# Coalescence of Viscoelastic Latex Particles

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ABSTRACT: Previous hypotheses for the mechanism of film formation of latexes are extended to include particles composed of general linear viscoelastic materials. The use of integral operator constitutive relations permits calculation of the distance of approach of two particles as a function of time for arbitrary contact pressures. The time required for sintering of a polystyrene latex near the glass transition temperature is calculated and compared with the experimental value obtained by thermal analytical methods.

## I. Introduction

The use of polymer latexes in such applications as paints, paper coatings, or textile sizings and the production of thin-walled articles by a coagulant dipping process requires that the latex form a continuous film on drying. Therefore, an understanding of the mechanism and forces involved in the coalescence of latex particles is not only desirable, but also has obvious practical importance.

Bradford[1,2] and coworkers proposed that the sintering of latex particles occurs as a result of the viscous flow of polymer, according to a well-known equation of Frenkel.[3] The shearing stress necessary for particle coalescence is provided by the polymer surface tension.

Brown[4] suggested that water evaporation from the capillaries in a partially dried latex provides the driving force for coalescence. As a first approximation he considered the deformation of two purely elastic spheres and assumed that the shear modulus of the material relaxes with time while the deformation remains constant. Brown then proposed that the minimum temperature for film formation is that temperature at which the shear modulus relaxes to some specified value during the time available for complete evaporation of the water.

Brodnyan and Konen[5] attempted to test Brown's hypotheses by determining the minimum film formation temperatures of several polymers and comparing these values with the temperature dependence of the dynamic shear modulus at an arbitrary frequency of 0.055 cps. They found that Brown's theory was a good first approximation but it could not account for the influence that the chemical nature of polymers have on the film-forming temperatures. Furthermore, it is well known that in many cases latex particles continue to coalesce even after all the water has been removed and the rate of this coalescence depends on the temperature.

In this article, the theory of latex particle coalescence is extended to include directly the viscoelastic character of the polymer. The approach taken employs the well-known solution of the contact problem in the linear theory of viscoelasticity.[6–8] It is found that the time dependence of an auxiliary response function, or approximately the shear creep function, following a stepwise application of the stress determines the rate of coalescence. By this direct approach the time required for complete film formation can be calculated once the rheological properties of the polymer are known and the capillary forces which cause coalescence have been specified.

As mentioned above, Brown[4] chose the time and temperature dependence of the shear relaxation function $G(t)$ rather than its Stieltjes inverse, the creep function $J(t)$, as the characteristic property of the polymer which determines the rate of coalescence. From the Boltzmann superposition principle, it can be shown[9] that $J(t)G(t) \leq 1$ for all values of $t$, so that each drop in $G(t)$ always occurs at a shorter time than the corresponding rise in $J(t)$. Thus, one would expect Brown's approach to provide a lower limit for the time required for coalescence to occur, and the degree of approximation should depend on the rate of change of $G(t)$ with time.

Voyutskii[10] has pointed that other factors, such as autohesion and the nature of the surfactant, should also be taken into consideration in a complete study of the mechanism of film formation. Since these have been neglected, the present paper remains as an approximation which is valid only when the contributions from these factors are known to be small.

## II. Theory

Consider as an analog of latex particle coalescence two spherical particles of radius $R$ in contact. It is assumed that the particles are composed of the same isotropic linearly viscoelastic material with constitutive equations of the form[9]

$$s_{ij} = G\cdot \mathrm{d}e_{ij} \tag{1}$$

$$\sigma_{ii} = K\cdot \mathrm{d}\epsilon_{ii} \tag{2}$$

where $G(t)$ is the shear relaxation function relating the deviatoric stress tensor $s_{ij}$ to the deviatoric strain tensor $e_{ij}$ and $K(t)$ is the dilatational relaxation function relating the stress and strain invariants $\sigma_{ii}$ and $\epsilon_{ii}$. The

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(1) R. E. Dillon, L. A. Matheson, and E. B. Bradford, *J. Colloid Sci.*, **6**, 108 (1951).

(2) W. A. Henson, D. A. Taber, and E. B. Bradford, *Ind. Eng. Chem.*, **45**, 735 (1953).

(3) J. Frenkel, *J. Phys. USSR*, **9**, 385 (1945).

(4) G. L. Brown, *J. Polym. Sci.*, **22**, 423 (1956).

(5) J. G. Brodnyan and T. Konen, *J. Appl. Polym. Sci.*, **8**, 687 (1964).

(6) J. R. M. Radok, *Quart. Appl. Math.*, **15**, 198 (1957).

(7) E. H. Lee and J. R. M. Radok, *J. Appl. Mech.*, **27**, 438 (1960).

(8) W. H. Yang, *ibid.*, **33**, 395 (1966).

(9) J. D. Ferry, "Viscoelastic Properties of Polymers," Wiley, New York, N. Y., 1961.

(10) S. S. Voyutskii, *J. Polym. Sci.*, **32**, 528 (1958).

restriction that the particles be identical is chosen only to illustrate the method and is easily removed. The notation for Stieltjes convolutions, introduced by Gurtin and Sternberg,[11] is used in eq 1 and 2. Thus, if $\Phi$ and $\Psi$ are functions of position and time, $\Phi \cdot \mathrm{d}\Psi$ stands for the function defined by the Riemann–Stieltjes integral

$$\Phi \cdot \mathrm{d}\Psi = \int_{\tau = -\infty}^{\tau = t} \Phi(t - \tau)\mathrm{d}\Psi(\tau) \qquad (3)$$

provided the integral is meaningful. Also, $\Phi$ is said to have Stieltjes inverse $\Phi^{-1}$ if

$$\Phi \cdot \mathrm{d}\Phi^{-1} = H(t) \qquad (4)$$

where $H(t)$ stands for the Heaviside unit step function·

If the contact region is comparatively much smaller than the dimensions of the spheres, it can be assumed that the displacement field set up in each sphere is the same as that set up in a half-space with the appropriate boundary and initial conditions. Thus, if $a(t)$ denotes the radius of the circle of contact, then the total thrust $W(t)$ acting over the contact region is given by the expression[12]

$$W(t) = \left(\frac{4}{3R}\right)[k^{-1} \cdot \mathrm{d}(a^3)] \qquad (5)$$

which may be inverted to give

$$a^3(t) = \left(\frac{3R}{4}\right)[k \cdot \mathrm{d}W] \qquad (6)$$

where $k$ is the auxiliary response function defined by the integral equation

$$k(t) = (3K + 4G) \cdot \mathrm{d}(2G + 6K)^{-1} \cdot \mathrm{d}(2G)^{-1} \qquad (7)$$

Equation 5 reduces to the result obtained by Brown[4] if the radius of contact is assumed to vary with time according to the expression

$$a^3(t) = a_0{}^3H(t) \qquad (8)$$

where $a_0$ is a constant.

From geometrical considerations, the total distance of approach of the two spheres, $\alpha(t)$, from the state of point contact is related to the radius of the contact circle $a(t)$ by the expression

$$\alpha(t) = \frac{2a^2(t)}{R} \qquad (9)$$

If the viscoelastic material has similar behavior in shear and dilatation, then the Poisson's ratio for the material is a constant. For spheres composed of an incompressible viscoelastic solid, $K = \infty$ and

$$k(t) = (4G)^{-1} \qquad (10)$$

The shear creep and relaxation functions for an arbitrary viscoelastic material can be deduced from spring-dashpot model representations or they may be obtained directly by measurements.[9] In principle then, one can determine the total distance of approach of the spheres as a function of time if the total thrust is specified.

Vanderhoff[13] and coworkers considered in detail the interfacial forces involved in latex particle coalescence. They found that the pressure forcing the spheres together as a result of the polymer water interfacial tension depends on the radii of curvature involved in coalescence and remains quite small until the contact area reaches some critical value. After the critical area has been reached, the contact pressure increases suddenly to some constant value. Therefore, it appears that the interfacial forces which cause latex particle coalescence can be approximated with the use of the Heaviside unit step function.

In general, the rate of particle coalescence for an arbitrary viscoelastic material can only be obtained by numerical methods. However, analytic solutions can be obtained for certain simplified models which serve to illustrate the important features of the method. As an example, consider the coalescence of two incompressible viscoelastic spheres whose relaxation modulus can be expressed by an equation of the form

$$G(t) = E(t/b)^{-m} \qquad (11)$$

where $b$ is a suitable unit of time, say 1 min, and $E$ and $m$ are experimentally determined constants; $m$ may be of the order of 0.5. This expression provides a good approximation for a number of materials over a limited range of values of time.

From eq 10, the auxiliary response function is found to be

$$k(t) = (1/4)J(t) = (\sin m\pi/4Em\pi)(t/b)^m \qquad (12)$$

It is assumed that the total pressure forcing the spheres together has the form of a step function so that the total thrust is given by

$$W(t) = \pi a^2(t)P_0H(t) \qquad (13)$$

where $P_0$ is a constant and $\pi a^2(t)$ is the total contact area at time $t$. If this expression is substituted into eq 6, it is found that the total distance of approach of the two spheres must satisfy the equation

$$a^3 = (3\pi P_0R/16)(\sin m\pi/E\pi)\int_0^t [a(\tau)]^2(t - \tau)^{m-1}\mathrm{d}\tau \qquad (14)$$

where $R$ is the radius of both spheres. This integral equation can be solved to yield

$$a(t) = (P_0R \sin m\pi/8E)[\Gamma(m)\Gamma(2m)/\Gamma(3m)]t^m \qquad (15)$$

for the time dependence of the contact radius, where $\Gamma(m)$ denotes the gamma function. If one follows Brown[4] and assumes that film formation is complete when $a(t) = 0.308R$, then eq 15 can be used to calculate the time required for film formation.

The procedure used above to derive eq 15 can also be followed for a pressure which is applied at time $t = 0$ and is suddenly removed at some later time $t = \tau$. Such time dependence would be required, for example, to describe the air drying of partially coalesced latex

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(11) M. E. Gurtin and E. Sternberg, *Arch. Rat. Mech. Anal.*, **11** (4), 291 (1962).

(12) G. A. C. Graham, *Int. J. Eng. Sci.*, **3**, 27 (1965).

(13) J. W. Vanderhoff, H. L. Tarkowski, M. C. Jenkins, and E. B. Bradford, *J. Macromol. Chem.*, **1**, 361 (1966).

films. The total thrust in eq 13 should then be replaced with the expression

$$W(t) = \pi a^2(t)P_0[H(t) - H(t - \tau)] \qquad (16)$$

where $\tau$ denotes the drying time and $P_0$ denotes the tensile strength of water.[13] Materials which exhibit instantaneous elasticity and long-term viscous flow will recover partially under these conditions, whereas materials which do not exhibit long-term flow will recover completely.[8] However, if any mutual interdiffusion of free polymer chains across the contact area occurs, this would tend to knit the particles together[10] and would inhibit recovery to some extent.

## III. Experimental Section

There is very little information in the literature which can be used to test critically the above theory. The reason for this is that in the past, experimentalists have usually determined only the minimum conditions under which a particular latex will form a continuous film on drying, but they have neither characterized the viscoelastic nature of the polymer in sufficient detail nor have they specified the total time during which coalescence actually occurs under these so-called minimum conditions.

Recently, Mahr[14] developed a technique for following the coalescence of latex particles with time and temperature by differential thermal analytical methods. This technique can be used to study both sintering of freeze-dried latexes and coalescence in the presence of water.[15] At the present time, however, the only data available for an amorphous polymer are on the sintering of a series of well-defined Dow polystyrene latexes.

It is found, using Mahr's calorimetric compensation method[14] (ccm), that as the sample and reference are heated at a slow rate, there is no discernible exotherm until some characteristic temperature is reached which is somewhat greater than the glass transition temperature of the polymer. The differential temperature slowly rises and reaches a plateau as the latex coalesces and then it quickly drops after coalescence is complete. If a very slow heating rate and the highest sensitivity are used, it is found that the entire process can take place within a 1-deg change in temperature. This method thus provides an estimate of the time required for coalescence near the characteristic temperature. At lower temperatures the rate of coalescence is too slow to be measured by the ccm, and sufficient data are not available in the literature using other methods.

In order to separate sintering of latex particles from effects due to evaporation of the dispersion medium, Mahr[14] exhaustively dialyzed and then freeze-dried the latexes. He found that coalescence proceeds even in the absence of water and the rate of coalescence strongly depends on the temperature. The capillary forces which come into play in this case are then due to the polymer–air interfacial tensions as described by Vanderhoff.[13] For the well-defined Dow polystyrene latexes studied, it is found that the characteristic temperature for coalescence is 102° and at this temperature coalescence is complete within 1.2 min. The glass transition temperature of polystyrene is approximately 96°.

The dynamic mechanical properties of polystyrene covering the temperature range from glassy consistency to rubbery flow is known.[16] To a very good approximation over a moderate interval of time, log $G(t)$ is a linear function of log $t$. Then

$$G(t) = E(t/b)^{-m} \qquad (17)$$

where $b$ is chosen to have the value $b = 1$ min. At a temperature of 102° $E = 7 \times 10^6$ dyn/cm$^2$ and $m = 0.5$. Since the temperature region of interest is in the transition zone, these results are independent of molecular weight.

To predict the rate of coalescence using the theory, a value must be chosen for the radius of curvature $r$, in the pulleylike interfacial region between two polystyrene latex particles. From electron micrographs, this value is found to be approximately 250 Å. Since the surface tension $\sigma$ of polystyrene at 102° is approximately 25 dyn/cm, the pressure $P_0$ in eq 13 is calculated, following Vernderhoff,[13] to have the value $P_0 = \sigma/r = 10^7$ dyn/cm$^2$. If these values are substituted into eq 15 it is found that at 102° the time required for film formation to be complete[4] is predicted by the theory to be 0.95 min as compared with the observed value of 1.2 min.

## IV. Summary

It is assumed that latex particles come into contact as the result of collision, after the stabilizing layers have been destroyed, or they are pressed together as the result of water evaporation. The small radii of curvature in the contact region between two particles provide the driving force for coalescence. It is also assumed that the latex particles are composed of a linearly viscoelastic material so that well-known techniques can be employed to treat the contact problem. If one measures the relaxation modulus of the material in shear and selects a functional form for the pressure, then one can use the expressions given above to predict the rate of particle coalescence. In general, this requires numerical methods unless certain simplified models are chosen. An example is given for the sintering of polystyrene latex particles and the value obtained is compared with experimental results.

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(14) T. G. Mahr, *J. Phys. Chem.*, **74**, 2160 (1970).

(15) T. G. Mahr, unpublished results.

(16) H. Fujita and K. Ninomiya, *J. Polym. Sci.*, **24**, 233 (1957)