Contact of Polymer Latex Particles with Metals

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Polymer latex has been widely used in decorative paints and adhesives. It is now beginning to find applications in steel protection where coalescence to form an impermeable coating is a prime requirement. The mechanism by which latex particles coalesce into a coherent and adhering coating is described. Electron microscope observations demonstrate that latex spheres deform elastically as coalescence occurs, this elastic deformation being driven by interfacial attractive forces. Direct measurement of the deformation allows the calculation of the interfacial energy both for the polymer-polymer interaction and for the metal—polymer interface.

KEY WORDS Coalescence mechanism; electron microscope study; interfacial energy; latex–latex contact; latex–metal contact; latex particles.

1 INTRODUCTION

The ability of polymer latex to solidify on drying, thus forming a protective adherent coating, was noted by the early South American natives who used natural rubber latex to waterproof cloth.[1] Modern latex technology is based on this same process but now has at its disposal a wide range of synthetic polymer materials, far superior in properties to natural rubber, together with fine control over the physical form of the polymer to enhance film-forming.

Synthetic latex is grown by emulsion polymerisation[2] to produce spheres of polymer, sometimes of remarkably uniform diameter in
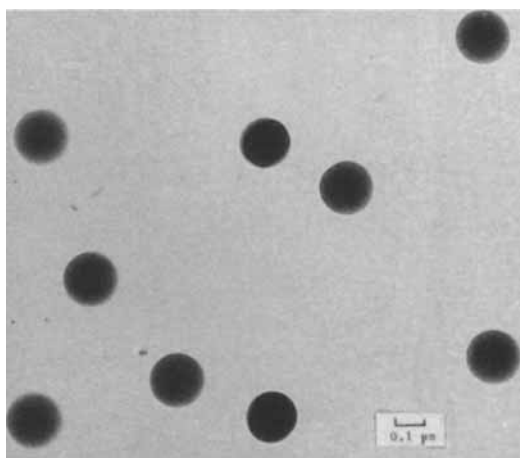
FIGURE 1   Transmission electron micrograph of vinyl chloride-vinylidene chloride copolymer latex particles.

the 0.1 to 1 μm range, suspended in water (Figure 1). The most popular materials for decorative coatings have been based on poly(vinyl acetate) which is manufactured on a 1 million tons per annum scale worldwide.[3]

A recent advance in latex technology has been the development of latex coatings for corrosion protection of steel.[4-6] In this application, the chemical properties of the polymer are important through their influence on the corrosion process, for example by reducing water and oxygen permeability. However, the physical structure of the coating brought about by the coalescence of the polymer particles is also vital. In addition, the contact of the particles with the metal surface determines the interface bond.

This paper addresses two key problems of latex coatings on metals. Consider the latex particles freely dispersed in the film of material applied to the metal (Figure 2):

1) How do these polymer particles cohere to form a solid impermeable coating?

2) How do they adhere to the metal substrate?

These questions have been studied by direct observation of latex spheres using the transmission electron microscope.
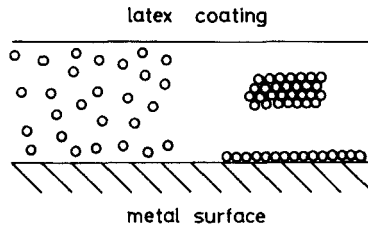
latex coating

metal surface

FIGURE 2 Schematic showing the coalescence of latex particles during drying of a coating on a metal surface.

2 THE COALESCENCE PROBLEM

The mechanism of latex coalescence has been ill understood until recently. Formerly[7,8] it had been thought that latex particles behaved as fluid droplets which coalesced according to Frenkel's well-known theory,[9] in which the process of fusion was driven by the surface energy of the particles and resisted by the viscosity of the polymer. According to that argument, the diameter of the contact between two latex spheres would increase with time as shown by the broken line in Figure 3.

Experiment shows, as Brown[10] first suggested, that such viscous flow does not occur with rubber latex particles. Instead, the contact diameter rises quickly and then maintains an approximately constant value with time[11] (Figure 3). Such a result is consistent with elastic deformation of the particles. This fits with the known properties of dried latex polymers. A dried rod of latex is a solid, elastic substance, not a viscous fluid.

The theory of elastic contact between spheres has been developed by Johnson, Kendall and Roberts[12] (JKR theory) to describe the diameter d of the contact region between two spheres of diameters D_1 and D_2. Young modulus E_1 and E_2, and Poisson ratio v_1 and v_2, with a contact energy Γ, and an applied load W. Contact energy is defined as the surface energy released in forming unit area of contact.

$$d^3 = \frac{3D}{E}(W + \tfrac{3}{2}\pi\Gamma D + (3\pi\Gamma DW + (\tfrac{3}{2}\pi\Gamma D)^2)^{1/2}) \qquad (1)$$
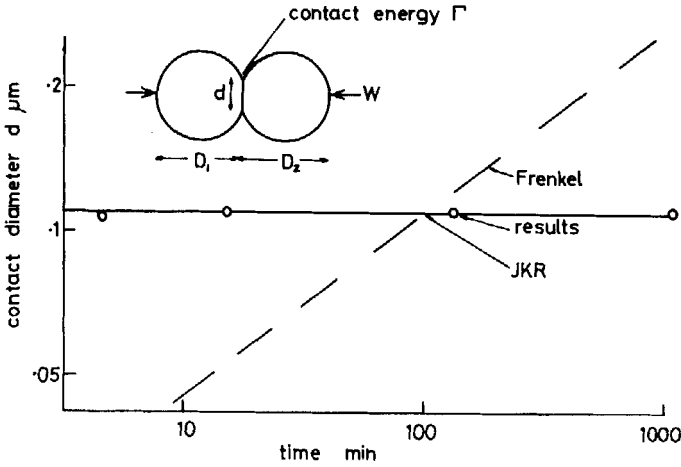
FIGURE 3   Measured contact diameter between latex spheres as a function of time gave a better fit to the JKR than the Frenkel theory.

where

$$\frac{1}{E} = \frac{1 - v_1^2}{E_1} + \frac{1 - v_2^2}{E_2} \quad \text{and} \quad \frac{1}{D} = \frac{1}{D_1} + \frac{1}{D_2}$$

with the geometry shown in Figure 3.

This equation reverts to the famous Hertz equation[13] of elastic contact when there is no surface force, at $\Gamma = 0$.

$$d^3 = \frac{3DW}{E} \tag{2}$$

More relevant here is the situation which arises when the external load W is zero, so that the spheres are drawn together only by surface attractions. In this case the contact diameter is

$$d^3 = \frac{9\pi\Gamma D^2}{E} \tag{3}$$

This is the equation which has been used to calculate the interfacial energy from measurements of contact diameter made in the electron microscope.

These equations apply to purely elastic spheres and so are applicable to high molecular weight polymers, away from the glass transition temperature. In practice, many latex materials only partly satisfy these conditions and are viscoelastic. Unfortunately, no theory has yet been established to cover the viscoelastic problem.

3 LATEX-LATEX CONTACT

The contact energy of latex particles to each other was measured by spraying a fine mist of diluted latex (Haloflex, ICI) onto carbon-coated grids, and inspecting pairs of particles in the transmission electron microscope. One such pair is shown in Figure 4. From the micrographs, the diameter d of the contact region between the spheres and the diameters D_1 and D_2 of the particles were measured, allowing the calculation of the contact energy from Eq. (3). Young's modulus E was 5.64 MPa determined by tensile testing a coalesced film of latex and Poisson's ratio was assumed to be 0.5. Typical results are given in Table I.

In order to investigate the validity of Eq. (3), a series of latex contacts was studied in the electron microscope and the measurements plotted in Figure 5 for a range of particle sizes. The results
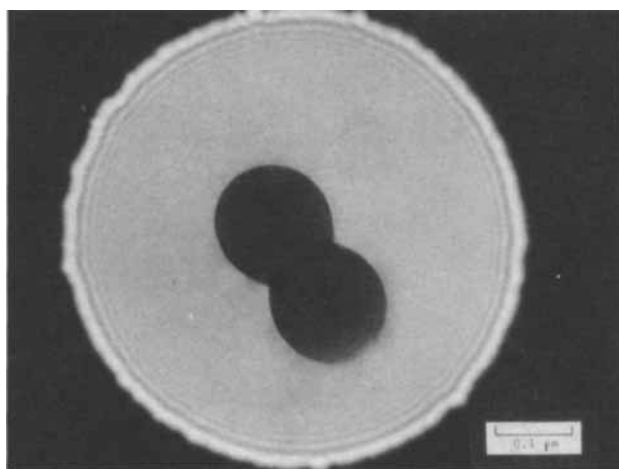

FIGURE 4   Electron micrograph of two latex particles in contact.

TABLE I
Determination of contact energy for Latex-Latex
adhesion

Sphere diameter D_1 μm	Sphere diameter D_2 μm	Contact diameter d μm	Contact energy mJm^{-2}
0.162	0.160	0.105	23.5
0.163	0.150	0.105	25.1
0.162	0.160	0.105	23.5
0.160	0.170	0.105	22.5
0.170	0.150	0.110	27.5
			Mean 24.4 ± 1.7

were in fair agreement with Eq. (3) which was plotted as a solid line, taking $\Gamma = 26.5\,\text{mJm}^{-2}$, to fit a macrocontact experiment in which a cast spherical surface of latex, 152 mm in diameter, was brought into contact with a latex-coated glass slide under zero load, to give a contact diameter of 1.0 mm. Within experimental error, this agreed with the results in Table I. It is interesting that the evidence supports the JKR theory, illustrating the 2/3 power law relating contact diameter to sphere size. In contrast, the Frenkel theory does not predict such a relationship.
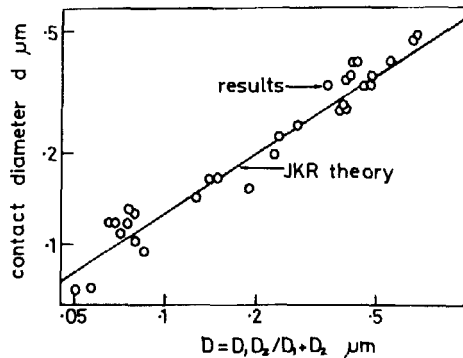

FIGURE 5 Contact diameters for various latex sizes gave a reasonable fit to the JKR theory.

4 LATEX-METAL CONTACT

To study the contact between latex spheres and metal surfaces, a different method was used to prepare samples for electron microscopy. Finely powdered metal was employed in the form of spheres, some $5\,\mu m$ in diameter. Grids were dipped into the dry metal powder and were then found to have metal particles adhering to the grid bars. These spherical particles were sprayed with highly diluted latex and on inspection in the microscope were seen to be covered with latex spheres. It was necessary to rotate the samples within the microscope to bring the contact region between metal and polymer into the correct plane for observation. The contact diameter was then photographed and measured as before. Figure 6 shows three such contacts between metal and latex spheres.

The latex was an acrylate-modified vinyl chloride-vinylidene chloride copolymer used at pH 2 to prevent dehydrochlorination and flash rusting. Slight surface darkening of mild steel under these acid conditions has been shown to result from formation of a protective surface film.[15] Three metals were studied; copper, aluminium/lithium (from Dr W. Clyne) and nickel/chromium (BSA). The compositions of the materials and the measured values of contact energy are given in Table II.

These results were somewhat surprising. In the first place it was expected that the metal oxide surface would exhibit a high surface energy and would thus exert a substantial attractive force on the polymer spheres. However, the results show that the polymer latex particles attract each other better than they do a metal surface by a factor around two. There was no significant difference in adhesion for the three metals, presumably because each metal is covered by an adsorbed film of organic material which reduces its surface energy to a low and nearly constant value. This result is consistent with that of Roberts[14] who studied macroscopic contacts between rubber spheres and glass plates. He found that the contact energy between two isoprene rubber spheres (cross-linked with 2% dicumyl peroxide) was $63 \pm 2\,mJm^{-2}$ whereas that between a rubber sphere and a glass plate was $41 \pm 1\,mJm^{-2}$. This effect has not been satisfactorily explained.

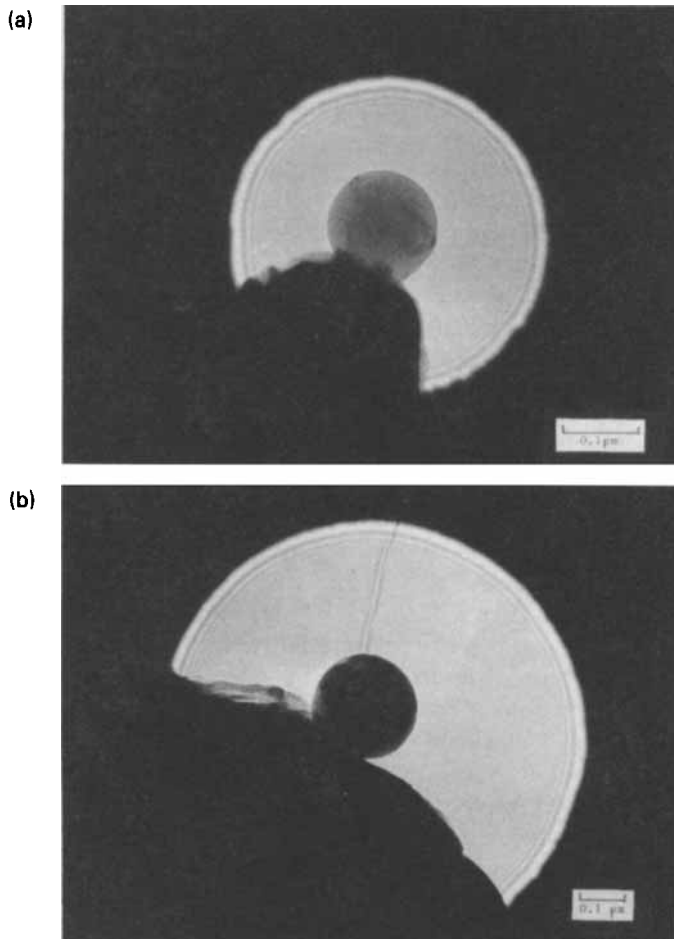In forming latex coatings, it is imperative that the contact energy

(a)

(b)

FIGURE 6 Contact of latex particles with a) copper, b) aluminium/lithium, c) nickel/chromium.

to the metal surface be maximised. It may be seen that the coalescence required at a smooth metal is larger than that in a close-packed latex because of the cubic packing imposed by the surface (Figure 7). Gaps will be left at the interface unless the contact energy is high, particularly if the surface has roughness which further inhibits contact. In addition, strong latex–metal
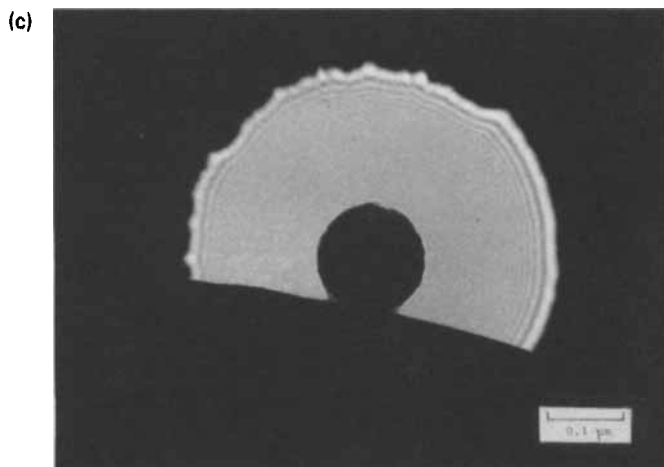
(c)

FIGURE 6 *(contd.)*

TABLE II
Contact energy for Metal-Latex adhesion

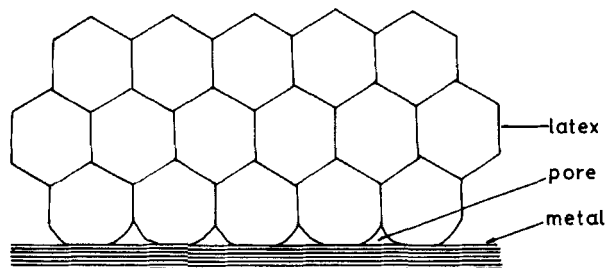| Alloy	Composition	Contact energy mJm^{-2}
copper	Cu, 99%	16 ± 2
nickel–chromium	Ni, 71%; Cr, 17%; Si, 4%; Fe, 4%; B, 3%; C, 1%.	11 ± 2
aluminium–lithium	Al, 97%; Li, 3%.	12 ± 2

FIGURE 7   Pore formation at the metal/latex interface at low contact energy.

adhesion is desirable in the event of mechanical damage to the coating, when it is helpful if failure occurs within the polymer, leaving some residual film of protective latex particles on the metal.

5 CONCLUSIONS

Polymer latex particles coalesce by an elastic deformation mechanism, pulled together by the surface energy of the latex spheres. Electron microscope observations allow this contact energy to be measured. The latex spheres are also attracted towards metal surfaces and the latex-metal contact energies have been measured. Surprisingly, these are lower than expected. For protective surface coatings, it is desired that the latex-metal contact energy be as high as possible.

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