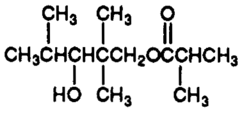
*Macromolecules* **1990,** *23,* 4731–4732 **4731**

# Effect of a Coalescing Aid on Polymer Diffusion in Latex Films[1]

Latex film formation describes the process in which the evaporation of water from a latex dispersion leads to particle coalescence and formation of a continuous film coating.[2] In commercial latex formulations, certain organic liquids (coalescing aids) are often added to promote film formation.[3] Little is known about the mechanism of coalescence enhancement. Few aspects of the process have been studied. Normally the only variables that can be examined involve practical tests of performance (e.g., the "scrub test" for latex paints) or the effect of the additive on the minimum film formation temperature (MFT) of the latex.[4] The MFT is the minimum temperature at which the force of water evaporating from the dispersion can deform the particle into a void-free film. In this sense, the coalescing aid is seen to act only as a fugitive plasticizer, lowering the effective modulus of the latex particles,[5] promoting polymer flow, and eventually evaporating from the film.

From a mechanistic perspective, the important question is whether these additives promote the diffusion of polymer molecules across the particle–particle interface. This diffusion controls the degree of interparticle penetration and the final mechanical properties of the film. Now that techniques are available to study polymer diffusion in such systems,[6–9] it is possible to examine in some detail the role of these additives in promoting film formation. Here we report the first such experiments, focusing on 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (Texanol, Eastman Kodak; 1). This substance was chosen for initial studies because of its low water solubility and its slow rate of evaporation. The first factor simplifies the issue of where the coalescing aid is located in the aqueous dispersion, and the second should enhance the time frame during which it is active in promoting polymer diffusion.



$CH_3CH(CH_3)CH(OH)C(CH_3)_2CH_2OC(=O)CH(CH_3)CH_3$

**1**

Our experiments employ direct nonradiative energy transfer [DET] measurements[9] in conjunction with mixtures of latex particles labeled with phenanthrene and anthracence, respectively, as donor and acceptor dyes. Previous experiments in our laboratory[6,7] employed these techniques to establish that, in two specific systems, annealing latex films above the glass transition temperature led to polymer diffusion and mixing as the polymer interface healed. One of those systems, consisting of 100-nm-diameter poly(butyl methacrylate) (PBMA) aqueous latex particles,[7] is nearly identical with that used here to examine the influence of 1 on polymer diffusion during film formation and film aging.

Texanol, 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (Eastman Kodak), was distilled under vacuum before use. Procedures for preparation and characterization of phenanthrene (Phe) and anthracene (An) labeled PBMA aqueous latex particles were reported previously.[6] In the present experiments, the particles have a diameter of 130 nm for the Phe–PBMA latex and 106 nm for the An–PBMA latex. We determined (gel permeation chromatography, poly(methyl methacrylate) standards) nominal values of $M_w = 6.3 \times 10^5$ for Phe–PBMA and $5.5 \times 10^5$ for An–PBMA, with $M_w/M_n$ values of 2.52 and 3.25, respectively. The label contents are ca. 1 monomer mol %.

A given amount of 1 was added to a mixture containing an equal amount of Phe-labeled and An-labeled PBMA latices (solid content: 37 wt %). The sample was allowed to equilibrate at room temperature for more than 48 h. The samples were then transferred onto a quartz plate at room temperature (22 °C) and allowed to dry (30 min to 1 h). The film coated on the quartz plate was then placed in a quartz tube, sealed under nitrogen with a rubber septum, and tempered at 95 °C (10 min to 24 h). Samples were then removed from the oven for fluorescence measurements and cooled to 22 °C.

Fluorescence decay profiles were measured by the single-photon timing technique.[11] Samples were excited at 296 nm, and emission was detected at 366 nm. Detailed procedures for the experiment and data analysis are reported elsewhere.[6,7] Here, we obtained the volume fraction of mixing at a particular annealing time by analyzing the donor fluorescence decay profile using the following expression:

$$I_D(t) = B_1 \exp\left(-\frac{t}{\tau_D} - C\left(\frac{t}{\tau_D}\right)^{1/2}\right) + B_2 \exp\left(-\frac{t}{\tau_D}\right) \qquad (1)$$

Equation 1 considers the donor decay profile to have two independent contributions: the term $B_2 \exp(-t/\tau_D)$ describes the unquenched donor fluorescence in the "unmixed" domains. The energy transfer term, with the preexponential coefficient $B_1$, describes the consequences of energy transfer on the $I_D(t)$ profile in the domains where polymer diffusion has led to mixing of the constituents of Phe-labeled and An-labeled particles, with the coefficient $C$ giving the effective acceptor concentrations in that region. The volume fraction of mixing ($f_m$) at any particular annealing time can then be calculated by

$$f_m = B_1/(B_1 + B_2) \qquad (2)$$

Figure 1 compares the $f_m$ values for PBMA latex samples containing 0, 3.0, and 6.0 wt % 1 (based on the weight of dried polymers) as a function of annealing time at 95 °C. We see that the coalescing aid has a dramatic effect on the film formation process. For example, at an annealing time of about 30 min, the $f_m$ value is increased from 30% for PBMA latex film alone to 44% with 3.0 wt % additive and 70% with 6.0 wt % 1.

To obtain quantitative information about the polymer diffusion rate, we fitted our data to a spherical diffusion model.[12] If the diffusing substances are initially distributed uniformly through a sphere of radius $R$, the concentration $C(r,t)$ at radius $r$ and time $t$ is given by[13]

$$C(r,t) = \frac{C_0}{2}\left\{\operatorname{erf}\left(\frac{R+r}{2(Dt)^{1/2}}\right) + \operatorname{erf}\left(\frac{R-r}{2(Dt)^{1/2}}\right)\right\} - \frac{C_0}{r}\left(\frac{Dt}{\pi}\right)^{1/2}\left\{\exp\left(-\frac{(R-r)^2}{4Dt}\right) - \exp\left(-\frac{(R+r)^2}{4Dt}\right)\right\} \qquad (3)$$

The fraction of the substance that has not diffused across the boundaries at time $t$ becomes

$$f_s = \frac{3}{4\pi R^3}\int_0^R C(r,t)\, 4\pi r^2\, dr \qquad (4)$$

The $f_m(t)$ values shown in Figure 1 may be related to the fraction of the donor-labeled polymers, which have diffused across the boundary of a sphere in which the donor-labeled polymers are distributed uniformly at $t = 0$. We set the $f_m(t)$ value at a particular diffusion time $t$ to $1 - f_s$ for the spherical model and then use a numerical procedure to fit the best $D$ value that satisfies eq 4. The $D$ values obtained in such a manner are compared in Figure 2 for PBMA latex film containing 0, 3.0, and 6.0 wt % 1.

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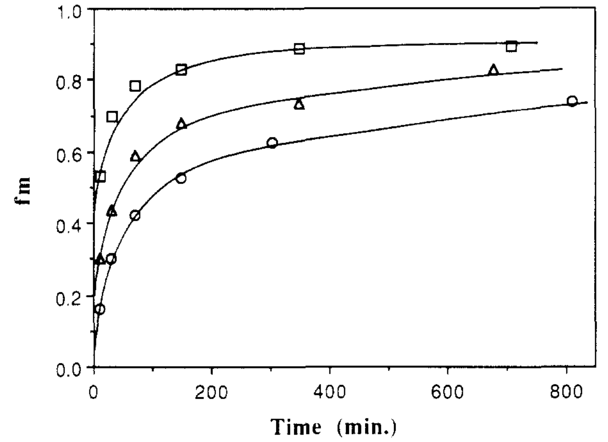

**Figure 1.** Volume fraction of mixing ($f_m$) as a function of annealing time at 95 °C for 100-nm PBMA latex film containing 0 (○), 3.0 (△), and 6.0 (□) wt % 1.

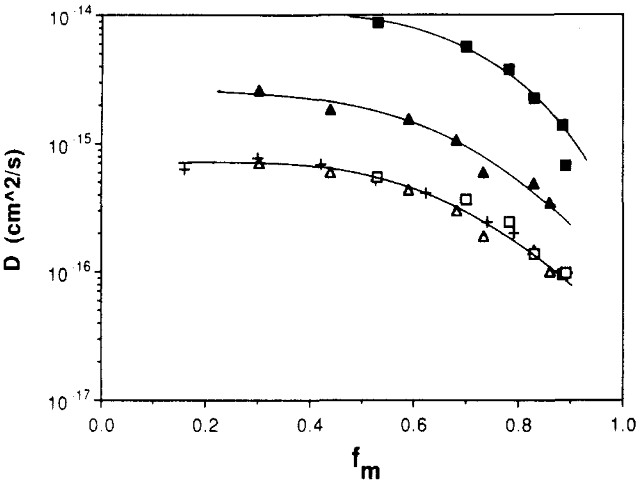

**Figure 2.** Diffusion coefficient $D$ as a function of volume fraction of mixing for the PBMA latex film described in Figure 1: 0 (+), 3.0 (▲), and 6.0 (■) wt % 1. The symbols (△) and (□) represent $D$ values recalculated from eq 6 using shift temperatures of 9.5 and 20 K, respectively.

We see that there is a marked increase in the polymer diffusion rate by addition of a small amount of film-forming additive. One notes in Figure 2 that $D$ decreases with the increase in $f_m$ for all three sets of samples. In the absence of the additive, this decrease can be explained in terms of the molecular weight polydispersity of the latex polymer: the low molecular weight chains dominate the diffusion at short times, with diffusion of high molecular weight chains becoming more prominent at long times.

While 1 might contribute in several ways to the enhancement of polymer diffusion, the most likely mechanism is one in which it acts as a plasticizer to increase the free volume in the film. We can test this idea in the following way: We have shown that the temperature dependence of $D$ values in these films is described by the Williams–Landel–Ferry [WLF] equation[5]

$$\log\left(\frac{DT_0}{D_0T}\right) = \frac{C_1(T-T_0)}{C_2+T-T_0} \tag{5}$$

where $D_0$ is the diffusion coefficient at the reference temperature $T_0$. $C_1$ and $C_2$ are parameters appropriate to PBMA and, for $T$ = 368 K (95 °C), take the values 15.5 and 249 K, respectively.

Assume that adding a small amount of plasticizer of weight fraction $w_1$ increases the free volume by the same amount as an increase in temperature $\Delta T = T' - T_0$. Under these circumstances, the three curves in Figure 2 should be related by shift factor $\Delta T$, which can be evaluated from the expression[16]

$$\log\left(\frac{D(w_1)T_0}{D(T_0+\Delta T)}\right) = \frac{C_1\Delta T}{C_2+\Delta T} \tag{6}$$

In Figure 2 we show that eq 6 is very effective in describing the diffusion enhancement. The open points on the lowermost curve were recalculated from the $D$ values by using the shift temperatures of 9.5 K (3.0 wt % 1) and 20 K (6.0 wt % 1) calculated from eq 6.

From the effectiveness of the analysis we conclude, first, that the major role of 1 in this system is to act as a plasticizer and, second, that no significant evaporation[14] of 1 occurs during our experiments.

**Acknowledgment.** We thank the Institute for Chemical Science and Technology for their support of this research. We are grateful for additional support from NSERC Canada and the Province of Ontario.

## References and Notes

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(16) This model is, of course, more simple than the Fujita–Doolittle model which has been used to describe the diffusion of small molecules in polymer matrices (ref 5, p 492).

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*Received June 1, 1990*
*Revised Manuscript Received August 20, 1990*