Resolving the Film Formation Dilemma with Infrared Radiation-Assisted Sintering

Argyrios Georgiadis,¹ Peter A. Bryant,¹ Martin Murray,² Philip Beharrell,²

and Joseph L. Keddie^{1}*

1. Department of Physics, University of Surrey, Guildford, Surrey GU2 7XH, United Kingdom

2. Akzo Nobel Decorative R&D, Wexham Road, Slough, SL2 5DS, United Kingdom

*e-mail: j.keddie@surrey.ac.uk

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ABSTRACT: The film formation of an acrylate latex with a glass transition temperature of 38 °C has been achieved through the use of near-infrared (NIR) radiative heating. A hard, crack-free coating was obtained without the addition of plasticizers. Sintering of acrylate particles was confirmed through measurements using atomic force microscopy. The addition of an NIR-absorbing polymer increased the rate of particle deformation such that it was significantly greater than obtained in a convection oven at 60 °C. The results are consistent with a lower polymer viscosity under infrared radiation, according to a simple analysis using a standard model of sintering.

KEYWORDS: Atomic force microscopy; sintering; latex film formation; coalescence; infrared heating; polymer colloid

There is continued interest in the creation of coatings from colloidal dispersions of polymers in water, also known as latex. A key attraction of latex is that its film formation can occur without the emission of volatile organic compounds (VOCs) into the environment. Despite this benefit, the so-called “film formation dilemma” limits the wide use of latex in hard, scratch-resistant coatings.^{1,2} Specifically, a choice must be made between two problematic options for thermoplastic latex films for coatings applications: The glass transition temperature (T_g) of the polymer must be either greater than *or* less than the usage temperature, T_u , which is often near room temperature.

When $T_g > T_u$, the polymer is in its glassy state in use and will make a hard coating, but latex particle deformation and coalescence is not possible at T_u . A cracked and brittle film will result.^{3,4} To obtain a coalesced, crack-free film the processing temperature for film formation, T_{ff} , must be greater than T_g (which usually equals the minimum film formation temperature, MFFT).^{1,2} One approach to achieve film formation is to reduce the polymer's T_g below T_{ff} through the addition of a volatile plasticizer or coalescing aid.⁵⁻⁸ After film formation, the plasticizer evaporates, and T_g is raised above T_u , so that the polymer is vitrified and the film hardens. The formulation is no longer free of VOCs, which is an obvious drawback as plasticisers are under scrutiny for environmental and health reasons.⁹ (Note that the water within a latex can plasticize the polymer,¹⁰ such that the dry polymer T_g is greater than both the MFFT and the T_g in the wet state.) Another approach is to place the film in a convection oven¹ so that T_{ff} is greater than T_g during the critical drying period. However, this processing method uses a higher level of energy, in comparison to natural drying.

When $T_g < T_u$, the polymer is in its rubbery state, and the film is said to be soft. When $T_{ff} > T_g$, particle deformation and coalescence will proceed to yield a continuous film. In thermosetting latex films, crosslinking can be used to raise the polymer's hardness,¹¹ but thermoplastic materials will remain in the soft state when $T_u > T_g$ and hence will not be suitable as a protective coating. Composites of hard and

soft polymers – created with particle blends,^{2,12,13} core-shell particles,^{14,15} or heterogeneous particles^{16,17} – also offer a means to enable film formation while also achieving film hardness. The past approaches to the film formation of hard latex coatings, along with their limitations, are listed in Table 1.

The dilemma is choosing between a “hard” latex in which film formation is problematic and a “soft” latex in which film formation is effective but the mechanical properties are less desirable. There is a choice between a soft coating that is VOC-free *or* a hard coating that emits VOCs. In this Letter, we describe a new method to resolve the film formation dilemma. A crack-free, smooth film is created from a hard latex.

Table 1. Ways to Achieve the Film Formation of a Hard Latex Film

Action	Effect	Drawback
Add a plasticiser ⁵⁻⁸	Reduces T_g and MFFT	Can introduce VOCs
Place in an oven ¹	Raises $T_{ff} > T_g$ (and MFFT)	Increased energy use
Modify polymer ^{2,14-17}	Reduces T_g and MFFT	Reduced hardness
Use a crosslinker ¹¹	Raises $T_g > T_u$ after film formation	Requires chemical functionality
NIR heating	Raises $T_{ff} > T_g$ (and MFFT)	Energy use – but less than in oven ¹⁸

Whereas convection and conduction are established methods of heating materials, radiation from infrared (IR) sources has gained greater prominence recently. IR radiation has been reported as a means to dry foods¹⁸ and waterborne polymers.^{19,20} IR radiative drying processes are energy efficient. In food processing, the energy consumed by an IR lamp combined with a convection oven in removing water is 245% less than that used by the oven alone.¹⁸ The drying time of aqueous solutions of poly(vinyl alcohol) was reduced from 120 min. for convective drying to only 15 min. for combined convective and IR radiative drying.¹⁹ In the latex film formation process, however, the removal of water is just the first step. Drying must be followed (or accompanied) by particle deformation and molecular diffusion between particles.¹ Previously, an electrically-conducting polymer – polypyrrole – has been employed as

a thermal transducer to raise the temperature of microspheres²¹ and hot-melt adhesives²² under NIR radiation. More recently, other conducting polymers²³ (polyaniline and poly(3,4-ethylenedioxythiophene) [PEDOT]) have likewise been shown to be effective in enhancing IR heating, because of their strong absorption characteristics.

During latex film formation, spherical particles at a film surface will flatten because surface energy provides a driving force to reduce the surface area. In a pioneering experiment, Wang *et al.*²⁴ demonstrated that atomic force microscopy (AFM) provides an excellent means to measure the rate at which particles flatten in a dry sintering process. This rate increases as the annealing temperature increases and the polymer viscosity, resisting particle deformation, decreases.²⁵ Particle corrugation heights²⁶ and film roughness²⁷ have previously been measured over time using AFM and successfully compared to the prediction of sintering models. Although the film formation of soft latices containing IR absorbers has been reported,²² we are unaware of previous reports on the effect of IR radiation and absorbers on particle sintering, although surface melting of polypyrrole composites was reported by Li *et al.*²² Interestingly, polypyrrole shells on latex particles have been reported previously to hinder film formation, so that plasticizers were used to achieve film formation at room temperature.²⁸

Materials and Methods

An acrylate latex comprised of a copolymer of methyl methacrylate, butyl acrylate, and methacrylic acid (in a weight ratio of 18.3:13.3:1) was prepared by semi-continuous emulsion polymerization using an ammonium persulfate initiator and an anionic, ethoxylated alcohol surfactant (Rhodafac RK500A, Rhodia). The monomers and surfactants were fed over three hr. at 75 °C. The T_g of the dry latex, measured by differential scanning calorimetry (Q1000, TA Instruments) at a heating rate of 10 °C/min, was 37.9 °C. The average particle diameter, according to photon correlation spectroscopy (Coulter N4 plus, Beckman-Coulter), was 420 nm. In some experiments, poly(3,4-ethylene dioxithiophene)/poly(styrene sulfonate) (PEDOT:PSS, Sigma-Aldrich), which is strongly absorbing in

the near-IR (NIR) (Supporting Information, Figure S1), was added at a concentration of 1 wt.% of the latex polymer mass.

In sintering experiments, the latex was diluted to 10 wt.% solids and then cast on glass slides and dried at room temperature to create 20 μm thick films, as was measured by stylus profilometry (Dektak 8, Veeco). Dry latex films were placed 21.5 cm beneath a 250 W NIR lamp (Model 470 IR, Interhatch). The lamp's peak emission is in the NIR range between 1.0 and 1.3 μm (Supporting Information, Figure S2). Preliminary experiments²⁹ found that the temperature of the latex films after 30 s varied approximately as the inverse-square of the distance from the lamp, but this distance was not used as a variable in the present study. Identical samples were placed in a convection oven (Model MOV-112F, Sanyo) with a set-point at 60 °C. In sintering experiments, film temperatures were monitored with a non-contact thermometer (Fisher Scientific).

Atomic force microscopy (NTEGRA, NT-MDT, Moscow) was performed in intermittent contact mode with silicon cantilevers (NSG01, NT-MDT, spring constant in the range between 1 and 15 N/m) to obtain images of dry latex film surfaces. For each sample, four separate 5 μm x 5 μm areas were scanned. The peak-to-valley height, h , was measured from randomly-chosen, neighbouring particles from each area to obtain approximately 30 measurements in total. The mean value was found for the as-cast film surface, h_0 , and after heating continuously under the lamp or in the oven for a time, t .

Results and Discussion

We start by comparing films made from wet latex after processing by two methods. After film formation in the convection oven at 60 °C, the film surface was irregular, with remnants of cracks, and the film was not fully transparent because of surface roughness and wrinkling. In contrast, a film heated under NIR is smoother and transparent (Figure 1). The likely explanation is that the particles were softened in the aqueous phase under NIR radiation, such that their deformation reduced capillary stresses³⁰ and prevented cracking.^{3,31} This concept will be expanded upon later in this Letter. With 1

wt.% PEDOT:PSS, film quality is also good, but there is a bluish tint. Because of the relatively high T_g of the polymer, the films are hard at room temperature. The NIR-irradiated acrylate films had a pencil hardness value (according to ISO 15184) of 8/9H, which means that they resist scratching by the hardest material on the scale.

Figure 1. Photographs of 20 μm thick films formed from the acrylate latex under various conditions: (a) NIR radiation; (b) in a convection oven at 60 $^{\circ}\text{C}$; (c) with 1 wt.% PEDOT:PSS under NIR radiation. Films were placed over printed paper to provide a qualitative indication of transparency.

In the oven at 60 $^{\circ}\text{C}$, it takes approximately 10 min. for a dried 20 μm acrylic film to reach a temperature of 48 $^{\circ}\text{C}$ (*i.e.* 10 $^{\circ}\text{C}$ above T_g). By comparison, the latex with 1 wt.% PEDOT:PSS under NIR radiation reaches this temperature within approximately two min. and reaches 75 $^{\circ}\text{C}$ within 5 min. This result is explained by the fact that with conductive heating in an oven, heat diffuses from the film surface, which defines the time dependence of the temperature. On the other hand, in a radiative heating process, energy is deposited directly into the film (varying with depth according to the Lambert-Beer Law³²).

Figure 2 shows a series of AFM topographic images obtained from latex films. Initially, the particles are spherical, and interparticle voids are seen between them. After just four minutes of NIR radiation, the voids have decreased in size and the particles have flattened. After 30 min., the particle identity is

less clear. A similar development is found for the latex containing PEDOT:PSS, but the effects are more pronounced; in the oven at 60 °C, less particle flattening is found (see Supporting Information, Figure S3.)

AFM topographical profiles were obtained for the standard acrylic latex in the as-cast state and after NIR radiation; examples are shown in Figure 3A and Supporting Information, Figure S4. Values of $h(t)$ are obtained from such profiles to enable a quantitative analysis of particle flattening. Measurements of $h(t)$ from a series of NIR radiation experiments are summarized in Figure 3B. Data obtained in the 60 °C oven are shown for comparison.

During the first 10 min. for samples in the oven, there was no significant decrease in $h(t)$ (Supporting Information, Figure S5). This result is explained by the slow rate at which films are heated in the oven. Particle deformation on realistic time scales does not occur until a temperature at least 10 °C above T_g .^{31,33} Therefore at shorter times, the temperature was not above the polymer T_g , and hence there was no significant sintering. Consequently, the data from the oven samples in Figure 3B have been shifted so that 10 min. corresponds to $t = 0$.

Figure 2. (a) AFM height images of an acrylate latex film after deposition at room temperature; (b) after 4 min. of irradiation from the NIR lamp; and (c) after 30 min. Image sizes are 5 μm x 5 μm; the vertical scales are as shown for each image.

Figure 3. (a) Topographic profiles corresponding to selected particles in AFM height images of an acrylic latex film after deposition at room temperature (solid line), after 4 min. of irradiation from the NIR lamp (dotted line) and after 30 min. (dashed-dotted line). (b) The dependence of the peak-to-valley height, h , on the time of continuous exposure to NIR radiation for the acrylic latex (filled circles) and acrylic latex with 1 wt.% PEDOT:PSS (open circles) and time in an oven at 60 °C (filled squares). The solid lines are the best-fit to the data using Eq. 2 with $\gamma = 0.041 \text{ J/m}^2$. Error bars are shown, but most span the size of the symbols and are not visible.

Perez and Lang²⁷ considered the flattening of a dry latex film made from particles with a radius of a . The polymer is described as having a viscosity η that varies with time, and flattening is driven by the

particle/air surface energy, γ . They derived an equation to describe how the particle peak-to-valley height, h , varies as a function of time:

$$\frac{1}{h^3(t)} = \frac{1}{h_0^3} + \frac{24\gamma}{a^4} \int_0^t \frac{ds}{\eta(s)}. \quad (1)$$

At a constant temperature, η will not vary over time for a thermoplastic, so that:

$$\frac{1}{h^3(t)} = \frac{1}{h_0^3} + \frac{24\gamma}{a^4\eta}. \quad (2)$$

The predictions of Equation 2 are compared to the experimental data in Figure 3B. In this analysis, γ was taken to be 0.041 J/m² (as reported for an acrylate³⁴), and η was varied to obtain the best fit to the data (neglecting the temperature variation). In the 60 °C oven, η was found to be 7.1×10⁷ Pa-s, whereas it was 2.7×10⁵ Pa-s for the PEDOT:PSS latex under NIR radiation.

The temperature-dependence of the polymer viscosity can be described by the Vogel-Fulcher equation:

$$\eta = \eta_{\infty} \exp\left(\frac{B}{T - T_0}\right), \quad (3)$$

where B and the pre-factor η_{∞} are constants for a material. T_0 is typically 50 K less than T_g ,³⁵ and hence is taken to be 261 K here. Noting that the average temperature of the PEDOT:PSS film under NIR radiation was *ca.* 390 K, and using the fitted viscosity values, the Vogel-Fulcher parameters are estimated to be $B = 773$ K and $\eta_{\infty} = 600$ Pa-s. The best-fit viscosity for the acrylate latex under IR radiation is 1.4×10⁶ Pa-s, which corresponds to an average temperature of *ca.* 360 K. This is a reasonable value, according to independent measurements, and it gives some credibility to the assumptions behind our analysis.

It is reasonable to expect that during the film formation of a wet latex, the viscosity of the polymer particles will be lower when under IR radiation than when in a 60 °C oven. According to film formation models,^{28,A} a lower viscosity will favor the deformation of particles while in the wet state (*i.e.* wet

sintering). Moreover, for a wet film of thickness, H , the value of the capillary pressure that is necessary for cracking, p_{cap}^{crack} , is predicted³¹ to be:

$$-\frac{Hp_{cap}^{crack}}{\gamma} \cong 2.06 \left(\frac{\bar{G}H}{\gamma} \right)^{2/5} + \frac{2.91}{\tau}, \quad (4)$$

where $\bar{G}$ is an effective shear modulus for the packed particles with Hertzian contacts, and τ is a relaxation time that is proportional to η . Russel *et al.*³¹ have explained that decreasing the polymer viscosity will suppress cracking in a latex film by increasing the p_{cap}^{crack} required to recover sufficient elastic energy when the crack is propagating. In the 60 °C oven, the polymer's viscosity is lower, especially during the heating up period. Hence, the films crack during film formation. These cracks subsequently heal by viscous flow of the dry polymer, but surface roughness and irregularities are remnants. The lower η obtained under NIR avoids cracking during film formation.

In summary, a new processing method has been reported to resolve the film formation dilemma. NIR radiation has been employed to achieve the film formation of a high- T_g latex to make a crack-free hard coating.³⁶ IR-assisted latex film formation offers key advantages. NIR radiation heats the polymer phase directly, along with the water, softening the particles and reducing capillary stresses, and ultimately leading to good film quality. The rate of particle sintering is significantly greater than in an oven at 60 °C. No plasticizers are required, and no VOCs are released in the process.

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Supporting Information Available. IR absorption spectra of acrylate latex and latex with 1 wt.% PEDOT:PSS; emission spectra from NIR lamp; AFM images of acrylate latex with PEDOT:PSS under

NIR radiation and acrylate latex after being in an oven; topographic profiles of these images; $h(t)$ for an acrylate latex in an oven at 60 °C.

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