymer. Various researchers [38–41] have attempted to produce 'core-shell-type' particle structures, in which the cores of the latex particles are prepared using a different monomer to the shells by the staged addition of a second monomer to a polymerisation reaction. Such reactions can, however, lead to unusual (e.g. half-moon, current bun or raspberry-like) particle morphologies [42,43], due to a minimisation in the interfacial energy [44–46] between the typically hydrophobic core and hydrophilic (functionalised) shell. Similarly, the method of feed of a second stage monomer (e.g. graduated blend, seeded growth or shot growth) can lead to a variation in the MFFT of the resultant latex due to the change in particle morphology [47]. The effect of core-shell morphology on the MFFT has, however, been found to depend on shell thickness [48]: thin soft shells on hard cores requiring higher drying temperatures than thicker soft shells due to the necessity to deform the core of the former in order to form a film. (see Section 3.1)

Brodnyan and Konan [49] and Kast [50] consider that comonomers which impart hydrophilic properties (e.g. methyl and ethyl acrylates, etc.) into a polymer may reduce the MFFT to below the $T_g$ in the case of the wet film (as opposed to these properties being measured for the dry polymer) by allowing water to act as a plasticiser. Similarly, surfactant that is compatible with the polymer may also plasticise the polymer, lowering both the $T_g$ and/or the MFFT [51–53].

Eckersley and Rudin [35], Jensen and Morgan [36] and Sperry et al. [54] found the MFFT to be related to latex particle size, although this is not always the case [49] (see Section 2.2.2). Eckersley found the MFFT to be dependent on latex particle diameter and even in the case of a series of polydisperse copolymer latices, the results suggested that the MFFT was proportional to the number average particle diameter. However, the increase in MFFT between a 150- and a 1200-nm diameter latex was only 5 K. Jensen and Morgan [36] found, that as the (monodisperse) latex particle size decreased by a factor of seven, the MFFT was reduced



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by approximately 10 K. Sperry [54] found the time-dependent dry MFFT (i.e. the transition from a cloudy to clear film in a latex pre-dried below its MFFT) increased with increasing particle size, and concluded that this was due to a simple viscous flow process which accounted for the larger interstitial voids which were present between larger particles and the longer time required for them to be filled (by particle deformation) to give a transparent film (see Section 3.1).

Sperry showed that the MFFT gradually decreased over long periods in a manner predicted by the Williams–Landel–Ferry (WLF) equation [55] such that upon extrapolation to zero time, it corresponded closely to the $T_g$. Also, MFFT curves were coincident whether the latex was initially wet or dry except in cases where water was significantly soluble in the polymer and plasticised it.

It has been proposed [56–58] that the $T_g$ at the surface of amorphous polymers is lower than in the bulk, as a consequence of the molecular weight distribution of polymer chains, with a concentration of shorter chains [59] and chain ends [60] at the particle surface, leading to enhanced polymer mobility.

Observing the evaporative drying process, typically by gravimetric methods (although Cansell et al. [61] described an alternate method using dielectric measurements), from beginning (i.e. wet latex) to end (i.e. film) leads to a sigmoidal curve, which can be divided into a number of stages for analysis. Vanderhoff et al. [62,63] describe three stages in the drying process (Fig. 1), studying drying both with and without the aid of a 'windtunnel' (to remove the humidity of the evaporating water). The drying process may be complicated, however, by virtue of it being non-uniform (i.e. different areas of the film may dry at different rates) and, hence, quantitative evaluations of the rate of drying typically involve the use of estimates of the size of, for example, dried areas of film or else the use of averages to give a mean value for the film as a whole. Despite this, attempts have been made to mathematically model the evaporative process for non-porous [64] and even porous substrates [65,66].

*Stage I.* Water evaporates from the latex surface, concentrating the latex solids content: the rate of evaporation has been determined by a number of workers [63,67,68] as being the same as the rate of evaporation from water alone, or of water from a dilute solution of surfactant plus electrolyte, i.e. such as that which constitutes the aqueous phase of a latex prepared via an emulsion polymerisation. This first stage is the longest of the three and lasts until the polymer has reached approximately 60–70% volume fraction, $\Phi$ (dependent on the stability of the latex) (74% for close packed spheres) or until the surface area of the latex's liquid–air interface starts to decrease as a result of, for example, solid film formation. Initially the particles move with Brownian motion but this ceases as the electrical double layers undergo significant interaction once a critical volume of the water has evaporated.

*Stage II.* This starts when the particles first come into irreversible contact, and iridescence (in the case of uniform sized, surfactant-free latices capable of colloidal crystal formation with its accompanying Bragg diffraction [69]) may be observed [70,71] on the latex surface. The rate of evaporation per unit area of open wet latex remains constant, but the overall rate of evaporation decreases greatly during this



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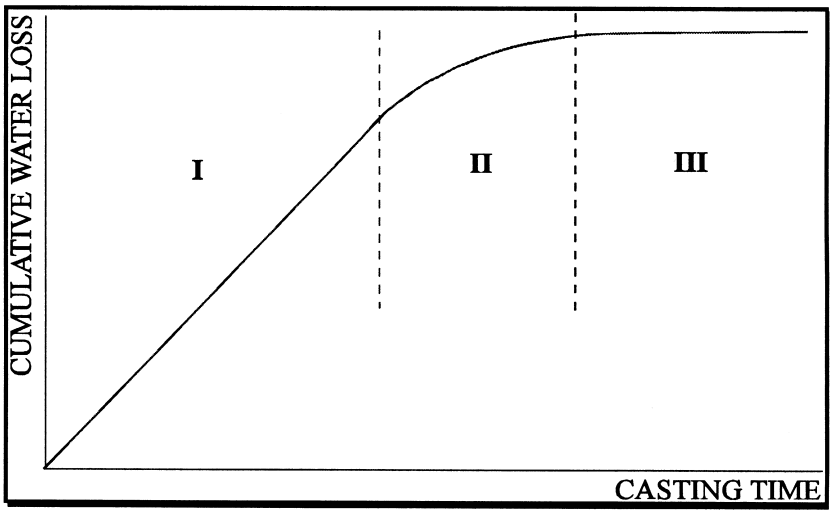


Fig. 1. Schematic plot of the water loss occurring on latex drying.

stage. (Reducing the rate of evaporation can lead to better quality films by allowing the particles more time to pack into an ordered structure before flocculation occurs. Casting at high temperatures gives the particles sufficient energy to overcome their mutual repulsion and the films are formed before the particles are fully ordered [72]). Particle deformation occurs in soft latices, in some instances, even before particle contact [73,74] as shown by the absence of a discontinuity in the rate of decrease of interparticle spacing at the volume fraction associated with the close packing of spheres in SANS data and the modelling of WANS data. Vanderhoff stated that the completion of 'coalescence' (i.e. particle deformation) marks the end of the second stage of film formation. (Less relevant to a paper on film formation, but still of interest, Ming et al. [75] have followed the re-wetting and redispersion of dip cast carboxylated styrene-butadiene latex films using the technique of cryogenic SEM, finding that even particle deformation can be reversible under certain conditions.)

*Stage III.* This stage starts with the initial formation of a continuous film. The remaining water leaves the film initially via any remaining interparticle channels and then by diffusion through the fused polymer skin, but the rate of evaporation eventually slows to (asymptotically) approach that of diffusion alone. The rate of water removal may be decreased by film additives that are impermeable (as a result of the increased diffusion path length) or hydrophilic (due to polar interactions). It is during this final stage that a soft latex becomes more homogeneous and gains its mechanical properties as polymer chain interdiffusion occurs (a process variously termed maturation, autohesion or further gradual coalescence) and particle interfaces tend to become less distinct. Researchers [76] have noted a drastic change in



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film properties between stages II and III, as the initially brittle cohered particles become more ductile due to polymer chain entanglements.

Croll [67,77] unlike Vanderhoff, describes the process of drying in just two stages consisting of an initially rapid water loss followed by a declining loss. An evaporation front was envisaged to move into the coating leaving behind a 'dry' porous layer, containing no continuous water, with ahead of it a concentration gradient across a 'transition zone', losing water via interparticle percolation, to the dry layer above and supplied with water from the still wet latex below. The rapid rate is maintained for as long as wet latex remains at the substrate, then the rate progressively decreases. Eckersley and Rudin [78,79] found that gravimetric water loss studies supported a mechanism similar to Croll's percolation-type process. Using the technique of ESEM, the formation of a skin was observed, which the authors postulated was sufficiently hydrophilic or porous not to impede the flux of water. ESEM [80] allows imaging of insulating surfaces (i.e. there is no need for a thin conducting coating of metal) under various atmospheric conditions (e.g. hydrated samples, such as wet latices [81]) by the use of a 'vacuum gradient' throughout the electron path. A system of apertures and differential pumping overcomes the problem of the high vacuum requirements of the electron gun found in conventional SEM and TEM: the atmosphere around the sample and its interaction with the electron beam, back-scattered from the sample, produces environmental secondary electrons and positive ions, making the imaging mechanism possible. Control of pressure (up to 20 torr) and of temperature (down to −150°C) in the sample chamber can, for example, enable water vapour saturation to be maintained.

Keddie et al. [82,83] using ESEM to monitor film morphology and multiple-angle-of-incidence ellipsometry (MAIE) to monitor mean refractive index and the kinetics of drying, showed that voids could remain in the film when evaporation was complete but film formation was ongoing. This is in agreement with Croll [67,77], and Eckersley and Rudin who also showed that clear films were not necessarily completely dry but could contain water-filled domains significantly smaller than the wavelength of light.

Bierwagon [84] considered film formation in relation to the same three regimes as proposed by Vanderhoff, discussing drying in terms of film thickness and latex solids content. For example, a film of low solids content could dry faster than one of high solids content despite the lower quantity of water to be removed from the latter which, however, reaches the diffusion-controlled stage (i.e. surface closure) sooner, and then loses water more slowly. As the film dries from the surface down, a fixed film area is then subject to contraction in the $z$-plane, thereby producing stress in the $x$–$y$-plane. If polymer elasticity is insufficient, then the stress can be overcome by slippage between the coalesced layer and the fluid beneath giving rise to the 'mud-cracked' surface effect that is often observed in latex cast films (see Section 3).

Although the mechanistic processes of film formation may not stay rigorously within the bounds proposed by Vanderhoff [63,63] across the full range of film forming conditions, e.g. where drying is non-uniform (see below) and processes may



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occur concurrently, it is still considered useful to order the more detailed discussion below in terms of three stages:

I Evaporation, particle concentration and ordering.
II Particle deformation.
III Polymer chain diffusion across particle boundaries.

*2.2.1. Evaporation and particle concentration: film drying stage I*

Croll [67] found similarities in the drying rates of film-forming acrylic latex and non-film-forming slurries such as mica and clay. Water loss was linear over much of the drying process, at 85% of the rate for water alone, i.e. in the absence of particles. It was proposed that it was the surface area reduction caused by the presence of particles, which reduced the rate, since at high dilutions, early in the drying process, the rate was comparable to that of water alone. Changes in size and chemical composition of the particles did not significantly alter the rate. Winnik and Feng [85], however, found that a surfactant-free non-film-forming latex (MFFT > casting temperature) dried faster than an acrylic film forming latex under the same conditions, and that a blend of the two dried slowest. This was explained in terms of the size of the capillaries available for water transport being reduced by the deforming soft latex. Surfactant added to the soft latex increased the drying rate to that of the hard latex by providing hydrophilic pathways for the diffusion process. Keddie [83] also has reported that a harder latex dried twice as fast as a softer latex.

Initially linear drying rates in the early stages of film formation have been found by Eckersley et al. [78] and Steward et al. [86].

The ending of the constant rate period of water loss is attributed by Okubo et al. [87] to skin formation overlying the wet latex. Others have also reported visual observations of skin formation [18,88] whilst Butt et al. [89,90] detected skin formation by AFM. Keddie [83], using ellipsometry, reports that the velocities of vertical drying fronts are dependent on temperature because of the effect on rate of evaporation of water and upon particle deformation. For temperatures near the $T_g$ of the polymer, voids are created near the air surface (cf. cloudy flocculated region of the Hwa [91] observations below), which then decrease in size over time to produce an optically clear film.

Although a vertical concentration of water might be anticipated as a consequence of water evaporating from the top of the film, non-uniform lateral drying is observed, as first reported by Hwa [91], even when the films are cast from a constant wet thickness with a view to producing a dried film of uniform thickness. Hwa determined that as the aqueous phase evaporated, three distinct regions could be observed, e.g. a dry region (transparent), a wet (dispersed latex) region (milky appearance), and an intermediate region of flocculated latex (some turbidity) such that the film as a whole embodied all three periods of Vanderhoff's drying regime. In Hwa's circular films, these regions formed concentric bands and the films dried from the outside inwards. It was noted that these rings differed, dependent on the



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$T_g$ of the polymer. In the case of a low $T_g$ polymer, the flocculated and dry regions were both continuous, whereas for hard polymers, fine radial cracks were apparent, due to the relief of stresses, and the dry region was more opaque (due to cracks) than the flocculated region. Hwa was able to show that the flocculated region had some mechanical strength (i.e. it was not washed away in a stream of water, as was the wet latex), presumed to result from van der Waals' forces and that the particles were not close packed (the volume fraction, $\Phi$, was between 0.49 and 0.62) such that the region was porous. The flocculation was found to be dependent, to some extent, on the nature of the surfactant used: easily desorbed soaps were proposed to be squeezed away from the points of particle–particle contact to form micelles in the particle interstices and, hence, aid flocculation when compared to the surfactant-free latices. Surfactants, which were not easily desorbed, however, delayed the onset of flocculation to high volume fractions.

The fact that latices of differing stability will flocculate at different particle–particle separations (i.e. at different rates) has been used to advantage by Okubo and He [92] in the preparation of asymmetric film from latex blends. Such films showed side-dependent (i.e. polymer–substrate or polymer–air interface) variation in properties such as film tackiness and permeability.

The constant rate ($r_c$) period of drying was studied by Poehlein et al. [62] in a wind tunnel with 50% relative humidity (RH) and with an air speed in the range of 1–4 mph (2.25–9 m $s^{-1}$), with respect to latex particle size, using an equation to account for the non-uniform drying. If the three regions described by Hwa [91] are expressed in terms of film areas [e.g. $A_I$ = area of wet latex; $A_{III}$ = area of dry film (the rate of evaporation in this region was assumed to be negligible)]; and $A_{II}$ = flocculated region area, then:

$$r_c = \frac{1}{A_I + A_{II}} \frac{dW}{dt} \tag{1}$$

where $W$ = gross film weight and $t$ = time.

It was shown that the rate, $r_c$, increased with increasing particle size (although this was not so apparent in still air, and was not predicted by a theoretical equation based on heat transfer theory). Poehlein et al. [62] speculated that the rate increase with particle size was a result of the differences in water content in the double layer, or the particle surface area available for surfactant adsorption, although the latter was minimised by attempted adjustment of the surface tension of the latices to a constant value.

Armtrong and Wright [93] noted that the films prepared from latices of a relatively large particle size (750 nm) were of a poorer quality (i.e. poorer corrosion resistance due to greater porosity) than those films prepared from latices of a smaller particle size (105 nm). This was ascribed to the larger particles showing less coalescence, but it was not clear whether the poor quality of the film was the result of differing rates of drying resulting from the differing particles sizes, or simply due to the larger interparticle voids that would be found for the larger-sized uncoalesced particles.



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As a result of non-uniform drying [62,85,87,91,94], films cast on a flat surface (without containing-walls) dry first at the edges as a consequence of the convex nature of the meniscus, whereas dish cast films, having a concave meniscus, dry first at the centre. Recently Deegan et al. [95] considered evaporation from a liquid drop, such as a coffee drop, and predicted the deposition of dispersed solids at the edge. This was ascribed to a form of capillary flow towards a pinned contact line at the edge of the drying drop. The mechanism predicted a power law growth with time, independent of the particular substrate, carrier fluid or deposited solids.

Denkov et al. [96] have used optical microscopy to study the ordering of (large uniform) polystyrene latices in thin (monolayer-to-multilayer) films upon drying. In a cell which produced a concave liquid surface, the thinnest part of the film, i.e. at the centre, approached the substrate until the particles came into contact with it. When the meniscus fell below the top of the particles, continued evaporation drew a flux of water from the surrounding regions, first ordering the particles at the centre and then transporting particles to extend growth of the ordered assembly around the nucleated region. This process was termed 'convective self-assembly'. It was found the flux could be sufficient to lift the particles to form bilayers or multilayers of different thickness. Although low ionic strength latices are believed to dry uniformly (e.g. Juhué et al. [97]), surface irregularities consisting of over-riding layers of ordered particles have been observed on the surface of PBMA latex-cast films [71]. The development of surface iridescence in such a film as a function of drying time is illustrated in Fig. 2 whilst Fig. 3 shows the conditions [88] inside the laboratory oven (as measured just above the latex) during drying.

Juhué [97] reported that the presence of 2% (by weight) sodium dodecyl sulphate (SDS) in a PBMA latex resulted in particles which were much more ordered at the 'last spot to dry' than in the rest of the film and Winnik [98] stresses an indirect consequence of this result in relation to modern instrumental methods, which may focus on only a small area of film, and the caution needed in generalising results from such observations.

Feng et al. [99] found that surfactant-containing films were 25% thinner at the centre than at the edges and they attributed this to the aforementioned process of 'convective self-assembly'.

Routh and Russel [100] have modelled the propagation of drying fronts (of close packed particles) arising from surface tension-driven horizontal flow and compared results from non-uniform drying with experimental data. The total recession of the waterfront, at the instant that the entire film dried, was predicted to increase with: (i) dispersion viscosity; (ii) initial film thickness; and (iii) decreased particle size. The 'opentime' before the edge dried was predicted to increase with: (i) surface tension; (ii) dispersion viscosity; and (iii) particle size. Experimental selective drying illustrated the predicted non-monotonic variation in film thickness between the evaporating and non-evaporating (covered) regions.

From cryogenic SEM studies, Sheehan et al. [101] considered that the extent of the 'flocculated' region or 'consolidation front' (i.e. the region consisting of ordered particles which have lost water) depended on the strength of the repulsive forces relative to capillary forces arising from a drying front meniscus.



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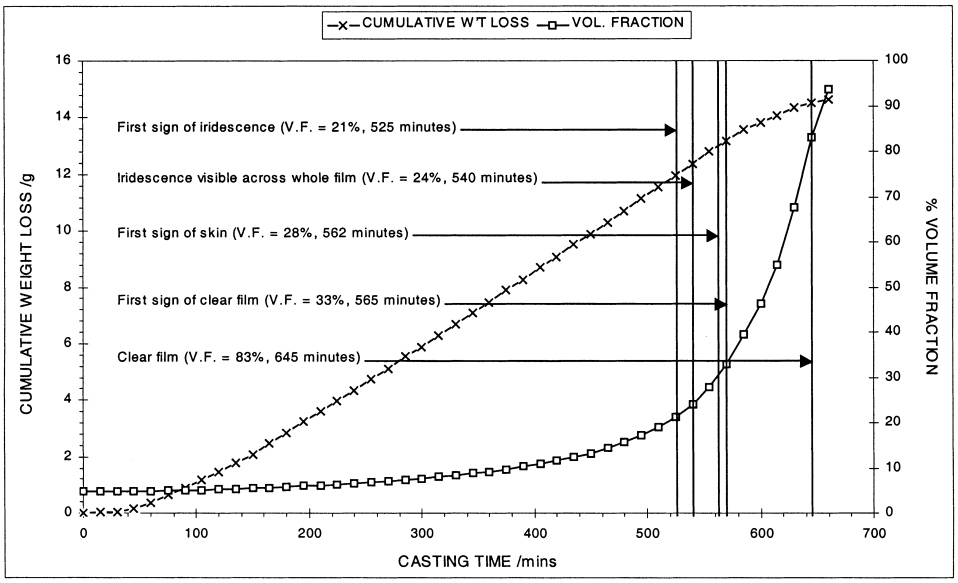


Fig. 2. Plots of cumulative weight-loss, and percentage volume fraction of polymer solids content during the casting of a surfactant-free poly($n$-butyl methacrylate) latex film at 313 K.

### 2.2.2. Latex particle deformation: film drying stage II

Over the years a number of theories regarding the driving forces for latex particle deformation have been considered. These include:

- dry sintering [102,103];
- capillary theory [104] and wet sintering [105–107];
- piston-like compression [68] arising from the preferentially dried surface layer building in thickness from the top down; and
- interparticle cohesion promoted by surface forces [108].

*Dry sintering* is driven by the polymer–air surface tension. Dillon et al. [102] discuss the coalescence processes in terms of the viscous flow of the polymer. This viscous flow results from the shearing stresses caused by the decrease in the polymer–particle surface area, and the resultant decrease in polymer surface energy, as the film is formed. By using values relevant to the typical polymer latex, Dillon considered the forces acting on the interparticle 'holes' (of radius $R$), as denoted by the Young–Laplace equation:

$$P_i - P_e = \frac{2\gamma_{pa}}{R} \tag{2}$$

where $P_i$ = internal pressure (see Fig. 4), $P_e$ = external pressure; $\gamma_{pa}$ = polymer–air interfacial tension.



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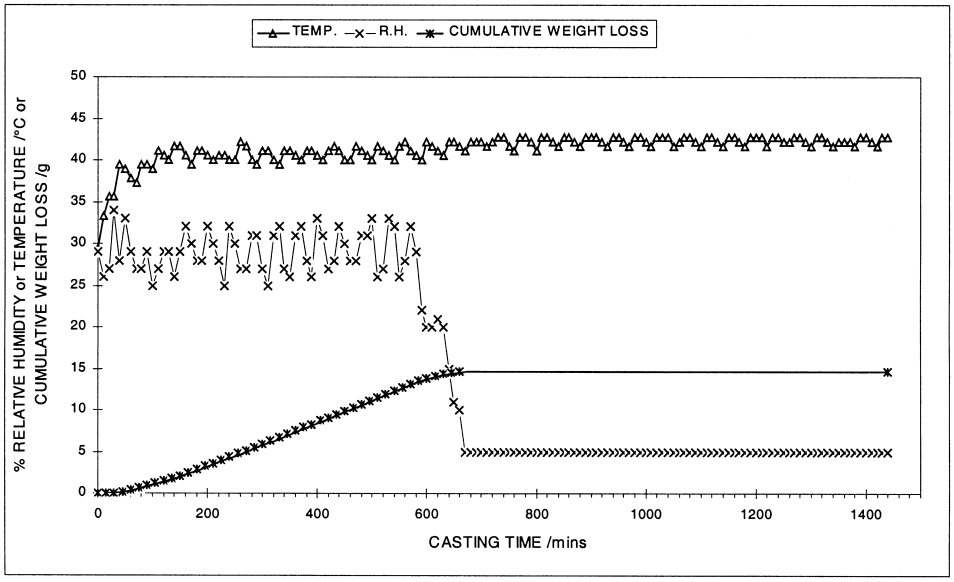


Fig. 3. Oven conditions during the casting of a surfactant-free poly($n$-butyl methacrylate) latex film at 313 K.

This concluded that the pressure acting on the void could not be contained as a result of the polymer, being permeable to the trapped air and water vapour. The extent of coalescence (as determined from the half-angle of coalescence) was then related to an equation developed by Frenkel [103]:

$$\theta^2 = \frac{3\gamma_{pa} t}{2\pi\eta r} \tag{3}$$

where $\theta$ = angle seen in Fig. 4, i.e. the half angle of contact, $t$ = time, $\eta$ = polymer viscosity and $r$ = particle radius.

Dillon showed that a plot of $\theta^2$ as a function of $1/r$, as measured by electron microscopic observation of shadowed particle pairs, gave the expected linear relationship. Recently Pekcan [109,110] has studied the kinetics of void closure by viscous flow of dry hard latex particles annealed above their $T_g$ values by measuring their optical clarity and steady state fluorescence.

Brown [104] who considered that dry sintering driven by the polymer–air interfacial tension was irrelevant to film formation, which he assumed finished when water evaporation ended, discussed capillarity theory where deformation of the particles was driven by the air–water interfacial/surface tension, $\gamma$, in the interstitial capillary system between particles, during drying. He considered the forces acting both for and against the coalesence of the latex particles, with the conclusion that for coalescence to occur, an inequality must exist in which the capillary force, $F_c$, (resulting from the surface tension of the interstitial water,



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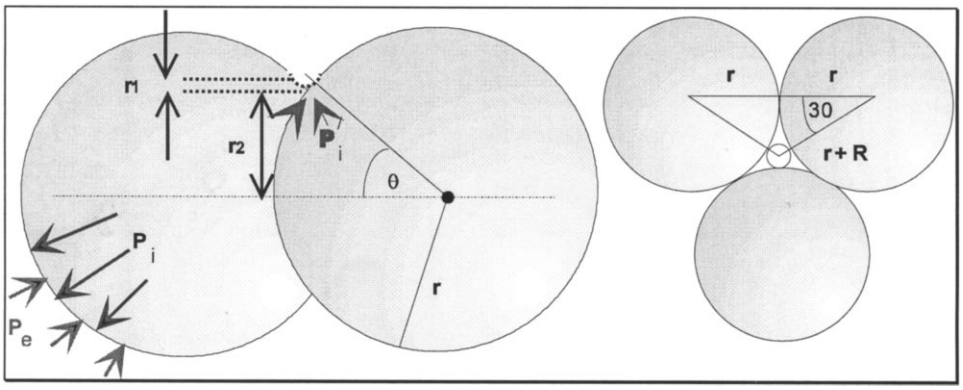


Fig. 4. A cross-section of sintered latex particles and a plan view showing the interparticle capillary.

caused by the formation of small radii of curvature between the particles as the water evaporated) must overcome the forces of resistance to deformation. $F_G$, of the latex spheres: i.e. $F_C > F_G$. These forces, Brown presumed, were proportional to the relevant pressures, with the area over which they act as the constant of proportionality and, hence $P_C > P_G$. From Laplace's equation, Brown derived the capillary pressure, $P_C$, for the cylinder of radius $R$, between three contiguous latex particles (see Fig. 4), in terms of the latex particle radii, $r$:

$$P_C = \left(\frac{2\gamma}{R}\right) = \frac{12.9\gamma}{r} \tag{4}$$

$$\frac{R}{R+r} = \cos 30^\circ \tag{5}$$

By treating the particles as elastic bodies, the pressure on the area of contact was also calculated in terms of the elastic shear modulus, $G$, of the polymer and, hence, Brown derived an expression for coalescence:

$$G_t < \frac{35\gamma}{r} \tag{6}$$

where $r$ = latex particle radius and $G_t$ = time-dependent shear modulus. (The theory is based on the deformation of two elastic spheres with elastic shear modulus $G$. The time-dependent shear modulus, $G_t$, is necessary to compensate for the fact that the particles are in fact viscoelastic i.e. they exhibit a stress response which is out of phase with the applied strain [111].)

Sheetz [68] later amended Brown's equation for capillary pressure to account for



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the situation when the contact angle, $\vartheta$, between the polymer and water did not equal zero:

$$P_C = \frac{12.9\gamma\cos\vartheta}{r} \tag{7}$$

Sheetz also formulated his own theory of latex film formation based on closure of the surface layer. In qualitative terms, as the latex becomes concentrated by evaporation of the water, flocculation occurs as the repulsive forces of the particles are overcome. Particles at the latex–air interface are then subject to the forces of capillarity and therefore, film formation, leading to compaction and deformation of the particles under the surface, i.e. a film forms from the surface downwards. Water in the film's interior must then diffuse through the upper surface layers to escape and this generates a further vacuum-like compressive force acting in a direction normal to the film's surface or piston-like compression. The mechanism is, therefore, seen to be based on Brown's capillary mechanism and diffusion producing an osmotic pressure. Sheetz analysed the thermodynamics of the system and showed that the source of the energy for the particles' fusion was the heat in the environment — converted for film formation by the evaporation of the water. As evidence that the diffusion was involved in the coalescence mechanism, Sheetz cited the facts that: (i) a film containing a water-permeable polymer dried at a rate faster than one that was less water permeable; and (ii) that a film in which capillary action was prevented (by means of a thin solvent-cast film) could form a continuous film, whilst the same polymer without the solvent-cast deposit formed a discontinuous film.

Although Dobler et al. [112] generally agreed with the mechanism of Sheetz, they believed, from observations of iridescence, that the surface of the latex closes (i.e. complete surface iridescence followed, presumably, by skin formation) long before the particles become close packed in the bulk latex.

Like Sheetz, Mason [113] also identified a number of erroneous assumptions and points of error in Brown's work. Firstly, in converting his forces (capillary and deformation) to pressures, Brown assumed the same constant of proportionality (i.e. an undefined area, $A$, over which the capillary force and contact pressures are exerted) for each, e.g. see Eq. (4):

$$F_C = \frac{12.9\gamma A}{r} \tag{8}$$

Mason points out that these areas (for $F_C$ and $F_G$) are not necessarily identical and repeated the analysis using corrected values for the areas, such that the condition Brown quoted in Eq. (6) became:

$$G < \frac{67.6\gamma}{r} \tag{9}$$



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Mason also criticises the fact that Brown assumed that the capillary pressure remained constant whilst the latex particles coalesced, and derived a new equation for the capillary pressure based on the deformation of the (elastic) spheres. From this, the criterion for film formation moved yet further from Brown's inequality to give:

$$G < \frac{266\gamma}{r} \tag{10}$$

It has also been noticed [54,114] that Brown's work has also been criticised for using a polymer modulus which was obtained for the dried polymer, rather than a polymer in an aqueous environment.

Despite Brown's differences with Dillon over the role of the evaporating aqueous phase in latex coalescence mechanisms, both research groups presumed that the forces of coalescence were inversely proportional to the latex particle radii. Vanderhoff et al. [105–107] indicated that the pressures for coalescence, resulting from the works of Dillon and Brown, were insufficient to cause the coalescence of particles greater than 1 μm in diameter and extended the theories accordingly. These extensions to the theory were again based on determining the forces acting to cause coalescence. Vanderhoff's 'wet sintering' mechanism proposed that as the water evaporated, the particle coalescence was initially hindered by repulsion of their stabilising layers. Further evaporation then resulted in particle–particle contact, and the force increased due to: (i) the polymer–water interfacial tension ($\gamma_{pw}$); and (ii) the small radii of curvature in the region of coalescence ($r_1$ and $r_2$ as seen in Fig. 4). Hence:

$$P_i - P_i' = \gamma_{pw}\left(\frac{1}{r_1} - \frac{1}{r_2} + \frac{2}{r}\right) \tag{11}$$

where $P_i$ = internal pressure, $P_i'$ = internal pressure in the region of coalescence, $r$ = particle radius and $r_1$ and $r_2$ are radii as seen in Fig. 4 [see Eq. (2)].

As with the work of Brown [104], Mason [113] criticised Vanderhoff's work for mathematically confusing force with pressure. However, whereas the error in Brown's model led to the error being less that an order of magnitude, Mason claimed Vanderhoff's error completely invalidated the work. Stewart and Johnson [115] investigating the dry sintering of freeze-dried samples of a polystyrene latex by differential scanning calorimetry (DSC) used an equation derived from that of Vanderhoff for wet sintering, but in which the particle–water interfacial tension was replaced by the polymer surface tension. The good correlation between the experimental and calculated results was claimed to validate Vanderhoff's equation.

Dobler et al. [70] demonstrated that wet sintering driven by the polymer–water interfacial tension alone without concurrent evaporation of water, i.e. for films which remained soaked in water, did occur, but that under normal film-forming conditions, with evaporation of water, it would make an insignificant contribution [112].



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The aforementioned theories assumed that the latex particles acted as viscous fluids (as depicted by the Dillon model) or elastic spheres (as depicted by Brown and Mason, etc.). Kendall and Padget [108] noted that particles are not truly viscous from the fact that latex films can show a residual particulate structure, and that they were in actuality elastic with a viscous component. Similarly, they reasoned that the fact that a film does not attain its full strength until after the point when all of the water is removed [116–118] implied modifications were necessary to Brown's model. Accordingly, Kendall and Padget introduced a new model of interparticle cohesion based on the Johnson, Kendall and Roberts theory [119] derived from the classical Hertz Theory (1822) for non-attracting elastic bodies but allowing for van der Waals' attractions of adhesion and interfacial surface energy between elastic spheres — again, its applicability is limited by its foundation on elastic spheres which would instantly deform, in contrast to particles undergoing viscous flow. For a hexagonal close-packed array of spheres, Padget states that voids are eliminated (i.e. opaque film to clear film) when:

$$\frac{2Er}{\gamma(1-\nu^2)} = \frac{9\pi}{2} \tag{12}$$

i.e. the condition for film formation:

$$E < \frac{9\pi\gamma(1-\nu^2)}{4r} \tag{13}$$

where $\gamma$ = energy released when two spheres of unit move into contact, $\nu$ = Poisson's ratio[2] and $E$ = Young's modulus — Note that:

$$G = \frac{E}{2(1+\nu)} \tag{14}$$

The dimensionless ratio on the left of Eq. (12) is described by Kendall and Padget [108] as the 'crumble number'. If this number is high, then coalescence will not occur; if the crumble number is low, then a transparent non-porous film will form. The transition was said to occur at a crumble number of 'approximately 10'. Kan [114] indirectly investigated the deforming forces during latex coalescence at the MFFT, by measuring the moduli of water saturated latices. The magnitude of the results showed good agreement with the Kendall theory.

Lamprecht [120] studied film formation by treating the latex particles as linear viscoelastic bodies (as opposed to treating particle deformation as an elastic phenomenon, but still a simplification compared to the non-linear case), and included dynamic factors such as creep deformation in relation to the rate of water removal. A mistake in Lamprecht's calculation was indicated by Eckersley and

[2] $\nu$ = lateral contraction per unit breadth/longitudinal extension per unit length.



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Rudin [35] who derived a corrected criterion for film formation assuming viscoelastic spheres:

$$\frac{1}{J_c(t')} \leq \frac{34\gamma}{r} \tag{15}$$

where $t'$ = time when the two spheres are in closest proximity to one another and $J_c(t)$ = the polymer's time-dependent creep compliance (i.e. time-dependent modulus, $G(t)$, in the linear viscoelastic region).

Eckersley and Rudin [35,79,121] went on to develop their own (time-dependent) viscoelastic model of film formation based on the interfacial tension forces acting in a complementary manner with the capillary force to cause coalescence. Eckersley's model assumes that the contributions to deformation of the linear viscoelastic material by the capillary and interfacial forces is additive such that the radius of the area of contact between particles, $a$, (which is equivalent to $r_2$ in Fig. 4) is given by:

$$a = a_{\text{capillary}} + a_{\text{interfacial}} \tag{16}$$

$$a = \left(\frac{2.80r^2\gamma_i}{G^*}\right)^{1/3} + \left(\frac{3\gamma rt}{2\pi\eta^*}\right) \tag{17}$$

where $a$ = contact area as a function of particle radius $r$, $\gamma_i$ = interfacial tension (the model was experimentally evaluated under conditions of both wet and dry sintering such that the interfacial tension can be the polymer–air or polymer–water interfacial tension), $t$ = elapsed drying time, $G^*$ = complex modulus (see following paragraph) and $\eta^*$ = complex viscosity.

Note that the fact that latex particles are viscoelastic in nature, and have a complex modulus has been discussed by Richard [122]. Viscoelastic measurements consist of studying the complex viscoelastic modulus (in terms of, for example, shear, torsion or tensile deformation) as a function of frequency and temperature, using forced oscillation devices. The modulus is described as complex since the stress response is generally out of phase with the applied strain. The real part of the modulus, which is given by the in-phase stress–strain amplitude ratio, is the storage modulus and represents the elastic response of the latex. The viscous relaxation yields an out-of-phase amplitude ratio, defined as the loss modulus, which is the imaginary part of the complex modulus. If $G_s$ is the shear storage modulus, and $G_l$ is the shear loss modulus, then the shear complex modulus $G^*$ is given by: $G^* = G_s + iG_l$.

Mazur and Plazek [123] studied neck growth at a constant temperature between polymer spheres and plates of similar polymer using a development of the Johnson, Kendall and Roberts theory [119]. They found that the early stages were entirely elastic with viscous flow not developing until much longer times and that 'for colloidal polymer particles, quasi-elastic deformation should always be sufficient to



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achieve complete condensation'. Keddie similarly cites studies by Kim and Winnik [124] in which the early stages of the deformation of PBMA particles show flat faces and sharp necks rather than the rounded-out necks to be expected from viscous flow. Visschers et al. [125] noted that since a non-linear viscoclastic theory is not yet available then the viscoelastic problem tends to be simplified to a quasi-elastic one in which the elastic modulus is replaced by the asymptotic value of the shear modulus. As Mason [113] has pointed out, droplets of viscous liquid film form irrespective of particle size, but a particle size dependence is to be expected for quasi-elastic behaviour.

The kinetics of film formation have been studied by Keddie et al. [83,126] using two acrylic latices ($T_g$ values of 268 and 286 K) cast at temperatures between 278 and 318 K. At temperatures approximately $> 20$ K above the polymer $T_g$, the evaporation of the aqueous phase was said to be rate-limiting and both polymer films formed in comparable times. However, at temperatures closer to the $T_g$ then particle deformation was the rate-limiting factor: the lower $T_g$ latex taking longer to form a film. This was attributed to the softer latex deforming to a greater extent than the hard latex at similar times, and therefore decreasing the air–water interfacial area available for evaporation. In the case of the hard latex, evidence suggested a drying front moving inward from the film's periphery, initially creating air voids at the latex/film surface, followed by a coalescent front shrinking the voids due to a reduction in surface energy. A model based on the viscous flow of the polymer was used to describe the process.

The role of capillary forces in promoting particle deformation is still disputed. Sperry [54] has investigated the role of water in film formation using MFFT measurements on: (i) latices pre-dried at temperatures below their MFFT (which show the MFFT by a transition from an opaque to a clear film); and also (ii) wet latices. In the case of a hydrophobic polymer, the dry MFFT was virtually identical to the wet MFFT indicating the presence of water and, hence, capillary forces, contributed little to film formation. Plasticisation by water was said to be the cause of hydrophilic polymers yielding wet MFFTs which were lower than the dry MFFTs — by up to approximately 10 K. The dry MFFTs decreased linearly with log[time] which was attributed to (Williams–Landel–Ferry [55] type) viscoelastic relaxation[3] resulting from van der Waals' attractive forces/polymer–air surface tension and the collapse of interstitial voids. When extrapolated to zero time, they were close to the $T_g$. Lin and Meyer [127], however, found using AFM, that the corrugation height of a poly(isobutyl methacrylate) latex smoothed out 10 times slower under dry conditions than when water was condensed on the sample and thus concluded that capillary forces were important in deformation. Visschers et al. [128] have calculated, using modified forms of the Brown/Mason equations, that capillary forces are more than sufficient to overcome repulsive forces and are orders of magnitude greater than van der Waals' attractive forces.

[3] Viscoelastic behaviour can be characterised by the relaxation time, i.e. the time taken for residual stresses within the material to decay [111].hgb



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The role of water in latex film formation is uncertain, between the extremes of it being either a fundamental driving force for promoting particle deformation or merely a convenient vehicle to keep low $T_g$ 'sticky' polymers dispersed at ambient temperatures prior to film formation. In a recent review of the literature on latex film formation, Dobler and Holl [129,130] concluded that because experimental results can be found which support all of the main theories (i.e. wet and dry sintering, capillarity, diffusion through a surface layer), the process is obviously extremely complex and perplexing. The unifying mechanism that convinces the whole of the scientific community has yet to be presented.

The consequences of deforming forces acting upon uniform spherical particles, which have become concentrated during stage I of film formation are next considered.

As the volume fraction of stable monodisperse latex particles increases, they may pass, if the ionic strength is low so that double layers are extensive, from a disordered state into a liquid crystalline array capable of Bragg diffraction of light [69]. The approach to the ordered state is possible since the particles experience charge repulsion but still retain some mobility. As further water is removed, the diffuse double layers will become compressed to such an extent that interparticle repulsion is lost and particles will coagulate into a primary minimum [131], after which, a further close approach is said, for smooth surfaces, to be limited to 0.2 nm [125] by the considerable Born repulsion of electron cloud overlap. For marginally stable latices, both an increase in volume fraction and an increase in ionic strength, upon water evaporation, may promote coagulation. Films formed from the building blocks of fractal coagulates are poorly ordered with much greater surface roughness [94].

It was originally deduced by Lissant [132], whilst investigating high-internal-phase-ratio emulsions, that above the maximum packing volume available to close packed hard spheres, i.e. 74%, deformation of a sphere to fill all of the space (whilst keeping the same volume as the original sphere) will give rise to a rhomboidal dodecahedron. Joanicot et al. [94] apparently showed such polyhedra by staining the hydrophilic membrane (i.e. particle interfaces — which, on particle deformation, defined the polyhedra), when a latex had lost most of its water — comparing the structure to that of a foam.

Roulstone et al. [133] was first to show the results of using a freeze-fracture replication TEM technique, which combined the advantages of the high magnification and high resolution of the TEM but without the disadvantages of distortion caused by sample preparation or by beam damage. A tensile snap method was used at $\sim 413$ K (140°C) and $5 \times 10^{-3}$ torr followed by immediate replication. Films cast from PBMA latices at room temperature and low RH (approx. 25%) had been stored for at least 1 month at room temperature before FFTEM analysis. Extended areas of crystalline order could be seen with dislocations and grain boundaries. Features of both fractures across particles (rough textured hexagons) and between particles (smooth rhombohedral faces) could be seen. Raised trigonal and square-based pyramidal features from the vertices of particles below the plane of fracture could also be seen — all features felt to be compatible with fracture of an array of



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rhombic dodecahedral particles. Unless structural weakness within a film promotes fracture across a particular plane then a random snap fracture need not simply traverse the diameter of all particles but rather chords might be expected together with fracture between particle surfaces. Interestingly the FFTEM studies by Wang et al. [134], also using surfactant-free PBMA particles, but dried slowly at approximately 100% RH, appeared to show less mechanical strength arising from polymer chain interdiffusion since fracture took place entirely at the particle surfaces. A very regular array compatible with cleavage of rhombic dodecahedra was shown across some 40 particles as well as ordered regions separated by dislocations in structure. Further work by the same group using compression of hard polystyrene and PMMA particles produced micrographs of great clarity [20]. Joanicot et al. [73,94] have shown, using shear to induce order, that extensive long-range order could be produced in the wet and which was preserved upon drying. The work of Roulstone also showed that for PBMA cast at higher temperatures, the particle boundaries were less distinct and that upon annealing at 393 K were lost altogether. Similar featureless cross-sections were shown for soft ($T_g < 273$ K) poly(*n*-amayl methacrylate) (PAMA) and poly(*n*-hexyl methacrylate) (PHMA) particles cast at 313 K [88].

The use of neutron scattering experiments (SANS), together with SEM/TEM/AFM has permitted the 'observation' of the latex particle structure during film drying; allowing the three-dimensionally deformed shape of the latex particles to be studied. Joanicot et al. [94] and Chevalier et al. [73] have studied the particle packing of latices consisting of a soft hydrophobic polystyrene-poly(butyl acrylate) copolymer core, stabilised by a hydrophilic shell [either neutralised poly(acrylic acid) or a monolayer of zwitterionic (i.e. both positive and negative ionic parts, such that overall it is neutral) surfactant]. Such a stable configuration allows the close packing of the particles before coalescence occurs.

By the use of very thin films, the SANS scattering patterns, produced by latices as the dispersions concentrated (to between approx. 20 and 50%, by evaporation), were studied and interpreted in terms of each of the monodisperse particles being surrounded by 10–12 nearest neighbours, and forming face-centred cubic crystalline-like particle packing. Such ordering of the particles was lost (as shown by the replacement of the scattering pattern by Debye–Scherer rings) either: (i) when the dispersion was too dilute (i.e. latex volume fraction $< 20\%$); (ii) if salt was present to screen the interparticle electrostatic forces; or (iii) when the latex was polydisperse.

SANS has also been used by Rieger et al. [135,136] to investigate the structure of styrene/*n*-butyl acrylate copolymer latex film. Again, the scattering data was interpreted such that the structure evolved during film formation consisted of crystallite-like domains of latex particles arranged into a closed-packed face-centred cubic configuration. This work differed from the aforementioned work of Joanicot et al. in that the films were dried and then exposed to (deuterated) water, which diffused into the interstices between the particles. The size of the crystallite domains was dependent on film casting temperature: elevated temperatures and



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the resultant reduced time for particle packing leading to smaller domains and increased numbers of amorphous regions and domain boundaries.

If uniform latex particles remain stable, but do not have the extended double layers associated with low ionic strengths which promote colloidal crystalline order and a volume fraction of 0.74, then they could potentially randomly close pack at a volume fraction of 0.58. Isotropic deformation is then predicted [137] to yield space filling polyhedra with 14–17 faces having predominantly 4, 5 or 6 sides. Visschers [125] notes that where void closure results in a 26% reduction in film volume (i.e. for 0.74 volume fraction close packing of spheres) then isotropic shrinkage would lead to a 9.5% reduction in the former particle radius. Shrinkage along the particle–substrate interface may be inhibited (leading to stresses and possibly even cracks) when uniaxial shrinkage may be more realistic. In the latter case interparticle distances in the plane parallel to the film surface remain constant, but in the direction normal to it, a 14% reduction in the original particle radius occurs.

Meyer [138] has indicated that hexagonal close packing is theoretically possible, as well as cubic close packing. Of these, only a face-centred cubic (FCC) lattice leads to rhombic dodecahedra when the particles deform to fill available space, whereas a hexagonal close packed (HCP) lattice leads to a trapezo–rhombohedron. Since both shapes share many geometrical features, they are not easily distinguishable. Meyer notes that the FCC lattice is quoted most often in the literature, but also notes that the two techniques typically used to provide insight are electron microscopy or neutron scattering. He goes on to state that a trapezo–rhombohedra, when fractured along its dominant fracture plane, will yield the same hexagonally close packed particles showing three rhombi on the exposed surface as a rhombic dodecahedra. Whilst the micrographic evidence of the Joanicot paper does provide conclusive evidence of rhombic dodecahedra and, therefore, an FCC lattice, the detection of FCC packing in one or more cases is not sufficient justification that all latex particles will form such a lattice, and the neutron scattering results in Joanicot's paper, whilst also cited as evidence of such structure, are claimed by Meyer to be inconclusive of either FCC or HCP structure. Meyer concludes that current literature provides no conclusive evidence as to the geometric destiny of spherical latex particles. With respect to SANS scattering data, the predicted differences between various particle configurations (FCC, HCP and also body centred cubic) are discussed by Rieger et al. [135] so as to provide evidence that his results were those of an FCC lattice.

Chevalier et al. [73] also used the SANS evidence to describe particle 'coalescence'. Coalescence was observed to move through the drying surfactant-coated latex in the form of a 'coalescence front' progressing from the periphery of the film inwards: the progress of which could be reversibly halted by stopping the evaporation of the water. At the interface between dry film and wet latex (in which the packing fraction was $< 0.74$) a phase inversion occurred from a polymer in water to a water in polymer system. Coalescence was said to only occur if the hydrophilic layer was breached and this was seen to differ depending on whether the hydrophilic layer was the surfactant or the acrylic acid. The films stabilised by poorly adsorbed surfactant, formed a continuous matrix of polymer-containing hydrophilic



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domains, whilst those latices stabilised by the polymer retained the foam-like structure: as indicated by a collapse of the diffraction peak in the case of the former, but a peak which could be reinstated by swelling the film with water in the latter case. This work, thus, differentiated between 'coalescence', which was defined as the break-up of the hydrophilic layer and polymer chain interdiffusion, which occurred at a later stage.

In atomic force microscopy (AFM) [139,140], the film surface is scanned at a fixed distance with a sharp triangular tip mounted on a cantilever. The deflections of the cantilever in the height co-ordinate, $z$, are measured with a focused laser beam which is reflected to a two-element photodiode detector, whilst a piezoelectric scanner provides information about the stage movements in the $x$ and $y$ co-ordinate planes. Thus, an image processing system can give a three-dimensional image of surface topography and, hence, particle packing can be studied. When used in 'contact' mode, damage to soft surfaces and capillary attraction to surface water can cause problems which are overcome in 'tapping' mode operation when the cantilever is oscillated to avoid permanent 'contact'.

Caution is needed in directly relating observations from AFM measurements on monolayers of latex particles cast on mica [127,141,142], where adhesions may influence the outcome to thicker latex films. It should also be recognised that the situation in the surface of a latex film may be different from that in the bulk, e.g. Wang [143] found ordered PBMA particles in the surface of a film by AFM when FFTEM had revealed disordered arrangements in the bulk [134]. Not only do the particles have no nearest neighbours at the air interface to influence the shape of particle deformation, but also this is the site of water vapour removal so that the nature and number of film-forming mechanisms may be different in the surface from those in the bulk. Perez and Lang [144] have modelled the 'flattening' of PBMA particles upon annealing above the $T_g$ and driven by the excess pressure produced by the curvature of the particles in the surface and compared the results with AFM measurements.

Pekcan et al. [109,145–149] have recently shown photon transmission to be another technique suitable for studying the film formation process. Results are interpreted in terms of the 'crossing density' on void closure upon annealing hard particles and kinetic data was obtained.

Du Chesne et al. [150] have used interferometry to monitor film thickness and polymer volume fraction. Results are not averaged over the whole film but apply rather to the spot under investigation. The technique was said to be simple to set up for a wide range of experimental conditions.

### *2.2.3. Polymer chain diffusion across particle boundaries: film drying stage III*

The aforementioned theories of film formation considered a process in which, after the intermediate stage, the deformed latex particles were held together by purely physical forces. Voyutskii [116–118], from studies on adherence of rubber-coated fabric strips, judged that these forces alone were insufficient to account for the mechanical and physical properties of such a film. Voyutskii discussed film formation from a polymer dispersion in the typical three stages of, evaporation to a



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concentrated 'solution'; followed by polymer 'globules' coming into close contact, with deformation, due to capillary forces; and then in the final stage, the film gaining its mechanical strength by virtue of the fact that solvated stabiliser molecules migrated to regions between the polymer globules, as a result of the loss of water, allowing the self-diffusion of polymer chains and leading to an increase in the homogeneity of the polymer. This process of mutual interdiffusion between polymer chain ends was termed autohesion, and although not an innovative idea (the mechanism being based on the work of Josewitz and Mark [151]). Voyutskii was the first to apply it to the film formation of latex particles.

Bradford and Vanderhoff [4] studied the changes in structure occurring in a continuous, transparent, film as a function of film age. A styrene-butadiene copolymer film, which was replicated and viewed by TEM within hours of casting, showed the vestiges of the original latex particles. However, over a 14-day period the particle contours on the film surface eventually disappeared, accompanied by the exudation of material from within the film: presumed to be stabiliser (visible as blister-like eruptions), and in some cases electrolyte (visible as crystallites). Investigations involving a series of non-ionic surfactants showed that it was the long poly(oxyethylene) (i.e. $-CH_2-CH_2-O-CH_2-CH_2-$) chained stabiliser, which the film exuded and not the short chained oil-soluble stabiliser. It was, therefore, concluded that it was the additive, which was incompatible with the polymer that was secreted. The exuded surfactant was itself observed to change in appearance with time, being initially smooth but later becoming rough. This was attributed to oxidation, which was later shown could cause scission of the poly(oxyethylene) chain, thus making it more compatible and, hence, allowing it to diffuse back into the polymer.

Bradford and Vanderhoff went on to study the ageing process, which they termed further gradual coalescence, in detail [4,152], and Vanderhoff has discussed the results in a number of reviews of film formation [106,107]. They showed that it occurred at the film–substrate interface as well as at the film–air interface (albeit at possibly, but not necessarily, different rates), and also in the film's interior where stabiliser was exuded into 'pockets'. Porosity due to the leaching of surfactant was reduced if the film was aged before the surfactant was leached. The further gradual coalescence was independent of the casting substrate, with the exception of a mercury substrate, which it was proposed induced different stresses into the film when compared to casting on a solid substrate. The proportion of oxygen in the atmosphere also affected the rate of further gradual coalescence — particle contours disappearing rapidly in a high oxygen atmosphere (attributed to oxidative softening of the copolymer) whilst remaining unchanged in a nitrogen atmosphere. Bradford and Vanderhoff also found that reducing the polymer molecular weight (by using a chain transfer agent {*t*-dodecyl mercapton, i.e. $CH_3-(CH_2)_{10}-CH_2-SH$}), increased the rate of further gradual coalescence and, correspondingly, the exudations of incompatible components appeared earlier, whilst an increase in the three-dimensional nature of the polymer [by cross-linking with divinyl benzene (i.e. $H_2C=CH-C_6H_4-CH=CH_2$)], reduced the rate of ageing but did not halt it completely.



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Bradford and Vanderhoff [152] observed ageing in other polymers, including ethyl acrylate-methyl methacrylate copolymer, natural rubber and vinylidene chloride-vinyl chloride-ethyl acrylate[4] copolymer. Similarly, Roulstone has observed the disappearance of particle contours within films of surfactant-free PBMA. Bradford and Vanderhoff did not, however, find evidence of ageing in poly(vinyl acetate) (PVAc) films, even after 280 days. This they attributed to the surface hydrolysis of the acetate to poly(vinyl alcohol) (hereafter called PVOH) which prevented autohesion. The presence of PVOH in such films was later shown by Kast [50] (using osmium tetroxide staining of the hydroxyl groups and electron microscopy) as a continuous network throughout the film separating the PVAc core particles.

Although theories for the interdiffusion of polymer chains at an interface exist [153] (see Section 2.2.4; and have been shown [154,155] to be applicable to latex particle film formation), it was the introduction of newer techniques such as small-angle neutron scattering (SANS) and direct non-radiative energy transfer (DET) techniques that have, since the mid-1980s, provided a means of investigating the magnitude of the polymer chain interdiffusion/penetration depth and, hence, the reason for a film's strength.

The SANS technique [156] measures the increase in particle size as interdiffusion of (typically) deuterated species occurs. Scattering data provides information on, e.g. the weight average molecular weight of polymer molecules, their $z$-average radius of gyration, and in the case of mixtures, the interdiffusion coefficient, the interpenetration depth, and the extent of polymer mixing. Various models exist to obtain diffusion data from SANS, e.g. Eu and Ullman [157] have recently developed an equation, derived directly from Fick's laws of diffusion, relating the increase in the radii of gyration ($R_g$) of labelled latex particles during interdiffusion to the interdiffusion coefficient. Some of the research work utilising SANS has been reviewed by Sperling et al. [158].

The DET technique utilises an equal mixture of latex particles labelled with either: (i) a donor fluorescent chromophore (e.g. phenanthrene dye) and an acceptor dye [159] (e.g. anthracene); or (ii) two different fluors [23] (e.g. pyrene and naphthalene). In the former system, energy transfer due to intermixing of the donor and acceptor dyes during chain interdiffusion allows a decay profile to be analysed in terms of time resolved fluorescence (TRF) decay measurements [159–161] to provide data on the extent of mixing and (inter)diffusion coefficients, etc. In the second system, the naphthalene, for example, is initially excited and during interdiffusion, non-radiative[5] energy is transferred between the naphthalene and pyrene molecules allowing steady state fluoresence (SSF) measurements [23–30,162] based on models accounting for polymer chains crossing interfacial boundaries [163,164].

[4] Vinylidene chloride $H_2C = CCl_2$; vinyl chloride $H_2C = CHCl$.

[5] *Note*. There is also the possibility, which is accounted for in the statistics, of radiative energy transfer as a result of a naphthalene photon encountering a pyrene molecule without interdiffusion having occurred.



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DET is said by Pekcan [28] to be suitably sensitive for studying the early stages of interdiffusion, whereas SANS is more sensitive to the latter stages. Feng et al. [165] found by DET, for example, that for dried PBMA film ($T_g$ = 294 K) stored at ambient temperature, it took 4–5 days for interparticle chain penetration to reach 30–40 nm, whilst for a latex with a $T_g$ of 266 K and a similar molecular weight of $4 \times 10^4$, a similar level of penetration was reached in 25–40 min. Interdiffusion was not observed for any latex before 90% solids content was achieved on drying. The techniques of SANS and DET, when combined with the more traditional SEM and TEM microscopic and the newer atomic force microscopy (AFM) (the modes of use of AFM have been briefly reviewed by Gilicinski et al. [166]) together with spectroscopic techniques, such as X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), and Fourier transform infra-red-attenuated total-internal reflection (FTIR-ATR) spectroscopy, have coupled to provide the means to examine all aspects (e.g. mechanical, morphological and chemical compositional changes) of film formation stage III. This has led to an extensive collection of such literature in recent years (e.g. see [167]).

It is the interdiffusion of polymer chains that provide a latex film with its mechanical strength. Annealing increases the degree of chain interdiffusion and, therefore, acts to enhance film strength. Zosel and Ley [168–170] claim that after the initial quick formation of a continuous but brittle film due to particle sintering, the increase in strength occurs in two main steps: (i) the interdiffusion of chain ends and small chains in the interfacial (particulate) membranes; and (ii) the interdiffusion of longer chains and the formation of entanglements. The former step is apparent as a change from brittle to tough fracture behaviour whilst the latter step provides the film with increasing toughness. The process is hindered by cross-linking the chains, leading to reduced-strength films if the distance between the cross-links is less than the entanglement length; and this is also a factor which has been shown [171] to have deleterious effects on the corrosion resistance of protective coatings. Hahn et al. [172,173] used SANS experiments on PBMA to show that latex particle coalescence was as a result of the 'massive' interdiffusion of polymer from different latex particles. The diffusion coefficient, $D$, during further gradual coalescence at approximately 353 K was $10^{-16}$ cm$^2$ s$^{-1}$ and demonstrated a 30-fold increase as a result of a rise in temperature of 20 K. A factor of 2 change in molecular weight changed the diffusion coefficient sixfold. Yoo et al. [154,155] used similar methods to Hahn to investigate the interdiffusion penetration-depth at which the film attained its full tensile strength. Results were found to be dependent on the polymer molecular weight, the spatial distribution and location of chain ends at the polymer–polymer interface, and the ratio of the polymer chains' radii of gyration to the radius of the latex particle. Tensile strength measurements gave a plateau at an interpenetration depth of 0.8 $R_g$, which was in agreement with predictions by Zhang and Wool [174] who claimed maximum fracture energy occurred at an interpenetration distance of 0.81 $R_g$.

Zhao [161] found by non-radiative energy transfer, using a spherical diffusion model, that diffusion coefficients showed a dependence on both time and temperature in accord with the WLF equations. For PBMA films of comparable molecular



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weight, this technique yielded similar values for the diffusion coefficient as found by SANS.

Linné et al. [175] found, using SANS, for a small (approx. 38 nm diameter), high molecular weight ($6 \times 10^6$) polystyrene latex, that the molecules were fourfold constrained in the particles, and that an enhanced non-Fickian diffusion relaxation at $10^{-14}$ cm$^2$ s$^{-1}$ occurred by a modified reptation model (see Section 2.2.4) that accounted for the polymer chains' charged ends and hence, repulsion compared to $10^{-16}$ cm$^2$ s$^{-1}$ expected for translational diffusion at 443 K. Energy release also occurred during $T_g$ determination with the second run giving a value 6 K lower than the first, and close to the expected value for polystyrene. Linné [175] claimed that polymer chain interdiffusion over 110 Å was sufficient to give a tough coherent film, i.e. diffusion across the particle boundary of 50–60 Å; approximately $0.15 \times \Phi$. The chain end diffusion of high molecular weight (e.g. $> 7.6 \times 10^4$) polymers may not follow Fickian or reptation models due to polymer chain entanglement [176].

Kim et al. [177] studied particle coalescence using 'direct mini-emulsified' latex particles[6], which were claimed to show a narrower molecular weight and particle size distribution, when compared to conventional emulsion-polymerised particles, and also contained no ionic chain-endgroups. (Particles were prepared by anionic polymerisation to give hydrogen chain ends, which were distributed randomly throughout the particles, as opposed to being predominantly on the particle surface as in conventional ionic chain endgroups.) The rates of interparticle chain interdiffusion were found to be greater for Kim's particles when compared to the conventional latex particles of Yoo [154,155]: a feature ascribed to the smaller chain endgroups (compared to, for example, sulphate endgroups) and the fact that the need to overcome polar repulsions was not required. Full tensile strength in Kim's film was achieved at an interpenetration distance slightly higher than that predicted by Zhang and Wool [174].

Sperling et al. [158] conclude that the rate of coalescence depends on where the polymer chain ends lie with respect to the particle surface, and that films form faster when the ends lie *on* the particle surface. The rate of coalescence of latex particles, as determined by Padget and Moreland [178] using TEM and an AC impedance technique, increased with increasing concentration of block copolymer surfactant. This effect was attributed to plasticisation of the (dry) latex polymer by the surfactant. (When wet, the poly(ethylene oxide) groups were hydrated and were relatively incompatible with the polymer, such that the MFFT was not changed whilst water was still present.) Exudations of the surfactant were only significant at concentrations above surface coverage.

Distler and Kanig [179,180] assumed that latex-cast films would always retain some form of inhomogeneity due to the distribution of stabilising charge (e.g. polymer chain endgroups or grafted surfactant). Citing latex particle stability as proof of the particles having an exterior more hydrophilic than their interior, they

[6] Effectively pseudo-latex particles: the bulk polymer being dispersed at the colloidal level.



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reasoned that, on deformation of the particles into a film, these surface boundary layers of hydrophilicity would interdiffuse to form an interconnected 'honeycomb', which would then act to inhibit further interdiffusion by virtue of the incompatibility between the hydrophilic and hydrophobic polymer. As evidence of this, Distler and Kanig point to the fact that a normally transparent film may turn opaque, or even show Bragg diffraction iridescence, when swollen with water: showing the ability of water to penetrate the hydrophilic honeycomb and expose the colloidal crystalline features. Staining with hydrazine/osmium tetroxide (to provide contrast [181]) prior to electron microscopy also revealed the honeycomb features, which persisted over a period of years when stored at room temperature, and also remained after heat treatment. Rather than being the general result supposed, however, the persistence of the boundary layers was peculiar to the latex formulation used, i.e. poly(butyl acrylamide) with 2% methoxy methyl acrylamide, which cross-linked at the particle surfaces.

The effects on polymer interdiffusion of varying amounts carboxyl chain endgroups, arising from the incorporation of, for example, methacrylic acid (MAA), on the surface of a PBMA latex (prepared to give a PBMA-core, carboxylated-shell morphology) has been investigated by Kim et al. [182] using time resolved fluorescence DET measurements. Whilst not preventing chain interdiffusion, it was significantly retarded by the presence of a 'surface membrane', consisting of acid endgroups, on the particles. Problems of data interpretation arose, however, due to particle surface-composition heterogeneity, and it was presumed that the polymer chains of lowest molecular weight and lowest carboxyl content interdiffused earlier than those of higher molecular weight/carboxyl content: the latter, however, showed increased contribution to the energy transfer at longer annealing times. (Interdiffusion was possibly between miscible phases, e.g. PBMA with PBMA, and PBMA-co-MAA with PBMA-co-MAA.) In a more recent paper, which includes PBMA latices with particle surfaces consisting of MAA and additionally latices with surface 'membranes' consisting of either: (i) surface grafted polyethylene oxide (PEO) or (ii) added polyethylene glycol (PEG) containing non-ionic surfactant, Winnik [183] found that whilst the presence of acid groups (or their salts) inhibited interdiffusion, the PEO chains at the surface enhanced interdiffusion — albeit only in the early stages of film formation and annealing. The PEG-containing surfactant was, for comparison with the PEO, also seen to advance interdiffusion by way of acting as a traditional plasticiser (as did non-ionic nonyl-phenoxy-poly(ethylene oxide) surfactants [183,184]). Winnik concluded that for systems in which the particle membrane is relatively similar to the core polymer, any influence results from the $T_g$ of the shell. High $T_g$ carboxyl groups act to retard interdiffusion, and interdiffusion only occurs at temperatures above the $T_g$ of all components. However, if the membrane phase is miscible with the core, then plasticisation can occur and interdiffusion occurs more rapidly.

The effect of neutralisation of the (carboxyl and sulphate) acid endgroups was also investigated by Kim et al. [124,185] using a range of monovalent and divalent bases. Like the aforementioned carboxylated polymer, interdiffusion of the neutralised polymer showed an initial quick rate, followed by a longer lasting constant



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rate period. The presence of an ionomeric shell reduced the rates of interdiffusion further than carboxylation, in the order of $NH_4^+ < Na^+ < Ba^{2+}$, i.e. monovalent ions retard diffusion to a lesser extent than divalent ions. Kim was unable to distinguish the contribution of $T_g$ effects during this work.

Feng and Winnik [186] showed that for hydrophobic PBMA particles, water had little influence on polymer diffusion rates, although the films showed an increase in turbidity upon water absorption, even when well annealed. The inclusion of 5% methacrylic acid in a copolymer, however, led to a fivefold increase in diffusion rates in the presence of water, but no decrease in film transparency. Neutralisation with NaOH led to retarded diffusion in dry films, and a 100-fold enhanced diffusion rate in wet films. Neutralisation with ammonia gave an intermediate rate between those for un-neutralised and NaOH-neutralised films when both wet and dry.

Despite their effects on chain interdiffusion, carboxyl groups have been shown to contribute to the viscoelastic cohesive strength of particles in a film due to interfacial cross-linking [187] via either hydrogen bonding or ionic dipolar interactions when neutralised. [If the neutralising molecule was sufficiently large (e.g. diaminopolyoxyethylene), then coiled lamella could be formed which had the opposite effect (when compared to neutralised carboxyl groups) of plasticisation and, therefore, reduced cohesive strength.] Kan and Blackson [188] also investigated the viscoelastic properties of a series of carboxylated styrene-butadiene latices finding that pH, and therefore the ionomeric character of the latex, altered the film morphology. At low pH, the carboxylated polymer from the vestigial particulate interfaces acted as the dispersed phase due to it having a higher $T_g$ than the non-carboxylated bulk polymer (particle cores) — which acted as the continuous phase. Increasing the pH of the film increased the ionomeric character of the carboxylated shells, with a corresponding decrease in polymer chain mobility of these regions, such that film morphology changed to one in which the interfacial polymer was the continuous phase.

The (i) increased water absorbency, (ii) increased difficulty to leach surfactant and, (iii) reduced tendency of a copolymer latex film of vinyl acetate and a vinyl ester of Versatec 10 acid to whiten (swell) in water were attributed, by Aten and Wassenburg [189], to the redistribution of surfactant molecules from the surfaces of the latex particles (where they were sited on latex polymerisation) to a more even distribution throughout the film, following a period of secondary 'drying' above the polymer $T_g$. Such redistribution was ascribed to the increased polymer chain mobility above the polymer $T_g$, and was not apparent in films annealed below the $T_g$.

The aforementioned particle packing studies of Rieger et al. [135] on styrene-*n*-butyl acrylate copolymer latex film structure using the SANS technique, also provided evidence of non-polymeric material (e.g. surfactant and electrolyte) in the particle interstices. During annealing above the polymer $T_g$, at temperatures from 343 to 453 K, an increase in the amount of non-polymeric material was evident as, for example, surfactant from the particle surfaces was expelled into the interstices. Above a certain annealing temperature and time (453 K for 2 h), however,



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scattering data changed significantly as the percolation of deuterated water into the film was inhibited by the loss of the networked structure of the interstices (attributed to further polymer relaxation, and particle deformation).

Richard [190] has recently reviewed the research performed by the Rhône–Poulenc research group who used the techniques of dynamic micromechanical analysis (DMA), to investigate the viscoelastic properties, and SANS and TEM to investigate the structural properties of such films. Films were cast from either electrostatically stabilised latices (i.e. carboxylated copolymer latex particle shell, styrene-butadiene core) or sterically stabilised latices (i.e. PVOH grafted onto PVAc particles). For example, the DMA analysis of films prepared from latices of styrene-butadiene and stabilised by copolymerised carboxylic surface groups suggested that a segregated second phase (as opposed to a membrane network) of (high $T_g$) carboxylated polymer did not exist. However, based on the work of Zosel [191], Richard does infer that at high acrylic acid content (i.e. > 15% w/w), water soluble (i.e. low molecular weight) chains of poly(acrylic acid) may form in the aqueous phase during polymerisation and lead to a second phase of polymer within the film. The sterically stabilised PVAc core-PVOH membrane latex film also showed [190,192] a single glass-to-rubber relaxation transition in the DMA spectra before annealing. However, after annealing, a second transition was apparent: the first and second transitions being associated with the $T_g$ values of the core and shell, respectively, suggesting the presence of two discrete phases. The results were further confirmed by selectively staining the PVOH phase with osmium tetroxide, and viewing under the TEM. Micrographs of the unannealed film showed only isolated PVOH clusters, whereas the annealed film micrograph showed the PVAc cores embedded in the rebuilt PVOH matrix.

Richard [190] comments on the difference between the rebuilding process found when annealing sterically stabilised latex films which is the opposite to the fragmentation and expulsion process observed in charged stabilised polymers. Joanicot et al. [193,194] have investigated the effect of thermal annealing on the cellular network ('membrane') of electrostatically stabilised (carboxylated) hydrophilic particle boundaries: observing the fragmentation of the membranes by the use of SANS and TEM. Fragmentation of the hydrophilic membrane arose due to the high hydrophilic–hydrophobic interfacial surface area, such that the dispersion was not in a state of lowest free energy. The appearance of the final film was of coalesced hydrophobic cores with isolated 'nuggets' of hydrophilic material dispersed within it.

Under humid conditions, the hydrophilic cell walls of Joanicot's [194] latices dictated the mechanical strength of the films.[7] Exposure of the films to humidity, caused the films to become brittle since the hydrophilic polymer was susceptible to

[7] By stretching films, Rharbi et al. [10,11] have also investigated the mechanical strength and the effect of selective swelling of either the core or the shell. When the dispersed cores were weakened, macroscopic stretching of the films caused homogeneous stretching of all the individual cells of the matrix; when the continuous poly(acrylic acid) phase was weakened, macroscopic stretching led to shear deformation and slippage between the cells causing disruption of the lattice.



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water penetration, causing the walls to lose their cohesive strength. The process of annealing was, however, found to reinforce the films due to core–polymer chain interdiffusion between particles. At temperatures sufficiently high to cause fragmentation of the cell walls, SANS evidence showed interdiffusion of high molecular mass polymer, which caused the films to show increased resistance to humidity. At temperatures at which the polymer chains were mobile, but the particle shells did not fragment, there was evidence of extensive interdiffusion of low molecular mass polymer across the hydrophilic cell walls, but the mechanical properties of the films remained unaffected such that the films were still brittle when exposed to humidity. The results, therefore, indicated that the shells were effectively size selective being impermeable to high molecular weight core polymers.

Joanicot [193] discusses the fragmentation of the hydrophilic membrane in comparison with the evolution (droplet maturation) of high internal phase ratio oil-in-water emulsions. In such an emulsion, the thermal motion of the stabilising surfactant (surrounding the emulsion droplets) can lead to surfactant bridging through the aqueous phase, between droplets, which can in turn allow the oil droplets to combine. The requirement for such combination to occur is the attainment of a critical thickness of water between the particles. The water membranes between latex particles are thin (approx. 2 nm), and their fragmentation is thickness-independent but requires thermal treatment for the attainment of a threshold beyond which the hydrophilic and hydrophobic parts of the film segregate.

It has been determined [190,193–197] that membrane fragmentation is a function of: (i) mobility of the polymer from which the membrane is made (restricted by cross-linking through neutralisation of surface carboxylic groups, or temperature, etc.); (ii) the mobility of the particle core (i.e. a function of polymer $T_g$, or again restricted by cross-linking of the core polymer, etc.); and (iii) the anchoring (i.e. due to surface functionality) of the membrane polymers to the core. Once fragmentation has occurred, the hydrophilic polymer is found to form irregular clusters within the hydrophobic polymer. The irregularity was ascribed by Joanicot [193] to the method of cluster formation in which the hydrophilic membranes were said to be 'attached' to cores with a distribution of strengths (i.e. heterogeneous latex particle surface) and, hence, released at differing times: clusters of hydrophilic polymer occurring (in the hydrophobic polymer) at points where the membrane was released initially. This was again compared to the evolution of high internal phase ratio emulsions whereby large droplets capture smaller droplets to yield a distribution of small droplets and much larger ones: 'heterogeneous growth' (cf. homogeneous growth: the combination of equally sized smaller droplets to give a monodisperse emulsion which grows continuously).

Nicholson and Wasson [9] concluded, with regard to the effect of surface group functionality, that coalescence mechanisms may be divided into two groups: (i) those dependent on sintering or capillarity processes, which dominate when there are polar repulsions present; and (ii) those dependent on chain interdiffusion, when there is very little repulsion between particles. Whilst ionogenic groups may lead to polymer chain stiffening, this may be countered during latex film casting by



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increased water hydration leading to plasticisation. High concentrations of functional groups (e.g. methacrylic acid) can lead to interfacial cross-linking [198]. Covalent interfacial cross-linking systems have been reported [199–203] and films with satisfactory mechanical properties produced even when floc formation [201] had commenced in the dispersed state.

*2.2.4. Film healing and fracture*

The diffusion of a polymer chain in bulk polymer is the subject of de Gennes' [204] reptation theory[8]. This theory also provides the basis for various chain interdiffusion studies and models at a polymer–polymer interface [153,205–215] and, therefore, latex particle film formation, ageing, crack healing, adhesion, etc. each of which has much in common by virtue of each of the processes involving polymer chain (inter)diffusion and entanglement. Polymer chains in the bulk polymer have a Gaussian distribution of chain segments, whilst those chains adjacent to an interface have distorted conformations. Diffusion across the interface allows configurational relaxation and a return to Gaussian behaviour

Short polymer chains would follow Fick's Laws of diffusion as confirmed by Wang [159] for low molecular weight PBMA when mass transfer was proportional to $t^{0.5}$ (where $t$ = time). Mechanical strength is not developed until the polymer exceeds a critical molecular weight for entanglements and then diffusion occurs, by reptation. For reptating chains, the discontinuity in the concentration profile at the former interface between particles persists until surface chains have diffused a distance comparable to their radius of gyration [98].

The reptation model describes the restricted thermal motion of a linear polymer chain that is entangled in other polymer chains [204,207]: the 'average' motion of chains longer than a certain critical length effectively being confined to random longitudinal (back and forth) movement along the centre of a tube. Eventually the motion causes the chain to partially exit one or other end of the tube. (The aforementioned technique of DET has proved useful in measuring the activation energy and frequency of the reptation motion and (inter)diffusion.)

Reptation theories typically unite properties such as: polymer chain diffusion coefficients with molecular weight/chain length; fracture energy (i.e. film 'toughness') or fracture stress (i.e. tensile strength) with, for example, annealing time and molecular weight; or chain bridging density (i.e. number of chains crossing the interface, which have entanglements at both ends per unit area) with time and molecular weight. Many of these properties are dependent on the reptation (relaxation) time, $\tau_R (\propto M^3$ where $M$ = molecular weight)[9]. This is the time taken for a chain to disengage from its initial tube (i.e. the time taken for a chain to diffuse a sufficient distance to lose all memory of the initial tube). The centre of mass diffusion coefficient ($D$) is predicted to be inversely proportional to the

[8]The name originally arose from the snake-like movement of polymer chains in concentrated solution.

[9]Reptation has a second basic time scale, $t$, associated with the wriggling motion of the polymer chain within a tube. Unlike, $\tau$, $t \propto M^2$.



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square of the molecular weight which has been confirmed experimentally by Wang [176] for PBMA film when $D \propto 1/M^{2.3}$. Reptation models typically dictate that fracture stress (tensile strength) increases with healing time raised to the one-quarter power, and such a relationship has been observed experimentally in many of the papers discussed within this section.

Winnik et al. [98,159] have discussed the difficulties involved in identifying the consequences of reptation in latex film formation using SANS and DET techniques. Whilst the early stages of polymer chain interdiffusion would be expected to exhibit the time-dependence characteristics of reptation, in practice, Fickian diffusion models have been used successfully. He points out that usually there is a broad distribution of molecular weights leading to a distribution of diffusion coefficients and a broadening of the concentration profile at the interface, which reduces the sensitivity to the difference in diffusion mechanisms. Reptation effects would be greatest when the SANS technique is least sensitive, i.e. when the increase in the radius of gyration of the labelled polymer is smallest. Whilst DET would potentially be far more sensitive, experiments have yet to be reported using narrow molecular weight distribution polymers.

In simple terms, the fracture of a latex film may be considered as the inverse of coalescence. Whilst studies of coalescence and healing investigate polymer chain interdiffusion, studies of film fracture are often seen to result from chain pullout — both of which involve polymer chain diffusion at an interface. Sperling et al. [216] have investigated and reviewed both the interdiffusion of polymer chains at an interface followed by subsequent cleavage to reform the interface, showing that the film formation and film fracture processes are partly reversible. Polymer chains may be reversibly pulled free during fracture if interdiffusion is less than a certain depth.

Klein and Sperling et al. [217–221] examined fracture during annealing using a dental burr grinding instrument designed to cut to specific depths per pass. The fracture of monodisperse polystyrene latex films was investigated on a molecular level, measuring the total energy required to fracture the samples. Chain scission together with chain pullout were found to be the important, energy-consuming, molecular mechanisms. Results were found to be dependent on polymer molecular weight. At low molecular weights (approx. $32 \times 10^3$ g mol$^{-1}$) fracture of polystyrene was almost 100% by chains undergoing pullout. At molecular weights of between $150 \times 10^3$ and $180 \times 10^3$ g mol$^{-1}$, fracture resulted from equal contribution between chain pullout and chain scission. At the highest molecular weights, chain scission contributed 90% to the fracture. By comparison, scission contributed 75% to the fracture of $485 \times 10^3$ g mol$^{-1}$ PMMA. Analysis of the frictional coefficients involved allowed the temperatures of chain pullout to be estimated. These temperatures (515–641 K and 493 K for polystyrene and PMMA, respectively) were well above the $T_g$ values of the polymers involved, but were confined to within 1.5–2.3 nm of the crack tip in the case of polystyrene. (The molecular weight-dependent results were found to be equally applicable to the fracture at the blend interface between immiscible polymers in which block copolymers were used to provide compatibility [221].)



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The designer of the aforementioned burr grinding instrument, Mohammadi [222], together with Klein and Sperling, found that the fracture properties of $420 \times 10^3$ g mol$^{-1}$ polystyrene films, initially increased with annealing time, peaking at a time corresponding to when the fracture pathway changed from being between particle–particle interfaces to one which was through the particles themselves. Similarly, fracture energy in a PBMA latex film, when measured by Zosel and Ley [169], reached a limiting value when the interdiffusion depth was of the same order of magnitude as the radius of gyration of the PBMA chains. Relative to a latex film's final strength, this presumably corresponds to completion of film formation, and further polymer chain (inter)diffusion is comparable to that found in a solvent-cast film. (DET studies [159,176] of PBMA films have shown that activation energies for interdiffusion can almost equal those determined from studies of viscoelastic behaviour of the PBMA chain backbone in bulk polymer.)

Many of the papers discussed in this section of the review (and those mentioned previously which have considered interdiffusion) provide quantitative measurement of factors such as chain interdiffusion coefficients and various energies associated with chain interdiffusion or fracture. These values have not been reproduced here since they are generally prone to being 'case specific', i.e. specific to a particular type of polymer with a specific endgroup functionality, or specific to the temperature at which the variable was measured and whether the polymer was above or below its glass transition temperature, etc. The reader should be aware, however, that such data is available in the literature.

### *2.3. Solvent-casting of a film — a brief comparison with latex casting*

Whilst the formation of films from latices and from polymers in solution may seem to be fundamentally different processes (e.g. polymer in solution will film form at room temperature regardless of the $T_g$ of the polymer), there are aspects of similarity, e.g. macromolecules in solution can behave hydrodynamically as though they are molecular dispersions having solvent-impermeable cores and peripheral solvent-permeable segments [223]; a difference mainly of scale compared with uncharged sterically stabilised latex particles. Whether solvents will necessarily deposit pore-free films of the maximum density and lowest permeability is uncertain: different outcomes are predicted, depending upon the solvent power, when high concentrations are reached in the later stages of drying. Funke and Zorll [224] have suggested, based upon evidence from freeze-dried extracts of films in the gel stage, that good solvents would produce more open, porous structures, and Nicholson and Wassen [9] cite Gould [225] with a similar prediction that compact molecules in the solution will remain compact in the film state. Kesting [226], however, suggests that polymer coils in good solvents will interpenetrate to a more compact structure than in poorer solvents which will favour earlier polymer segment–segment contacts. Spitael and Kinget [227] concluded that the formation of a gel was the most important stage of solvent-cast film formation, and that solvents that did not gel yielded poorer films, which exhibited poorer transparency. Charmeau et al. [14,228] compared both latex cast films of various



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acrylic/methacrylic polymers and the corresponding solvent cast films (prepared by dissolving the latex in a solvent) so that the films had identical composition but differing structure. The latex cast film were shown to have Young's moduli which were greater than the comparable solvent cast films due to polar interactions between the hydrophilic shells of the latex particles, which increase the modulus.

Distler and Kanig [179] dissolved freeze-dried samples of poly(ethyl acrylate) and poly($n$-butyl acrylate) (PBA) in tetrahydrofuran, diluted to such an extent (0.1%) that the polymer chains were dispersed with no 'felting', i.e. the resultant solution was completely homogeneous. In films formed from such solutions, it was found, from analysis by electron microscopy, that there remained a residual particulate structure, with particles of approximately the same size as those of the original latex. This they attributed to sufficient self-cross-linking (i.e. acrylates have a labile tertiary hydrogen [229]) during the polymerisation process to allow the particles to simply swell (i.e. gel) rather than truly dissolve. This hypothesis of cross-linking was tested by repeating the experiment using PBMA, which lacks the ability to self-cross-link: such films cast from tetrahydrofuran showed no sign of residual structure.

The rate of evaporation of solvent from solvent-cast films depends upon $(t)^{1/2}$ as expected for a process controlled, or limited, by diffusion, i.e. Fickian desorption to the surface through a homogeneous solution of increasing concentration [230]. However, the removal of the final traces of solvent from solvent cast films is a problem — attributed to the fact that the polymer may be plasticised by the solvent. Elevated temperature (to assist diffusion of the solvent in the polymer), good vacuum and long drying times are used to overcome the problem, e.g. 323 K at 3 torr for 96 h [231]. The removal of the final traces of solvent can be important with regard to toxicity (in the case of pharmaceutical coatings) and also the permeability properties of solvent-cast coatings. List and Laun [232] found the water vapour permeability of isopropyl alcohol-cast poly(methacrylic acid, ethyl acrylate) (i.e. Eudragit® L[10]) copolymer films to be markedly increased by residual solvent. However, the effects of residual solvent were minimised by secondary drying, and the solvent could be almost completely removed in a very short time (8 h) if the film was held above its $T_g$.

### *2.3.1. Volatile organic components in aqueous latices*

It is common, for example, in the paint industry, to add volatile organic components to latices (e.g. as coalescing aids — to lower the elastic modulus and provide temporary plasticisation to promote polymer chain motion and, hence, provide a better film finish). Sullivan [233] investigated the removal of such volatile organic compounds from latices, concluding that the ease of removal was dependent on their molecular size and polarity: the more polar a compound, the more likely it was to partition into the hydrophilic network of the evaporating water (and hence find less diffusive resistance), and less residual solvent would remain in the

[10] Röhm Pharma GMBH.



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film. Sullivan found that the initial (steady-state) rate of evaporation of water was unaffected by the solvent but may ultimately be slowed if the additive is hygroscopic or interacts with the water, forming hydrogen bonds (e.g. as do both ethylene glycol {i.e. $OH-CH_2-CH_2-OH$} and propylene glycol {i.e. $OH-CH_2-CH_2-CH_2-OH$): in which case the evaporation will not be diffusion-controlled, as is the usual case.

Hansen [234] has also discussed the evaporation of various volatile organic components from aqueous latices. Comparing film formation by the evaporation from true solutions [i.e. internal diffusion-controlled (characterised by a concentration gradient across the film thickness, with a concentration of zero at the film surface)] to the system in which the volatile component is present as an additive. It was found, that in the latter case, since no concentration gradient (of volatile components) was apparent in the film, then evaporation of the volatile components was not controlled at the film surface. As in the work of Sullivan [233], however, the evaporation rate of the aqueous phase was independent of the organic phase.

In the case of diffusion-controlled evaporation, the ratio of the weight of volatiles to polymer can be related to a dimensionless reduced time variable, $T$, given by:

$$T = \frac{Dt}{L^2} \tag{18}$$

where $D$ = diffusion coefficient, $t$ = time and $L$ = film thickness.

Hence, in the case of diffusion-controlled (desorption-controlled) resistance:

$$\frac{W_{\text{volatiles}}}{W_{\text{dry polymer}}} \propto \frac{t}{L^2} \tag{19}$$

where $W$ = weight of (subscripted) component.

Whereas for surface-controlled resistance:

$$\frac{W_{\text{volatiles}}}{W_{\text{dry polymer}}} \propto \frac{t}{L} \tag{20}$$

The effects on polymer chain interdiffusion of small amounts of organic solvents, added to PBMA latices, has been investigated by Juhué and Lung [280]. Results depended on the nature of the solvent's properties (e.g. evaporation time, level of plasticisation) with respect to the polymer. Strong plasticisation was found not to be a desirable feature (to achieve high film strength by enhancing interdiffusion) if the solvent was not easily evaporated, and similarly neither was weak plasticisation and quick evaporation. Desirable properties to enhance film formation were, therefore, moderate evaporation rates and moderate plasticisation.



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## 3. Film morphology

Roulstone [18] observed that in the case of both solvent-cast and latex-cast films, drying occurred from the upper, open surface, downwards to the substrate. This appeared to result in the solvent-cast film having a higher density skin on the top surface in comparison to the substrate side. Similarly, a difference in appearance between the two surfaces was apparent for latex-cast films, with matt upper surfaces and glossy lower (substrate) faces. Replicas of the two surfaces subjected to the resolution of a TEM showed slippage of the layers of latex particles in the upper surface, presumably arising from mud-cracking. (Mud-cracking is used in this context to mean the uneven and apparently ridged polymer–air interface of the film, as opposed to the true hard-edged cracks as might be observed in a brittle polymer film.)

Monodisperse spherical latex particles are known to form ordered structures (as mentioned in Section 2.2.1) which diffract light and produce opalescence. This behaviour has been observed by both Roulstone [18] and Steward [88] as 'model' latex-cast PBMA films dried, producing 'islands' of iridescence. Such random and isolated regions of drying may possibly contribute to the surface irregularities, as regions overwhelm and possibly slide over/under each other. Film asymmetry was also manifest [18] in the permeability towards both water vapour and 4-nitrophenol — which varied according to the film orientation — for both solvent-cast and latex-cast films. When the face towards the donor (permeant-containing) compartment was the upper surface, it gave the greater permeability to water vapour, whilst the lower face gave the greater permeability to the 4-nitrophenol. This was explained in terms of desorption being the rate-controlling process, and the difference between the permeants arising from their relative affinities for the film: 4-nitrophenol being much more soluble in the film. Opposite trends were found for solvent-cast films in which it was the upper surface that had the greater density, in contrast to the latex-cast films. Abdel-Aziz [235] reported a similar effect for solvent-cast Eudragit® films, although the density was found to vary depending on the casting solvent used, and the films could be seen, under the SEM, to contain pores when cast from acetone containing 5% w/w ethanol [236]. Other researchers [19] have found the polarity of the casting substrate to influence the polarity of the lower surface of a film inducing an asymmetric effect.

Although it is generally assumed that latex particles exhibit sufficient colloidal stability to form a close packed-array prior to coalescence, it has been reported by Okubo et al. [87] that in the case of a surfactant-free latex, a porous, flocculated layer was apparent at the film interfaces. For a latex of only marginal stability, the film–air interface was observed to be porous. The addition of electrolyte to the latex, before casting, further destabilised the latex such that the film–substrate interface was also found to be porous. However, the addition of surfactant to increase the latex stability led to a close-packed, non-porous structure in agreement with the findings of Isaacs [237].

Both Vanderhoff et al. [4,152] and Chainey et al. [15,16] noted changes in the surface of latex films upon ageing. Vanderhoff found increased coalescence prior



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to surfactant exudation to the surface, whilst Chainey found that spray-cast surfaces which appeared rough under the SEM smoothed to the appearance of a solvent-cast film upon ageing for 1 month. Roulstone et al. [133], using a freeze-fracture replication TEM technique (in which the sample is frozen at the temperature of liquid nitrogen and fractured in-situ, so as to reduce any thermal effects of the fracture process), which showed structures in PBMA film, of close packed spheres deformed into rhombic dodecahedra, with the clarity of the interparticle regions dependent on the temperature of preparation. Only at very high casting temperatures (e.g. 405 K) was there no evidence of particulate structure, such that the film then resembled the appearance of the fracture section of a solvent-cast film. It was suggested, from visual observations and differential scanning calorimetry (DSC) evidence, that PBMA underwent a melting or softening transition in the region of 393 K. Long exposure to temperatures lower than 393 K were not investigated (e.g. 6 h at 368 K was the most extreme treatment where particle positions, if not the interparticle boundaries, could still be identified). Wood [238] remarks that whilst polymers are ductile at their $T_g$ they require heating to 40–50 K above their $T_g$ to produce a processable 'melt'. PAMA and PHMA latex film cast at 313 K (i.e. at least 40 K above their $T_g$ values) showed no evidence of particulate structure [133].

Wang et al. [134,176,277] performed similar work to Roulstone et al. [133] investigating the affect of annealing on surfactant-free PBMA films. Results showed a decrease in the visibility of particle boundaries on annealing at temperatures lower than those investigated by Roulstone. Wang [176,277] also investigated the degree of chain interdiffusion using fluorescent dyes and DET measurements. From this, it was concluded that there was extensive polymer interdiffusion: at 363 K for 2 h, an interpenetration depth of 6 nm (in particles of 337 nm diameter) was calculated, and this was shown in the fracture cross-sections as a change from fracturing along the interparticle boundaries (in the unannealed film) to fracturing through the particles. A decrease in the rate of polymer interdiffusion with annealing time was attributed to polymer polydispersity. Low molecular weight polymer dominating diffusion at early times [277] and high molecular weight after long annealing times; a phenomenon also observed via SANS experiments conducted by Eu and Ullman [157] on polystyrene-deuterated polystyrene latex films with a large mismatch in molecular weight. List and Kassis [72] attributed the fracture of particles (as opposed to particle boundaries) to the increased strength of the boundary resulting from the interaction of polar groups (which are situated predominantly on the particles' surfaces).

The existence of porosity in both solvent-cast and latex-cast films has been cited by a number of authors [239,240]. The structure of a solvent cast film is dependent on the solvent used. Greater enmeshment and density may result from the use of a good solvent (see Section 2.3) compared with a theta solvent.

Roulstone et al. [18,133] used mercury porosimetry[11] and krypton BET surface

[11]A technique to determine pore density and pore size in a sample by means of forcing mercury into the sample under increasing pressures.



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area measurements on both solvent-cast and latex-cast films of PBMA. They attributed the apparent uptake of mercury at high pressures to the compressibility of both film types, rather than true porosity, however, krypton BET surface areas were greatly in excess (by a factor of approx. 37 times) of the geometric areas of the films used, and similar values resulted from the two types of film The excess krypton adsorption could be attributed to microporosity at the low temperature (77 K) of the experiment. Mercury porosimetry, when performed on a harder polymer, did demonstrate the presence of porosity in core-shell (hard polymer core; soft shell) latex films designed to be porous, and also showed its removal when thermal treatment took the film above the $T_g$ of the cores.

Okor [240] cited fracture cross-section SEM evidence for mesoporosity in plasticised solvent-cast Eudragit® films. Roulstone et al. [18,133], however, using freeze-fracture TEM on solvent-cast, and latex-cast, PBMA films found no evidence of mesoporosity. (IUPAC [241] defines pore size according to: micropores, $< 20$ Å[12]; mesopores, 20–500 Å; and macropores, $> 500$ Å.) Nitrogen desorption analysis of the low levels of mesoporosity found to exist in such films is not practically feasible due to the low uptakes involved. Balik et al. [239] considered microporosity to be present in their terpolymer (vinyl chloride, butyl acrylate and vinyl acetate) latex films at 40 K above their $T_g$, however, whether this excess carbon dioxide sorption would be better described in terms of free-volume in the rubbery polymer is a matter of semantics. Balik considered solvent-cast films to be structureless and to furnish a baseline performance for permeability. For a poly(vinylidene chloride) copolymer latex, it has been shown that [242] storage of the latex prior to film casting resulted in films with decreased barrier properties and this was ascribed to an increasing crystalline content which also elevated the MFFT.

In a study [88] of permeation through latex films, it was shown by Steward et al. that the aqueous solute permeability of a latex could be enhanced by the leaching of a water soluble additive from a film, due to an increase in void volume, or the formation of hydrophilic (aqueous) pathways [243–245]. However, the rate of solute permeation depended on whether permeation occurred simultaneously with the additive leaching. Delaying the start of a permeation until after the additive had been leached caused a reduction in the measured solute permeability coefficient, implying that the film was undergoing a wet sintering process. Additionally, if the $T_g$ of the film was above ambient temperature, and the film was allowed to dry in between the leaching of the additive and the start of permeation, then the magnitude of the permeability coefficient was reduced to below the level of the comparable additive-free film. Only those films whose $T_g$ values were above ambient temperature were able to retain porosity following a period of leaching and drying (at ambient temperature). This was confirmed by using a film prepared from a mixed latex consisting of a water (pH 5.5) soluble hard latex, and a soft latex which was soluble in toluene but not water at pH 5.5. Leaching of the soft latex,

[12] 1Å $= 1 \times 10^{-10}$ m.



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and drying, led to a film showing the expected degree of porosity when observed under the SEM, whereas leaching of the hard polymer, and drying, left a pore-free film [86] of reduced thickness.

Before moving on to consider more complex latex systems, it is worth pointing out, in view of a number of factors discussed in earlier sections, that even for surfactant-free homopolymer model colloid latices, the mode of preparation, cleaning and characterisation are important in attempting to compare results from different workers or the same worker using different batches of latex. The molecular weight distribution in the surface layers, the surface charge density and the content of residual monomer may have an effect upon any of the three stages of the film formation process. Even for latices of the same polymer and similar particle sizes, subtle differences in preparative techniques and cleaning procedures [246] may make a vital difference, therefore, it is important that they are reported in sufficient detail.

### *3.1. Heterogeneous and blended latex films*

The blending of two or more latex types into a film may provide a means of achieving the desired film properties, or even a means to achieve a unique set of properties which cannot be achieved by the use of a single homopolymer. In terms of film formation, structure and properties, copolymer films may normally be considered as being effectively homogeneous in nature (assuming that the polymer composition within individual particles is uniform). However, the same is not necessarily true for copolymer films formed from blended latices or from core-shell polymers, e.g. when one of the comonomers is more hydrophilic in nature such that it may end up forming a (full or, more likely, partial) 'shell' around the core of the more hydrophobic comonomer. Kast [50] describes such particles as being heterogeneous or composite, and cites the aforementioned work of Distler and Kanig [179], which showed the vestiges of the carboxylated particle boundaries within a film, as being evidence of a heterogeneous network. In similar films, of either an acrylic acid-free or acid-containing butylacrylate copolymer, differences in the storage modulus$/T_g$ were cited as experimental confirmation of heterogeneity. Guyot [247] has stressed the importance of the morphology of the initial latex particles, e.g. core-shell in relation to the production of films with improved mechanical properties without the need for environmentally unfriendly volatile additives.

Marion et al. [248] used fully labelled core-shell particles and particles labelled only in the core for fluorescence non-radiative energy transfer (NET) studies to demonstrate the core-shell nature of the particles. Comparison of the rates of film formation for homogeneous particles and for core-shell particles established the internal structure of the particles and the method was recommended as particularly useful when the core and shell polymers were of a similar nature.

Films cast from core-shell type heterogeneous particles differ from films cast from a blend of two different latices in that in the case of composite particles, the two polymer types are less mobile than those of the blend. This is important, for



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example, if only one of the polymer types is film forming at the casting temperature. Rajatapiti et al. [249] investigated the film forming properties of systems consisting of PBA-PMMA core-shell latices with a graft copolymer consisting of PBA backbones and PMMA side chains acting as a compatibilising agent. At ambient temperature, only the PBA is film-forming. Comparing film formation of blended mixtures of PBA and PMMA latices with the composite latices, only the blended latex mixture was film forming since the PBA particles were mobile and able to come into contact, whilst the PMMA remained dispersed within the PBA matrix. In the case of the composite particles, the mobility of the PBA was reduced by the PMMA shell. Only when the shell was incomplete did the composite particles film form.

The process of film formation from a heterogeneous particle has been shown by Brodnyan and Konen [49] to be governed by the polymer of lowest $T_g$, unless that polymer is of a low volume fraction ($< 30–40\%$) or surrounded by a shell of high $T_g$, polymer (in which case the polymer may contain voids or will require heating to the MFFT of the higher $T_g$ polymer). The result is described, with experimental evidence from the polymer's viscoelastic properties, as a multidomain polymer with the high $T_g$ polymer dispersed in a matrix of the lower $T_g$ polymer, although this morphology may be inverted by heating above the $T_g$ of the hard polymer. Additionally, Brodnyan and Konen also investigated the effects of particle size on the MFFT: finding that size had no effect (albeit that the latices used were somewhat polydisperse).

In the same way that film formation from heterogeneous particles can be dependent on the $T_g$ of the polymer of lowest $T_g$, so can film formation from blends of latices. With the intention of investigating whether film transparency was dependent on a softer polymer filling the voids between close packed harder particles, Feng and Winnik et al. [99] cast films, from blends of high $T_g$ PMMA particles and lower $T_g$ (varied between approx. 238 and 283 K dependent on recipe) particles of poly(butyl methacrylate-co-butyl acrylate). The latter copolymer particles being of smaller diameter were intended to occupy the voids between the larger hard particles. Despite the hard particles not deforming, transparent films could be obtained by air drying, but were dependent an a critical volume fraction (40–50%)[13] and therefore, to a certain extent, the diameter of the soft copolymer particles. Transparency was independent of the copolymer's $T_g$ (albeit only tested for $T_g$ values below the film formation temperature). When viewed by SEM and FFTEM, the transparent film showed the harder particles to have retained their spherical shape, and to be uniformly distributed in a matrix of the softer polymer. This uniform packing was found to be disrupted by factors such as changing the size ratio between the particle types, or removing surfactant, etc., leading to turbid films. Blended films were further analysed [250] using Tapping Mode AFM, which showed, in the case of blends containing $> 40\%$ by volume of

[13] *Cf*. free volume between close packed spheres of 26 or 34% dependent on face-centred cubic or random packing.



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the softer copolymer, smoothed bumps, which were apparently sized larger than either of the particle types alone. The evidence suggested that the bumps consisted of coalesced copolymer covering submerged PMMA particles; such a morphology arising due to the lower surface energy of the softer copolymer. Despite the transition from an opaque to a transparent film when the volume fraction of soft polymer was varied between 0.4 and 0.6, the AFM micrographs showed no discernible evidence of a change in film topology. It was, therefore, suggested that the opacity resulted from air voids within the film.

The work of Jensen and Morgan [36] in the effect on the MFFT of monodisperse latex particle size has been mentioned previously, but Jensen and Morgan also investigated the effect of blending various ratios of two different sized (i.e. 63 and 458 nm) latices. With the larger particles exhibiting an MFFT of 309 K, and the smaller particles an MFFT of 299 K, the blended latices showed almost a linear increase in MFFT as the weight fraction of the larger particles increased. With a similar intent to that of Winnik (in the previous paragraph) and Jensen and Morgan, Peters et al. [251] have also cast films from latex dispersions, which were blended to provide bimodal size distributions, in order to provide a more detailed investigation of the effects of packing fraction (which is a function of particle size) on film properties such as drying rate, MFFT, tensile strength and water uptake. A blend of large (approx. 340 nm) to small (approx. 40 nm) particles in the ratio of approximately 80:20 was observed to be significant in yielding a minimum in MFFT together with a minimum in the films water absorption at short drying times, and the maximum in tensile strength. This was ascribed to the effects of particle packing: the 80:20 blend providing a minimum void volume and a higher maximum volume fraction than those of either individual component of the blend.

Comparisons of composite/heterogeneous latex film structure has been made by Cavaillé et al. [252–254]. Using films cast at room temperature from either: (i) blends of polystyrene latices and PBA from polymer latices; or (ii) composite polystyrene-PBA core-shell latices (prepared in a two-stage seeded polymerisation [255]) then, as in the aforementioned work of Winnik et al. [99,250], it was the softer polymer, in this case the PBA, that provided a matrix into which the higher $T_g$ polystyrene was dispersed. In the case of the latex blends, segregated clusters of polystyrene particles were detected, whereas using the core-shell type latices, this clustering was prevented. Clustering of the polystyrene particles in the blended latex films occurred even when the polystyrene was present at low (10%) volume fractions. In the case of the composite core-shell latices, two samples were studied, containing 40% by volume polystyrene and a shell of either pure PBA or a functionalised copolymer consisting of butyl acrylate and 10% methacrylic acid: the latter giving better coverage of the core. Segregation was dependent on the covering of the core by the shell, and the better the core coverage the greater the inhibiting effect, and the less the cores were found to aggregate. The mechanical properties of the polystyrene-pure PBA core-shell latex films were found to be affected by the size and volume fraction of the high $T_g$ polystyrene 'inclusions', and a continuous percolating network of the polystyrene particles was found to provide effective film reinforcement. Upon annealing of the polystyrene-pure PBA core-



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shell latex films at temperatures higher than the $T_g$ of the polystyrene, the polystyrene was found to coalesce, and the structure of the film was said to change from an inclusion (segregated) matrix to a bi-continuous two phase system. The presence of the methacrylic acid in the polymer, however, reduced the interactions between the polystyrene inclusions and lessened the enhanced mechanical properties of the film as a result of the aforementioned reduced aggregation. The methacrylic acid also acted to prevent the coalescence of the polystyrene during annealing due to a 'coalescence blocking mechanism', although this could be circumvented by modifying the heat treatment programme. Recently [256], the Cavaillé group have also investigated the properties of similar films with varying (amide) functionality (i.e. functionalising the PBA shell) and, therefore, hydrophilicity[14], in relation to the distribution of the functionality within the latex, again finding that this also inhibits the coalescence of the polystyrene (as was found with the polystyrene-pure PBA core-shell latices).

Heuts et al. [257] also examined the differences between: (i) blended mixtures of both high acid low $T_g$ latices; and (ii) latices prepared via a two-stage emulsion polymerisation, in relation to the requirements of the decorative paints industry, and the need for low MFFT coatings without the necessity of volatile organic solvents (or co-solvents in the case of waterborne coatings). Results showed that both the blends and the two-stage polymers gave films of low MFFT with improved mechanical properties, when compared to single component systems of comparable MFFT, which were ascribed to film morphology. In the case of the blended latices, the $T_g$ of the softer polymer was 278 K, and MFFT of the film remained within 5 K of this $T_g$, until the ratio of high to low $T_g$ polymers was 1:1, after which the MFFT rose rapidly and there was insufficient softer polymer to form a continuous film. By comparison, the two-stage polymers exhibited MFFTs which were between the MFFT of the blended films and those of the single stage polymer. The sequence of polymers (hard polymer core-soft shell, or soft polymer core-hard) showed little difference.

In fluorescence energy transfer experiments, Feng et al. [258] have shown that for surfactant-free immiscible polymer blend films of hard and soft latex particles, annealing at 373 K increased the limited extent of polymer mixing at the interface between the particles. In the presence of 4–6 wt.% SDS surfactant, energy transfer was reduced and a layer of surfactant appeared to be trapped on the surface of the hard particles.

Shellenberg et al. [259] have shown by AFM that for low $T_g$ low molecular weight core and cross-linked shell particles, that low cross-linking of the shell led to an even and mechanically homogeneous film, whilst for high degrees of cross-

[14] Note that this study also investigates the copolymerisation of the systems themselves: differences in hydrophilicity between the PBA and the functionalising polymer results in variation in the ability of the two to copolymerise and the location of the functionality (e.g. in the bulk of the shell or on its surface), although all led to a final incomplete core-shell type latex structure. Whilst coalescence of the polystyrene core was prevented, the film's mechanical properties were in some instances changed due to cross-linking of the functionality by annealing.



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linking the shell collapsed and released the core to form a continuous film containing collapsed units.

In the case of a single phase amorphous polymer, Gauthier and Perez [260] have explained how the rheological and mechanical properties, i.e. macroscopic stress–strain behaviour, and localised molecular processes, can be described in the form of theoretical equations, with the polymer both in its glassy state and as it changes to a rubbery polymer when moving through its $T_g$. In the case of heterogeneous polymers, however, local stress and strain have no simple relationship to the macroscopic properties since they are not uniform throughout the polymer. Gauthier and Perez went on to review various techniques that have been proposed by which the mechanical behaviour of blends and composite (binary and multi-phase) polymers may be predicted, e.g. by considering the phase in series or parallel, or by so-called 'homogenisation methods". Examples of heterogeneous systems were then examined and data about the morphology of such systems were obtained from comparison of experimentally measured and theoretical viscoelastic properties.

The heterogeneity of a polymer or film may be beneficially exploited in film usage. Heterogeneous carboxylated styrene-butadiene latices were prepared by Rigdahl et al. [261] by a process of seeded polymerisation which utilised seeds of different molecular weights of polystyrene and finally a copolymer of styrene-butadiene and either 1 or 10% w/w methacrylic acid. The latex was used to cast porous film containing (i.e. binding) kaolin; such as might be utilised for a paper coating. Coatings were cast at temperatures within the rubbery region of the polymer, and it was shown that a higher modulus in the rubbery region of the films led to coatings with higher porosity, and better light scattering/glossiness as a result of reduced shrinkage during drying.

Zheng et al. [262] have used lithium salts grafted on to the surface of poly(ethyl acrylate) latex films to show that ionic transfer in the surface layer on latex particles is an effective method of increasing the conductivity of polymeric electrolytes.

Permeation, which may provide useful information on structure, through such heterogeneous latex films has not been widely studied, although the situation in which a solid is dispersed in a continuous polymer phase is not unusual, e.g. pigmented or filled films. Core-shell latex particles in which the core is below its $T_g$ (at the film casting temperature), whilst the shell is soft, may provide the basis for an ideal model filled film is since the uniform distribution of the 'filler' core is promoted by its non-deformation and, hence, uniform packing in the latex films. As such, the theoretical treatments of Maxwell [263] (particle interactions neglected), Rayleigh [263] (cubic arrangement of identical spheres) and Higuchi [264] (spheres treated as points, but including particle interaction), for permeability should be applicable. Peterson [265] used blends of 28% (volume fraction) of latex polymers, [polystyrene, PMMA, and poly(vinylidene chloride)], in a soft continuous phase of PVAc, latex, and found good agreement with the Higuchi theory for oxygen permeability. Chainey et al. [15,266] studied the helium permeability of flash-cast films, formed from hard core-soft shell polymers prepared by a shot growth



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technique. The latices consisted of particles composed of a polystyrene core-PBMA shell, of varying coating thickness. The films aged in the same manner as for free PBMA films, but the extent of the permeability reduction was less, and decreased with decreasing coating thickness. This was attributed to graft copolymer inhibiting further gradual coalescence. When the solvent-cast polystyrene permeability value was used for the core, and the aged value for the PBMA at low volume fraction of core, or the initial value at high volume fractions of core, then reasonable agreement with the Higuchi equation was obtained, although experimental results tended to be high. For a PBMA core-PEA shell combination ageing was observed but could not be attributed to shell ageing, since PEA homopolymer did not age. Unfortunately, for this combination of polymer, the core polymer aged to the same permeability coefficient as the shell polymer, and thus this similarity gave an insensitive test of the Higuchi treatment. Good agreement for core-shell, and copolymers was found but not for blends, and this was attributed to imperfect film structure arising from incompatibility of the components.

Roulstone [18] investigated film ageing relative to shell thickness, for *4*-nitrophenol permeation through dish-cast PBMA-poly(methyl acrylate) core-shell latex films, and found results conforming with those of Chainey [15] for gas permeability. As in Chainey's study, there was some agreement with the Higuchi theory, but experimental results were higher than for aged films. Rather better agreement was found when water vapour was the permeant.

Lepizzera et al. [267] studied hard core, soft shell latex particle films under elongation using AFM. Originally, the particles formed long-range hexagonal ordering but upon elongation were pulled apart in the direction of elongation and pushed together in the direction perpendicular to it, thus forming linear 'necklaces' of core particles. At increased elongation, geometric rearrangement and breaks in the necklaces led to zigzag and chevron-like structures. The two main parameters controlling the mechanical behaviour of blend films were the mechanical properties of the soft polymer continuous phase and the weight fraction of hard particles. Debounding of hard particles and soft matrix occurred on elongation [268].

### *3.2. Film opacity*

It has been stated previously that non-film-forming latices dry to form an opaque, white, friable powder. Such opacity can be a desirable property of a coating, for example, a paint. Typically, an additive such as $TiO_2$ is used to achieve the opacity. The opacity results from light being scattered at an interface between substances of different refractive index (e.g. the interface between air and polymer, or air and $TiO_2$) — dependent on the laws of reflection and refraction [269]. Such scattering and hence, opacity can, therefore, also be achieved if a polymer film contains large numbers of voids (i.e. due to the high number of polymer–air boundaries) such as in 'microvoid coatings'. The degree of opacity is dependent on: (i) microvoid concentration; (ii) microvoid size and size distribution; and (iii) the aforementioned refractive index ratio. There exist a number of patents for the preparation of such coatings, and the methods have been reviewed by Seiner [270].



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By utilising a method of optimising microvoid size using a model system developed by El-Aasser et al. [271], Durbin et al. [272] were able to prepare a latex paint containing microvoids, in combination with a small film-forming latex, which used 50% less $TiO_2$ to yield comparable hiding power without loss of desirable physical properties (e.g. scrub resistance).

An effect similar to that found for microvoid coatings can be achieved through the use of hollow spheres. Such spheres have a large polymer–air interface (requisite for light scattering) as a result of the internal chamber [273].

Film turbidity and light scattering/interference measurements, combined with a knowledge of spherical particle-packing structures in latex films; has been used by Van Tent and te Nijenhuis [274,275] to provide models which allow visible light transmission measurements to be used to characterise the geometrical packing of latex particles during the process of latex film formation.

In the case of a latex paint, a rough film morphology may be desirable to increase the opacity of the paint. However, by way of contrast. a smooth topography is desirable in the quest for a glossy finish. Butt and Kuropka [276] have used atomic force microscopy to directly correlate the surface roughness of pure latex films with the gloss of the corresponding latex paints.

## 4. Latex film additives: plasticisers, surfactants, etc.

Polymer latex films may contain a number of additives, such as stabilising surfactant (endogenous to the reaction, or post-added) and plasticisers to aid film formation. These are in addition to additives utilised to enable the film to perform a function, e.g. colorants in latex paints or pharmaceuticals in controlled or sustained release matrix-type devices.

Typically, a plasticiser or coalescing aid may be added to ease the deformation of the latex particles so that a non-film-forming polymer can become film-forming at a given temperature. The plasticiser may then be required to soften the film or, more frequently, be fugitive to allow the film to harden since soft polymer films have a tendency to cohere. (The capacity to resist such self-adhesion is termed 'block resistance'.) In the case of fugitive plasticisers, which partition between the polymer and the aqueous phase, there is a compromise between the necessity of the plasticiser to remain in the latex for sufficient time for it to perform its function, but not to remain so long as to soften the film: a factor dependent on the plasticisers volatility. (Volatile organic components were considered in Section 2.3.1.)

The effect of coalescing aids on the interdiffusion of polymer chains during polymer annealing was investigated by Winnik et al. [277,278]. Organic solvents, typically used as coalescing aids (e.g. glycol derivatives), were found to provide a constant degree of enhancement in inter-diffusion rates (i.e. as a result of plasticisation by the coalescing aid) during annealing, and the effect was described by a modified Williams–Landel–Ferry equation. Deviations from the model (i.e. the degree of enhancement was not constant during the course of annealing) were as a



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result of evaporation of the coalescing aid from the film by a Fickian-type process. In addition, AFM showed that the presence of a coalescing agent (Texanol™) acted to promote the exudation of surfactant (SDS) from PBMA latex films [279]. Juhué and Lang [280] have also reported the effects of organic solvents of varying volatility and strength of plasticisation upon diffusion coefficients and penetration depths in PBMA film.

In addition to its usual role of plasticisation, several authors have added plasticiser to various types of polymer films in an attempt to control the permeability of the film [88,281] or to provide a means of control of the release rate in sustained release pharmaceutical devices [282,283]. Goodhart et al. [282] found that the addition of plasticiser (triethyl citrate or dibutyl sebacate) to Aquacoat® (pseudo-latex) coated drug cores (phenylpropanolamine HCl) changed the flux of the drug such that release rates were inversely proportional to the plasticiser concentration. Addition of plasticiser up to a concentration where it aided coalescence decreased the drug release rate, whilst above a certain level (not stated, but between 24 and 40% w/w) of addition, the solute permeability increased due to the increased solute diffusivity caused by the plasticiser's water solubility. Above the higher loading (40% w/w), an increase in film casting temperature did not effect the rate of drug release, whilst at a loading of 24%, an increase in casting temperature led to reduced release rates.

Hoy [284] provided experimental evidence which accredited the efficiency of various coalescing aids (including a number of acetates and ethoxy alcohols, as used in latex paints) to their degree of partition between the aqueous and polymer phases, and their $T_g$. (The ability of the plasticiser to undergo hydrogen bonding had a great effect on the results due to the tendency for the plasticiser to remain in the aqueous phase.) Casting (i.e. painting) on porous substrates was found to aid the removal of plasticiser that partitioned favourably into the aqueous phase, decreasing its efficiency.

Additionally, Hoy gave theoretical equations for predicting the action of a coalescing aid on the film's MFFT — based on the assumption that the MFFT was directly proportional to the $T_g$, where the constant of proportionality was a 'reduced film forming temperature', $K$:

$$\frac{\mathrm{MFFT}}{T_g} = K \tag{21}$$

Using a variation of the Fox equation (for determining the $T_g$ of copolymers) which accounted for the fact that the plasticiser was external to the polymer (correction factor, $\alpha$) and, hence, had greater mobility, the polymer's plasticised glass transition temperature, $T_g^p$, was given by:

$$\frac{1}{T_g^p} = \frac{V_p}{T_{gp}} + \frac{\alpha V_A}{T_{gA}} \tag{22}$$

where $V_p$ = volume fraction of the polymer, $\alpha V_A$ = volume fraction of the coalesc-



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ing aid, $T_{gp}$ = pure polymer glass transition temperature and $T_{gA}$ = glass transition temperature of the coalescing aid.

The volume fraction of coalescing aid, $V_A$, was then modified to account for its distribution in the latex:

$$V_A = \frac{Af_p/\rho_A}{S_0/\rho_p + Af_p/\rho_A} \tag{23}$$

where $A$ = weight of coalescing aid (parts per hundred of latex), $S_0$ = initial percentage solids of latex, $\rho_A$ = density of coalescing aid, $\rho_p$ = density of polymer and $f_p$ = fraction of coalescing aid contained in the polymer.

Knowing that $V_p = 1 - V_A$, and combining the above three equations:

$$\frac{1}{\text{MFFT}} = V_A\left[\frac{\alpha T_{gp} - T_{gA}}{K(T_{gp})(T_{gA})}\right] + \frac{1}{K(T_{gp})} \tag{24}$$

Toussaint et al. [285] have also proposed a model to predict the effect of a coalescing agent on the $T_g$ (or MFFT) of a latex. The model is based on the concept of free volume and the distribution coefficient of the agent between the polymer particles and the aqueous phase. The model is said to be applicable to mixtures of coalescing aids, and allows the calculation of the weight or volume fraction of agent required in order to give a required depression in $T_g$ (or MFFT). The mechanical properties of plasticised (and non-plasticised) films have also been modelled [286] in relation to the viscoelastic properties of the polymer.

Du Chesne et al. [287] has used Energy Filtering Transmission Electron Microscopy (EFTEM) to show that separated domains of surfactant/polymer were only detectable in films which were cast above the MFFT of dispersions of either poly(vinyl acetate) or polyacrylate. When samples were prepared at lower temperatures, the surfactant was retained at the particle surfaces. Du Chesne concludes that the mobility of the emulsifier is increased with particle deformation/coalescence and that such mobility is essential for domain segregation.

The effect of a surfactant on the ability of a protective coating to prevent corrosion have been studied by Satguru [171]. In addition to stabilising the latex, the addition of a non-ionic surfactant to a chloropolymer latex was found to additionally plasticise the polymer leading to increased rates of particle coalescence together with reduced particle flocculation during film formation. This provided better quality, defect-free films which yielded water vapour permeabilities that were comparable to solvent-cast films when the surfactant was present at a concentration equal to monolayer coverage. A decreased or increased surfactant concentration led to evidence of increased water ingress and hence poorer corrosion resistance. Roulstone et al. [18,288] have also studied the water vapour permeability of films cast from PBMA surfactant-free latices in the presence of post-polymerisation additives that included surfactants, polymers and inorganic electrolytes. The surfactants had a common $C_{12}$ backbone, but either anionic (sodium dodecyl sulphate or SDS {i.e. $CH_3(CH_2)_{11}SO_4^-Na^+$}), cationic (dodecy-



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lethyldimethylammonium bromide, or DEDAB {i.e. $CH_3(CH_2)_{11}N^+(C_2H_5)$-$(CH_3)_2Br^-$}), or non-ionic (dodecyl tetraoxyethylene glycol monoether, or $C_{12}E_4$ {i.e. $CH_3(CH_2)_{11}(OCH_2CH_2)_4OH$}) polar head groups. A minimum in the film's water vapour permeability was found at monolayer coverage of SDS, and this was interpreted as a consequence of improved particle packing order due to enhanced charge stabilisation since somewhat greater coalescence was apparent in freeze-fracture TEM replicas of such films. Below monolayer coverage, permeability decreased with increased SDS concentration, and tended to lower values on film ageing. Durbin [289], however, argued that at this level of addition, SDS decreased the particle packing order since the increased ionic strength outweighed the effects of increased charge density. At higher SDS concentrations, film permeabilities increased and 'islands' of SDS ware visible in micrographs as aggregate defects, with smaller aggregates in the particle interstices. Particle boundaries could be observed and the films did not age to give lower permeabilities. (Note, however, Tebelius et al. [290] provide evidence that water vapour or humidity, which causes water uptake by a film, can change the film's morphology or the distribution of surfactant within the film.)

For the cationic surfactant, at concentrations sufficient to give charge reversal and to maintain stability, a minima in permeability was observed by Roulstone et al. [18,288], at approximately monolayer coverage. However, permeabilities were higher than for the SDS additions and higher than for the surfactant-free films. This increased permeability was attributed to the DEDAB first forming a salt with the anionic surface groups in the interparticle regions, and then adsorbing tail first onto the surface — with multi-layers forming at higher concentrations. These films, like those with the higher concentration of SDS, also did not age to lower permeabilities.

Significantly different behaviour was observed [18,288] for $C_{12}E_4$, which plasticised the films making them more flexible but not tacky, and giving increased coalescence. Slightly reduced permeability at surface coverage, but then raised permeabilities at higher concentrations were also observed. Being well coalesced, the films did not age to lower permeabilities. Vanderhoff [106] found good compatibility between non-ionic surfactants of this type and the polymer with no surface exudations. However, when the ethylene oxide chain length was increased, incompatibility with the polymer did lead to surface exudations. Padget and Moreland [178], using a non-ionic block copolymer surfactant, found increased coalescence at surface coverage, with surface exudation at higher levels of addition. Vijayendran [52], Kientz and Holl [12,291], Kim et al. [292], Eckersley and Rudin [51] and Kawaguchi et al. [184,293] have also reported plasticisation and enhanced diffusion rates when non-ionic surfactants have been used in latex films.

Odrobina et al. [294] showed that nonylphenol ethoxylate, EO20, solubility was limited to approximately 2 wt.% in PBMA at room temperature, whilst an equivalent poly(ethylene glycol) (PEG) was even less soluble. Miscibility was determined by a lowering of $T_g$, whilst immiscibility was shown by a melting isotherm for the surfactant component as determined by modulated DSC measurements.

AFM was the technique favoured by Juhué and Lang [97,295,296] to investigate



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surfactant exudation. They measured the peak-to-valley distances in PBMA films as a function of their concentration of (post-polymerisation added) surfactant ($C_9H_{19}$–$C_6H_6$–O–$(CH_2CH_2$–$O)_{25}$–$SO_3^-Na^+$ or sodium nonylphenol-polyglycol-ether-sulphate) [295]. Surface coverage was again significant, providing a minimum in the peak-to-valley distance: attributed to a favourable delay in flocculation, due to enhanced particle stability and hence, the greatest degree of particle close-packing at the film surface. (Below surface coverage by surfactant, particle–particle repulsions are weak and flocculation occurs early during film formation, whilst at high surfactant concentrations, electrostatic repulsions are screened by the large concentration of sodium ions in the latex dispersion — again leading to early flocculation.) Additionally, it was found [296] by using a similar (but non-ionic) surfactant that depletion effects, as well as steric stabilisation (and, in the case of the ionic surfactant, electrostatic repulsion) contributed to the optimal packing of particles during film formation. [Polymer depletion regions (see Juhué [296] for references) occur for colloids in the presence of non-adsorbing polymers. When two particles approach within a distance of less than twice the polymer radius of gyration, exclusion of the polymer from the space between the particles leads to the development of an osmotic pressure which flocculates the particles.] The development of micelles at high surfactant concentrations, above surface coverage, contributes to the formation of poor quality films due to depletion flocculation.

Zhao et al. [297–299] used surface analytical techniques including XPS, SIMS, and FTIR-ATR spectroscopy to show that material which was incompatible with the polymer was exuded to the film surface. They revealed, by FTIR-ATR spectroscopy, that SDS was exuded from methyl methacrylate-butyl acrylate polymer latex films mostly during drying, but also during further gradual coalescence, to give a concentration gradient which increased towards both interfaces with a higher concentration at the film–air interface than at the film–substrate interface. The same trends were observed, but to a reduced degree, for a more compatible surfactant. In contrast to Zhao, but again by using ATR-FTIR, Amalvy and Soria [3] investigated the distribution of SDS in a terpolymer of methyl methacrylate-ethyl acrylate-methacrylic acid, finding that the surfactant was distributed with a parabolic profile between the upper and lower interfaces (as opposed to predominantly being found at the polymer–air interface). This result was attributed to the latex particle surface which consisted of the high $T_g$ hydrophilic, methacrylic acid groups, rather than the effects of the casting substrate being used. Urban and Evanson [300] found surfactant exudation during film formation to be initially dependent on the water flux, but ultimately on the difference in surface tension between the polymer and substrate. It was found that mechanical stretching of the film (as may be encountered during removal from a substrate) affected the distribution of surfactant throughout the film: as the surface area, is increased (by stretching), the surface concentration of surfactant is decreased and the resultant increase in surface tension is henceforth reduced by the diffusion of surfactant to the interface. Analogous to the ability of a liquid to wet a solid of higher surface energy; casting the film on a substrate of lower surface tension [e.g. PTFE (= 18.5 mN $m^{-1}$)] than the polymer (surface tension typically 25–60 mN $m^{-1}$) prevents the



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film from wetting the substrate and, hence, surfactant diffuses to the polymer–substrate interface to lower the interfacial tension. In addition to investigating the effect of substrate surface tension on surfactant mobility and distribution, Urban and colleagues have produced a number of papers [301–312] importing FTIR measurements detailing extensive investigations of mimic and non-ionic surfactants on ethyl acrylate-methacrylic acid and styrene-butyl acrylate copolymer films, looking at the surfactant molecular orientation and molecular stratification near the substrate–polymer and polymer–air interfaces, together with surfactant mobility, and have [313–317] also looked at the effect of both latex blends and modified (e.g. core-shell) latex particle composition, finding that these also affected both surfactant concentration and (molecular) orientation within the film. Urban [318,319] has also used step-scan photoacoustic FT-IR spectroscopy for depth profiling analysis of surfactant content.

Holl et al. [12,13,320,321] have produced a series of papers on the effects of surfactant concentration, migration and distribution, upon the adhesion between film and substrate, a topic also recently considered by Zosel and Schuler [322].

The AFM study of PBMA latex films, including SDS in the presence of Texanol™ coalescent aid by Juhué showed that for 2 wt.% SDS in the absence of the plasticising solvent, there was little tendency to exude to the surface, even upon annealing at 343 K. It was noted, however, that the 'last spot to dry' was highly ordered and that surfactant did exude solely in this region upon annealing. More general surfactant exudation was strongly promoted by just a few percent of the Texanol™.

Park et al. [323,324] used AFM to show that post-added poly(ethylene oxide-co-acrylic acid) gave enhanced diffusion rates in PBMA films, and this was attributed to the low molecular weight and low $T_g$ of the additive adsorbed at the latex particle surface. Park et al. [325] also used AFM to examine the effect of a carboxylated random copolymeric emulsifier upon PBMA latex film formation. For surfactant-free PBMA latex, cracks were seen to divide the surface into hexagonal regions consistent with the underlying polycrystalline film structure. In the presence of poly(styrene-acrylic acid), molecular weight 8600, more regular packing was observed and an inter-connected layer of polar material inhibited particle fusion.

Roulstone et al. [18,288] used two samples of poly(vinyl pyrrolidone) (PVP) of molecular weights 44 000 and 360 000 at 0.16 g $g^{-1}$ (cf. monolayer coverage 0.1 g $g^{-1}$ and 0.15 g $g^{-1}$ for the two molecular weights, respectively [326]). The PVP was deposited between the particles, which showed good packing but very limited evidence for coalescence and deformation. Limited ageing to a lower permeability was observed. List and Kassis [72] suggested that high molecular weight stabilisers immobilised particles in films and inhibited ageing. Bondy and Coleman [327] also noted retarded coalescence on film formation in the presence of stabilisers.

For post added KCl, at below the critical coagulation concentration (CCC) of a PBMA latex, Roulstone found a reduced packing order coupled with an increased permeability, with most of the inorganic material being exuded from the interstices to the surface layers: a tendency that increased on ageing.

The addition of sucrose to polymer latex films to study [244] its effect on



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permeation gave rise to a number of observations on film formation. The use of carbon-14 radiolabelled sucrose as a permeant had showed that a number of the methacrylate (co)polymer films studied were impermeable to sucrose, and yet, these same films showed enhanced solute/electrolyte permeability properties when cast with sucrose dissolved in the aqueous phase of the latex. This implied that sucrose was being entrapped within the film structure, and must either have been contained within the voids between the spherical particles or at the particle interfaces. The films were observed to dry from the polymer–air interface downwards, towards the substrate, and this was confirmed in SEMs of sucrose-containing (surfactant-free) PBMA films, which showed an ordered close-packed latex particle structure at the polymer–air interface, whilst at higher levels of sucrose addition, showed a phase inversion of individual latex particles in a matrix of solid sucrose at the polymer–substrate interface.

Pochan [328] found, by measuring the dielectric properties of a PBMA latex film containing a water soluble polymer additive [a carboxylated styrenic terpolymer (25% by weight)] that, when cast at ambient temperature, the additive was present in the interparticle interstices forming a continuous network. This morphology was, however, said not to be the equilibrium state, and thermal annealing of the film led to the additive forming isolated domains within the film if the annealing temperature was above the $T_g$ of the additive.

Bindschaedler et al. [329] note a broad diversity of works, and conclusions, concerning film additives in the literature with five possible fates for the emulsifier, as shown in Table 1.

Although not intentional additives, the exudation of water soluble impurities can occur as a consequence of the dissolution of components from the substrate, when wetted during film formation, into the aqueous phase. In the coating of steel, the occurrence of 'flash rusting' [330] is a consequence of the dissolution of ferrous ions from the substrate followed by convective diffusion to the film surface where they are oxidised to ferric ions to give rust brown spots. In the coating of drug cores the drug has similarly been found to exude to the film surface although in this case it was not necessarily a disadvantage since a time-lag prior to the initial release of drug by diffusion through the film, was avoided [71].

Table 1
Possible fates of emulsifier added to latex films

| Fate of emulsifier | Polymer compatibility |
|---|---|
| Migrates and dissolves in the polymer | Compatible |
| Exudes towards film surface | Incompatible |
| Forms independent islets, possibly corresponding to interstitial voids between particles | Incompatible |
| Forms a continuous network embedding globules | Incompatible |
| Adsorbs at the particle surface | Incompatible |



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### 4.1. Latex films and the critical pigment volume concentration

Certain applications that utilise latices, whilst necessitating the ability of the latex to film form, differ in the context to which the term film forming has been generally used in this review. This review of film formation has really been about the latex itself: how and why it film forms, and what factors might affect the quality of the cast film when looked at from an academic point of view. Many applications of latices only utilise the film forming ability, however, as a binder to other components; applications such as, e.g. drugs in pharmaceutical preparations or the pigments in an emulsion paint. Taking a paint as an example, whilst all of the aforementioned 'academic' factors that concern film formation are of relevance, there are also commercial factors to take into account. Film quality is of obvious importance in a decorative or protective coating, but cost is also important. From an academic point of view, a film additive is usually considered as something added to the latex, whereas in a coating formulation, the latex might be better considered as an additive to the film. Cost savings can be made by using just sufficient latex to bind the other components of the film, albeit at the expense of, for example, film permeability properties, etc.

The pigment volume concentration (PVC) [331] is a measure used in the paint industry to describe the volumetric percentage of hiding pigment present (+extenders), $V_P$, in the total volume of non-volatile vehicle solids content (polymer matrix), $V_B$, of a paint:

$$\mathrm{PVC} = \frac{V_P}{V_P + V_B} \tag{25}$$

In 1949, Asbeck and Van Loo [332] suggested an explanation as to why the properties of a coating underwent a dramatic change within a narrow band of the PVC. The properties (e.g. gloss, permeability, rust prevention) of a series of oil-based coatings of increasing values of PVC, but ground to the same degree of dispersion, showed a sudden break [e.g. the permeability increased sharply; the glossiness (and also blistering) decreased markedly; and the degree of resting increased markedly] at a value they termed the critical pigment volume concentration (CPVC). They showed that the CPVC was dependent not only on the type of pigment, and its degree of dispersion, but also on its physical relationship with the other components of the paint and, hence, the agglomeration[15] of the system (the higher the degree of agglomeration, the lower the CPVC) and noted the fact that systems with high CPVCs have a smoother texture. From work using different (oil-based) binders, it was reasoned that the degree of colloidal stability imparted to the particles resulted in changes to the packing density, and that this too could influence the CPVC (in addition to the packing properties resulting from the shape of the particles themselves). Further work allowed the CPVC to be defined as 'the

[15] Defined by Asbeck as, 'a group of two or more individual pigment particles that are held together so firmly by the force of adhesion that they tend to remain as an intact unit'.



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point in a pigment-vehicle system at which there is just sufficient binder to completely fill the interstices between randomly packed pigment particles after the volatilisation of the thinner, such that it represents the densest degree of packing of the pigment particles commensurate with the degree of dispersion of the system' [333]. The change in properties of the paint at the CPVC was ascribed to the formation of air voids due to insufficient binder to fill the interstices between the most densely packed particles. Thus, below the CPVC, the pigment packing fraction ($\Phi_p$) is equal to the PVC [Eq. (25)], whilst above the CPVC, if the total volume of air in the coating is given by $V_A$, then $\Phi_p$ is given by [334]:

$$\Phi_p = \frac{V_P}{V_P + V_B + V_A} \tag{26}$$

Various experimental methods of CPVC determination are mentioned by Anwari et al. [335]. However, the determination of an accurate method for the calculation of the CPVC (without preparing a formulation and investigating its properties) has proved elusive. Bierwagon et al. [336] describes a mathematical model based on the ideal random packing of spheres, their size distribution, and adsorbed layer thickness, etc, the results, however, were described (by Bierwagon) as 'good' for alkyd-type (acid + alcohol resin) paints, when compared to experimental results, but only as 'fair' in the case of latex paints which was presumed to result from pigment–polymer interactions.

Rasenberg and Huisman [334] describe a method which utilises porosity measurements (determined by mercury porosimetry) and the fact that $\Phi_p$ remains constant, above the CPVC (because it represents the highest possible pigment packing density) to determine the value of the CPVC from a knowledge of the pigment weight fraction (and the values of the densities of pigment and binder). By defining the weight fraction of the pigment as $c$:

$$c = \frac{m_p}{m_p + m_B} \tag{27}$$

where $m$ = mass, subscript p refers to the pigment and subscript B the binder, then the volume ratio, $\Phi_p$, can be determined in terms of $c$, $V_A$ and the respective densities of the binder and pigment ($\rho_B$ and $\rho_p$) if all properties are defined per unit mass (kg) of coating:

$$\Phi = \frac{m_p/\rho_p}{m_p/\rho_p + m_B/\rho_B + V_A} = \frac{c\rho_B}{V_A\rho_p\rho_B + c\rho_B + \rho_p - c\rho_p} \tag{28}$$

which can be re-arranged:

$$V_A = \left[\left(\frac{1}{\Phi_p\rho_p}\right) - \frac{1}{\rho_p} + \frac{1}{\rho_B}\right]c - \frac{1}{\rho_B} \tag{29}$$



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This is, thus, an equation for a straight line in which the term in the square bracket is a constant (because $\Phi_p$ is constant). A plot of porosity ($V_A$) vs. the pigment weight fraction ($c$) will yield the critical pigment concentration (CPC) as the intercept on the concentration axis, when $V_A = 0$. The CPC can then be converted to a CPVC if the densities of the pigment and binder are known.

Rasenberg notes that if $\Phi_p$ is constant (and the densities are known: in order to give the intercept, $\rho_B^{-1}$), then the CPVC may be determined from a single point (taken above the CPVC and extrapolated). However, this method of Rasenberg and Huisman also requires a film be prepared, rather than being a theoretical method.

Citing a previous paper [337] on the use of a polystyrene latex as a filler, Floyd and Holsworth [338] discussed a number of anomalies which may affect the CPVC. The fact that various properties of the film appeared to show differing values for the CPVC, was attributed to the fact that the polystyrene particles were shown to sinter at points of contact (despite it being non-film forming) and, hence, provide the film with some mechanical integrity at values of the PVC above the typical CPVC. Floyd also discussed certain factors that may change the concept of the CPVC, e.g. clustering [i.e. the association of the dispersed phase (pigment particles) as the concentration increases (even at low volume fractions, e.g. $< 10\%$) leading to the formation of doublets, triplets, multiplets, etc., a random process and not the same as flocculation due to colloidal instability] and percolation (which commences when the cluster size is sufficient to span the film). Floyd speculated that it was this latter feature which gave rise to the change in the film's permeability properties due to the formation of pathways, and also led to the decrease in film gloss by the introduction of light scattering. At high pigment concentrations, a phase inversion can occur as the primary phase changes from being one that is polymer rich to one that is pigment rich. (This can have important connotations with regard to, for example, the electrolytic properties of a film, e.g. zinc-rich paints for corrosion protection or any type of film requiring a continuous network of additive.)

Although the results of Asbeck's work have been shown to be equally applicable to latex paints, the CPVC is offset to a lower value by a fixed fractional amount which is termed the binder index [338] of a given latex. Floyd and Holsworth [338] note that air voids are present in all latex paints, for all values of PVC (and that their concentration increases as the CPVC is approached) due to the fact that particle deformation is hindered by the pigment. The voids are likened to a second dispersed phase and can undergo clustering and percolation as their concentration increases with increasing PVC. Because the pigment is typically impermeable, it is percolating voids that give the increased permeant flux. The CPVC of latex paints is, thus, attributed to a phase inversion [339] from a bi-continuous (polymer–air) system in which the polymer is the primary phase to one in which the primary phase is air.

Typically, a dispersing or wetting agent (surfactant) is added to a paint to prevent agglomeration of the pigment. For a latex (paint), it is not only important that the pigment itself does not destabilise the latex, but also that the pigment does not



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remove surfactant for its own stabilisation in detriment to the latex. In ensuring this, the CPVC of a latex paint is usually equal to the ultimate pigment volume concentration (UCPVC) [333], i.e. the CPVC at which all of the pigment particles are completely separated and act independently, whilst the polymer matrix acts as a continuous fluid [331]. Factors that affect the ability of the pigment particles to act independently (such as clustering and flocculation, etc.) all serve to decrease the CPVC, when compared to a new stable system.

Joanicot [139] has used SANS and AFM, obtaining good agreement between the techniques to study ordering, spreading and adhesion of latex particles to calcium carbonate pigment. At the low volume concentrations typical of gloss paint, there was no modification of polymer film structure by pigment, i.e. the pigment did not force the particles to coalesce. In high PVC paints, more typical of matt paints, the pigments were fixed by isolated latex particles at many discrete points.

## 5. Summary

At first sight, polymer latex film formation appears to be remarkable but simple. It is remarkable that a water-based dispersion, in contrast to polymers in aqueous solution can dry to a water insoluble coating. A uniformly spread wet film dried at a temperature above the $T_g$ of the polymer might simply be expected to dry to a uniform film with the spherical latex particles deformed to fill all interparticle space. The process has, however, been studied for over 50 years without universal agreement being reached as to the mechanisms involved. A considerable increase in interest has been shown in the last decade driven by the need for waterborne formulations in order to avoid the release of the environmentally harmful volatile organic compounds associated with solvent-based systems. Recent studies have benefited from the availability of new instrumental techniques such as SANS, DET, ESEM and AFM, etc. The roles played by water in the film-forming process are particularly contentious. If water does not plasticise the polymer, then the MFFT may coincide with the $T_g$ of the polymer seeming to make a mechanistic role for water doubtful. It is not necessarily the case, however, that film formation is complete when a transparent film is formed or that it coincides with the complete removal of water. A transparent film may still have inclusions of water or air if they are significantly smaller than the wavelength of light. The relative rates of water removal and polymer consolidation can influence the outcome. It is still useful to consider film formation as occurring in three stages: (i) the concentration of particles; (ii) deformation of particles: and (iii) polymer chain interdiffusion between particles. The stages may not, however, occur sequentially, e.g. deformation may commence before close packing, and interdiffusion of polymer chains may precede complete removal of water, depending upon the temperature of film formation relative to the $T_g$ and upon the uniformity of drying. Greater emphasis is now placed on the fact that the drying of latex films is seldom uniform. The progress of drying fronts, both horizontally and vertically, needs to be considered. Films may be thicker at the edges or at the centre depending on whether or not



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containing walls are used and the 'last point to dry' is believed to be structured differently. Whether or not a skin of film overlies wet latex during the drying process is still in need of clarification. All of the particle deforming mechanisms, i.e. dry sintering driven by $\gamma_{pa}$, wet sintering driven by $\gamma_{pw}$ capillarity driven by $\gamma_{aw}$ and piston compression driven by osmotic pressure have been shown to be feasible film forming mechanisms, but their relative importance in typical drying conditions is disputed. The possibility that latex particles are deformed predominantly elastically and then cohere (followed usually by chain interdiffusion) has not been ruled out. That rhombic dodecahedra are the outcome of the isotropic deformation of well ordered uniformed sized latex particles under typical film-forming conditions has yet to be unequivocally demonstrated. Care is needed in comparing results for apparently similar latices without due regard to the preparative and cleaning procedures actually employed as well as film formation conditions used.

Whilst penetrant barrier properties and mechanical strength development indicated that for polymers with $T_g$ values close to ambient temperature, polymer chain interdiffusion and entanglements continued over periods of days or weeks, it has been SANS and NET experiments which have shown the extent of interdiffusion and shown that particle identity would ultimately be lost. Particle boundaries may remain where particles themselves are cross-linked or where cross-linking reactions take place at the boundaries or where bound additives such as surfactants and polymers become trapped, therefore preventing interdiffusion. Whilst high molecular weight polymer chains would be expected to follow reptation theory, experimental verification has yet to be entirely convincing. Acid groups, or their salts, retard interdiffusion whilst short polyethylene oxide chain compounds tend to enhance it. Carboxyl groups do tend to increase cohesive strength due to hydrogen bonding and ion–dipole interactions whilst plasticisers reduce it. During film annealing, surfactants and polymers originally associated with the particle surfaces are, unless strongly bound to form a membrane phase, fragmented and expelled to the film surfaces or to the particle interstices to form islets of hydrophilic material dispersed in the predominating hydrophobic polymer. Whilst a hydrophilic membrane phase increases the water sensitivity of a dried film, it can, despite having prevented inter-particle diffusion, increase the mechanical strength of the film.

As well as copolymer particles, blends of homopolymer or core-shell particles can be used to give a compromise between good mechanical properties and good film-forming properties. Minima in polymer film permeabilities have been observed at monolayer coverage of surfactants, which is ascribed to better particle packing. Modern analytical techniques such as XPS, SIMS and FTIR-ATR have all proved useful in studying surfactant re-distribution and interactions. Water soluble additives can be used to increase the permeability of latex films for sustained and controlled release purposes. For polymers stored above their $T_g$ values the porosity created by the leaching of an additive is lost upon drying. Air voids with sizes approaching the wavelength of light create opacity and whiteness in films.

It is apparent then that latex film formation is far more complex than film formation for the equivalent solvent-based systems. A full understanding of the



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fundamental processes involved still provides a challenge to academic investigators whilst the extra complexity caused by additives necessitated by the choice of water as the continuous phase poses challenges to industrial formulators. Continuing environmental pressures will ensure, however, that both groups of workers will sustain and expand their interest in these difficult but versatile systems for the foreseeable future.

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