

Effect of Sintering on Surface Chemistry and Surface Energy of Pigmented Latex Coatings

H. AL-TURAIIF,* P. LEPOUTRE

Chemical Engineering Department, University of Maine, Orono, Maine 04469

Received 14 April 2000; accepted 25 January 2001

ABSTRACT: Drying in the absence of water (sintering) of pigmented coatings made of styrene–butadiene (SB) latex and kaolin clay at different levels of pigmentation was investigated. As found from X-ray photoelectron spectroscopy, sintered coatings showed a higher SB area percent on the surface than did latex with a high glass-transition temperature (T_g) and dried at room temperature. This was a result of latex spreading at the surface. Sintering the high- T_g coatings that were dried at room temperature caused a decrease in the surface energy. Drying in the presence of water (wet coalescing) was compared to drying in the absence of water (sintering). Even though sintered coatings were more porous and had higher gloss, no significant difference was found in the SB/clay ratio at the surface or in the surface energy above the critical pigment volume concentration (CPVC). However, at and below CPVC, the sintering process yielded a higher SB content at the surface and a lower surface energy than the wet-coalescing process. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 968–975, 2001

Key words: sintering; pigmented coatings; surface chemistry; surface energy

INTRODUCTION

Pigmented coatings are usually applied on paper products to improve optical properties and printability. They are applied as aqueous dispersions of pigment, usually as clay or calcium carbonate, a binder, soluble polymer or latex, and additives. Little is known about the binder–pigment interaction process and the role water plays in the coating consolidation. Watanabe and Lepoutre¹ used quenching and freeze-drying techniques to follow the process of the consolidation of clay–latex systems. They found that for slow drying at room temperature (wet coalescence), the coales-

cence and spreading of latex with the minimum film-formation temperature (MFT) at approximately 0°C occurred while water was still present. On the other hand, LePoutre and Alinec² investigated the effect of coalescence in the absence of water (sintering). Drying a coating below its MFT followed by a sintering process resulted in differences in the structure and an improvement in the final film optical properties. This made the commercial application for sintered coatings important. Figure 1 illustrates the difference between wet-coalesced and sintered coatings.

In their pioneer work, LePoutre and Alinec² showed that a significant increase in light scattering after sintering of the latex particles by thermal treatment resulted in an increase in void size caused by the coalescence of the latex particles in the absence of water. Also, coalescence in the absence of water improved the gloss of the coatings, causing a higher gloss than for the coat-

Correspondence to: H. Al-Turaif.

* Present address: King Abdulaziz University, Chemical Engineering Department, P.O. Box 80204, Jeddah 21589, Saudi Arabia.

Journal of Applied Polymer Science, Vol. 82, 968–975 (2001)
© 2001 John Wiley & Sons, Inc.

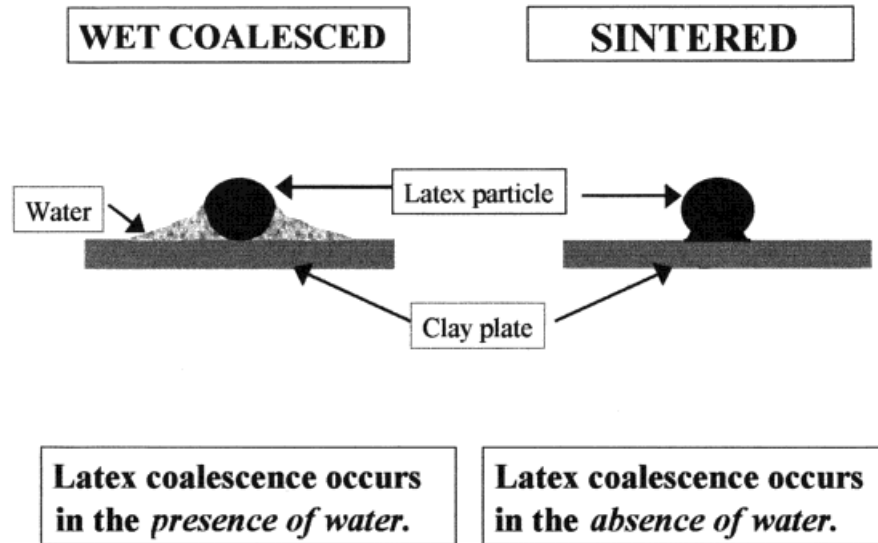


Figure 1 Wet-coalesced and sintered coatings.

ing dried in the presence of water, which shrank considerably during drying.

In our previous work,³ the evolution of surface structure and chemistry and the surface energy of wet-coalesced clay–latex coatings was followed. It was found that latex spreading rather than “binder migration” was responsible for the high styrene–butadiene (SB) area percent at the final stage of consolidation at the surface. In addition, the total surface energy and its polar component decreased with consolidation time.

To explain some of the different properties between the wet-coalesced and sintered coatings, this work was undertaken to compare the surface chemistry and surface energy of both wet-coalesced and sintered coatings.

EXPERIMENTAL

The coatings were based on premier kaolin pigment (ECC International, Sandersville, GA) and SB latex binder (OMONOVA Solutions Inc., Ak-

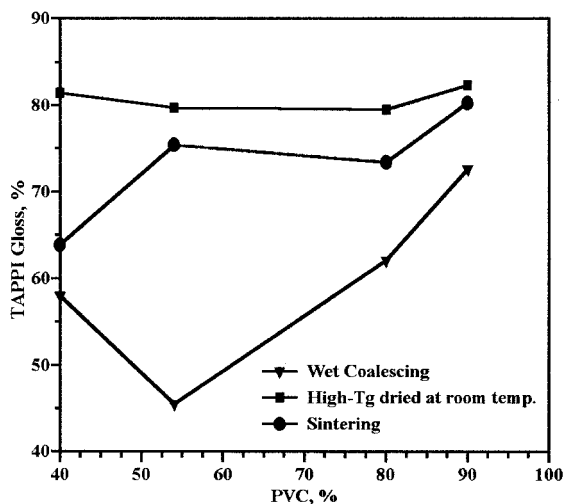


Figure 2 Gloss of wet-coalesced and sintered coatings [pooled standard deviation (*SD*) was on the order of 0.5%].

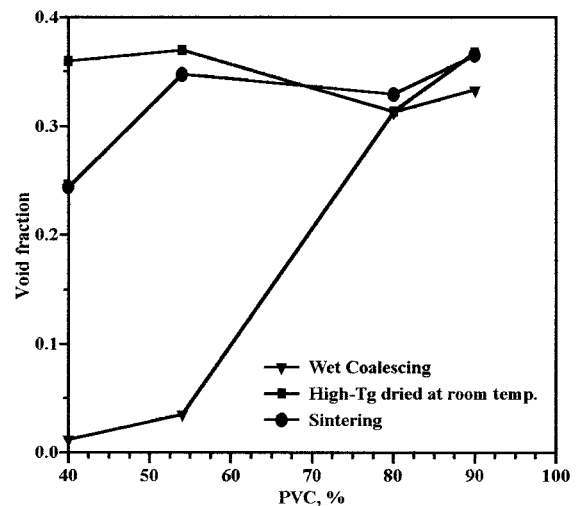


Figure 3 Void fraction for wet-coalesced and sintered coatings (pooled *SD* = 0.01).

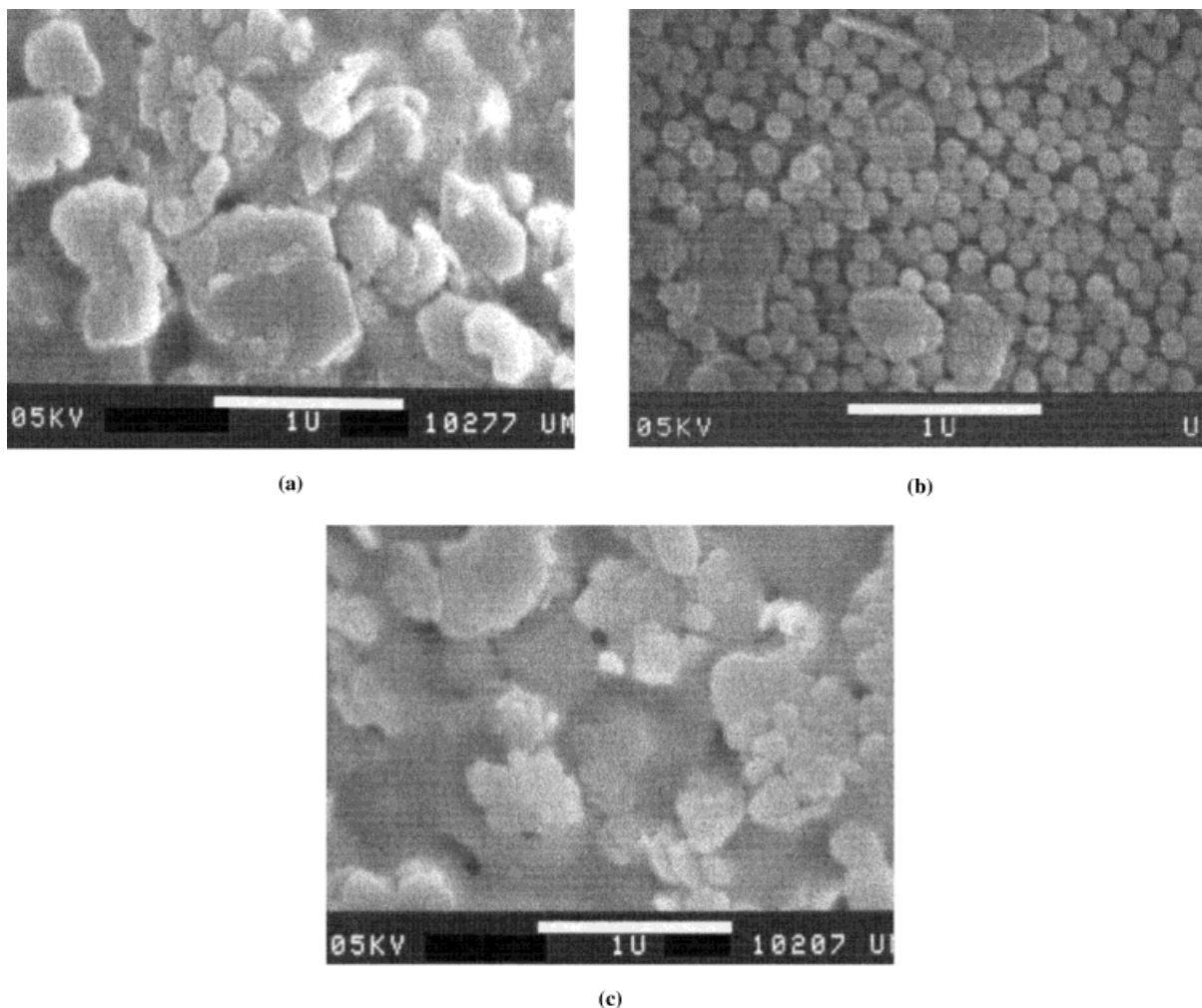


Figure 4 SEM micrographs for (a) wet-coalesced coating, (b) noncoalesced coating, and (c) sintered coating (54% PVC).

ron, OH). Two carboxylated SB latices with low (-3°C) and high glass-transition temperatures (T_g 's; 50°C) were used. The surfactant used for particle growth and stability in these latices was sodium lauryl sulfate, and both latices contained the same amount of acrylic acid for stability. The level of internal polymer crosslinking was the same and high for both latices, due to the presence of a chain-transfer agent.

The kaolin pigment was dispersed in water at 75% solids by weight, with 0.03 parts sodium polyacrylate (Dispex N-40, Allied Colloids, Inc., Suffolk, VA) per hundred parts of pigments. The desired level of pigmentation was prepared by mixing the clay suspension and the latex. To achieve smooth and applicable coatings, the coating color were further diluted to 60% solids by weight. The pH was adjusted to 8.5 with NH_4OH .

The coatings were prepared to cover a wide range of pigmentation levels: above the critical pigment volume concentration [CPVC; 90% and 80% pigment volume concentration (PVC)], at the CPVC (54% PVC), and below the CPVC (40% PVC). The CPVC of our SB-clay system was determined at the region where the gloss reached minimum value. The coating colors were applied with a rod-draw-down coater at a medium speed of 0.67 m/min on a nonabsorbent polyester film. The resulting coat weight was on the order of 40 g/m^2 , and the coatings thickness was on the order of $30\ \mu\text{m}$.

The sintering process was conducted with the high- T_g latex (50°C). At the beginning, the coatings were dried below the latex T_g (at room temperature) and were then heated in the oven at 105°C for 15 min.

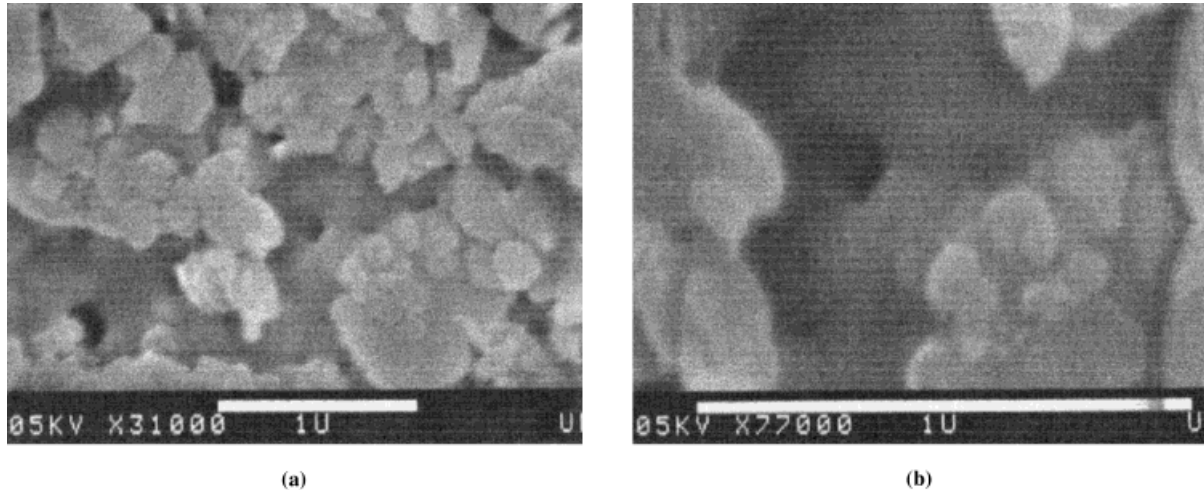


Figure 5 SEM micrographs of small features at sintered coatings.

RESULTS AND DISCUSSION

Effect of Wet Coalescing and Sintering on Gloss

Over pigmentation ranges from 40 to 90% PVC, the gloss variations between wet-coalesced coating, high- T_g coating dried at room temperature, and sintered coating are shown in Figure 2. Gloss was measured at an incident angle of 75° (TAPPI standard) with a Hunter glossmeter (Hunter Assoc. Lab Inc., Reston, VA). The gloss of wet-coalesced coatings decreased with increasing pigmentation level until the CPVC then increased. This was a typical curve for coatings formulated with conventional low- T_g latex.

The gloss of coatings with high- T_g latex dried at room temperature was always higher than that of both wet-coalesced and sintered coatings. This is what is normally found with coatings that contain clay and a high- T_g latex.² After heat treatment of the high- T_g latex dried at room temperature, a drop in the gloss was observed. The drop in gloss was very small at and above the CPVC. Below CPVC, the gloss drop was greater as the latex content increased but was always higher than that of the wet-coalesced coating. As a result, coalescing in the absence of water (sintering) produced a higher gloss than coalescing in the presence of water (wet coalescing). This can be explained as a result of the structural collapse that occurs in wet-coalesced coatings.

Traditionally, the structural collapse of the wet coating during coalescence is related to a decrease in void fraction. Measurement of the void fraction by an oil absorption technique, as explained by

LePoutre and Rezanowich,⁴ showed that little change in void fraction happened at and above the CPVC and that the decrease in void fraction took place only below the CPVC (Fig. 3). Therefore, the previous results indicate that at high levels of pigmentation, no collapse of the structure during the sintering process occurred. This happened even though the latex coalescence during the sintering process was confirmed from scanning electron microscopy (SEM) pictures [Fig. 4(C)].

In addition, in all cases investigated, the void fraction of the sintered coatings was found higher than that of the wet-coalesced coatings. This indicates large differences in coating structure be-

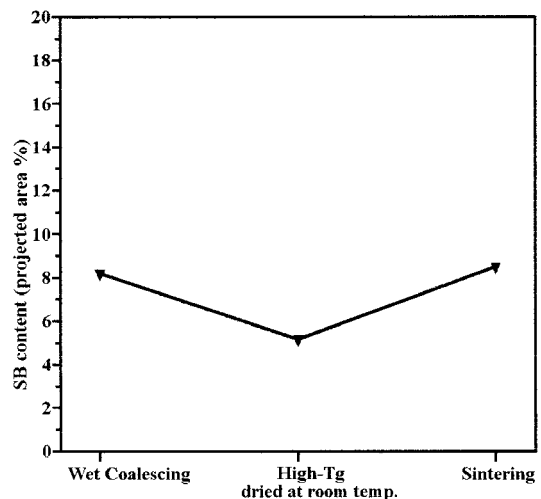


Figure 6 XPS for wet coalescing and sintering at 90% PVC.

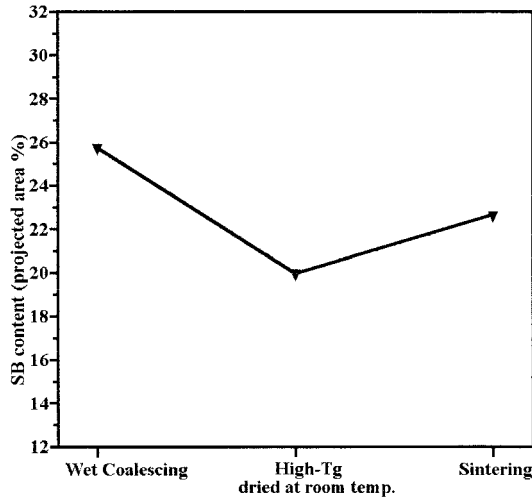


Figure 7 XPS for wet coalescing and sintering at 80% PVC.

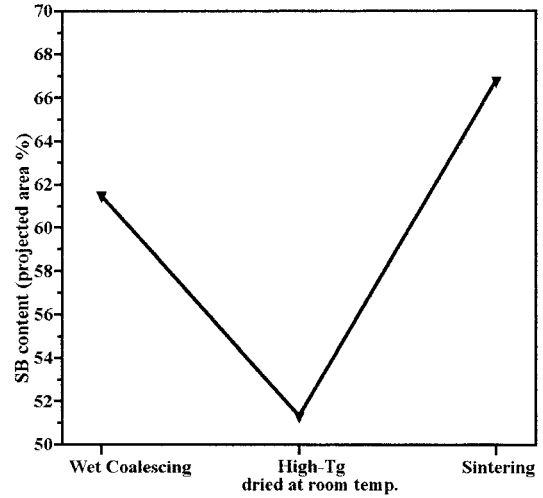


Figure 9 XPS for wet coalescing and sintering at 40% PVC.

tween the wet-coalesced and sintered coatings. It was speculated by LePoutre and Alinec² that in the presence of water, the surface tension or induced stress was distributed throughout the coating structure; this led to an overall shrinkage of the structure. In contrast, in the absence of water, only when there was enough latex present around the clay particles to form a continuum (in our case, this seemed to start happening below the CPVC) did the local stresses induced by the polymer-polymer and polymer-clay interfacial tensions distribute evenly and cause a general collapse or shrinkage. The local stresses causing the coating shrinkage should be investigated and es-

timated for the coatings dried in the absence of the water (sintering) and compared to the coatings dried in the presence of the water (wet coalescing).

SEM Examination After Wet Coalescing and Sintering

High- T_g coatings dried at room temperature, wet-coalesced coatings, and sintered coatings at all pigmentation levels (40, 54, 80, and 90% PVC) were examined with SEM.

Figure 4 illustrates the difference in surface morphology between the wet-coalesced coatings,

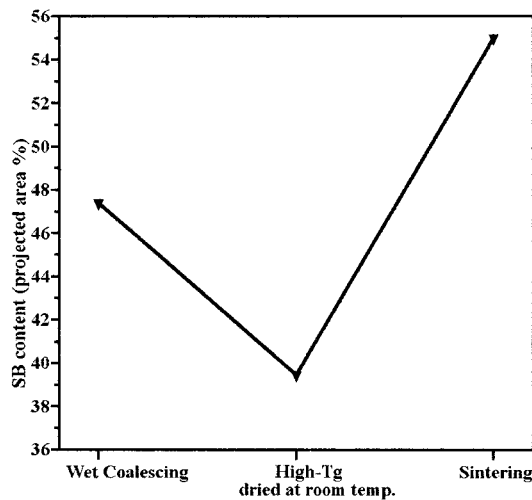


Figure 8 XPS for wet coalescing and sintering at CPVC (54% PVC).

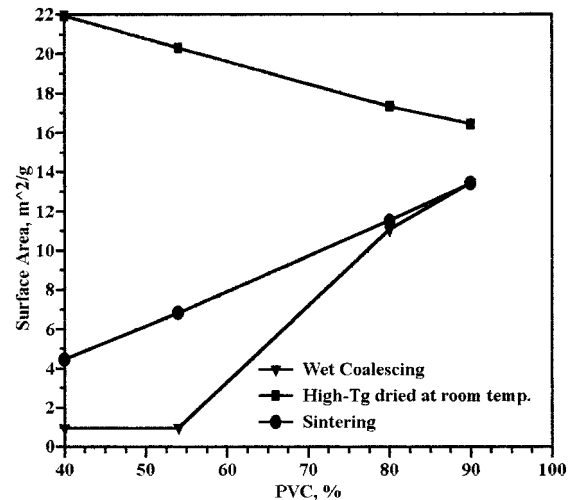


Figure 10 Surface area for wet-coalesced and sintered coatings (pooled $SD = 0.5 \text{ m}^2/\text{g}$).

Table I Surface Energy on Wet Coalesced and Sintered Coatings from Kaelble Equation (40% PVC), Where γ is the Total Surface Energy

Coating	γ^d (mJ/m ²)	γ^p (mJ/m ²)	γ (mJ/m ²)	Coefficient of Determination (R^2)
Wet coalesced	21.7	25.2	46.9	0.99
High T_g , dried at room temperature	30.1	29.5	59.6	0.97
Sintered	30.3	7.9	38.3	0.91

the noncoalesced coatings, and the sintered coatings at 54% PVC, as confirmed by SEM examination. The SEM micrographs showed that the gloss values obtained earlier (Fig. 2) reflected the difference in surface morphology. The coating with a high T_g dried at room temperature (noncoalesced) was very smooth [Fig. 4(B)]. After sintering of these high- T_g latex coatings, the latex particles fused together into a continuous film. During the sintering process, the surface remained quite smooth, as shown in the SEM micrograph [Fig. 4(C)]. In contrast, the wet-coalesced coatings showed a more disordered surface as a result of the structural collapse discussed earlier.

During the examination of the sintered coatings with SEM, small black features within the latex film attracted our attention (Fig. 5). These features were not seen in the wet-coalesced coatings. To explain these features, high-magnification micrographs of more than twice the original magnification were performed. These features were air voids (pores) within the latex film. Sintering produced coatings with larger voids; therefore, these pores could be seen in the sintered coatings and not in the wet-coalesced coatings. Initially, no physical explanation for these pores could be found. However, LePoutre and Alince² unexpectedly found that after heat treatment of the high- T_g coatings dried at room temperature (sintered), the oil absorption rate remained high, similar to that of the noncoalesced coatings. It appeared that these pores within the latex film

accounted for the high absorption rate in the sintered coatings after heat treatment.

Surface Chemistry: Wet Coalescing Versus Sintering: X-Ray Photoelectron Spectroscopy (XPS)

The effect of coalescing in the presence or absence of water on the surface content of the coatings at a wide level of pigmentation (40–90% PVC) was investigated with XPS. After the detection of each component signal at the surface, the coating surface content was calculated as area percent:

$$\text{Clay area \%} = \frac{\text{atom \%}(\text{Al} + \text{Si})_{\text{Coating}}}{\text{atom \%}(\text{Al} + \text{Si})_{\text{Pure Clay}}} \times 100 \quad (1)$$

$$\text{SB Area \%} = 100 - \text{Clay Area \%} \quad (2)$$

Figures 6–9 illustrate the SB surface content, as area percent, of the wet-coalesced coating, the high- T_g coating dried at room temperature, and the sintered coating at 90, 80, 54, and 40% PVC, respectively.

Over the pigmentation range studied, the sintered coatings showed an increase in the SB area percent after heat treatment of the high- T_g coatings dried at room temperature. This was caused by the latex spreading on the coating surface. This increase in the SB area percent increased with increasing latex content. This was similar to

Table II Surface Energy on Wet Coalesced and Sintered Coatings from Kaelble Equation (54% PVC), Where γ is the Total Surface Energy

Coating	γ^d (mJ/m ²)	γ^p (mJ/m ²)	γ (mJ/m ²)	Coefficient of Determination (R^2)
Wet coalesced	24.9	16.9	41.8	0.99
High T_g , dried at room temperature	30.8	27.8	58.7	0.98
Sintered	31.9	6.0	37.9	0.86

Table III Surface Energy on Wet Coalesced and Sintered Coatings from Kaelble Equation (80% PVC), Where γ is the Total Surface Energy

Coating	γ^d (mJ/m ²)	γ^p (mJ/m ²)	γ (mJ/m ²)	Coefficient of Determination (R^2)
Wet coalesced	30.4	18.0	48.3	0.95
High T_g , dried at room temperature	31.4	29.7	61.1	0.98
Sintered	28.8	19.3	48.2	0.92

the behavior of the conventional wet-coalesced coatings after latex coalescence.³

At high PVC (90 and 80% PVC), no significant difference was found in the SB area percent at the surface between the sintered and the coalesced coatings (Figs. 6 and 7). On the other hand, at and below the CPVC (54 and 40% PVC), the SB area percent at the sintered coatings surface was higher than that at the wet-coalesced coatings surface (Figs. 8 and 9). This indicates that at and below the CPVC, sintering enhanced the latex spreading at the coating surface more than the conventional wet coalescing. This behavior was the opposite of what was found in the coating bulk. In the bulk, the surface area, measured by the nitrogen-gas adsorption experiments, indicated that the wet-coalesced coatings always showed lower SB surface area than sintering coatings (Fig. 10). The difference between the wet-coalesced and sintered coatings increased with increasing latex content. Lower surface area for the wet-coalesced coatings indicated that the latex coverage and spreading, in the bulk, was better or more complete with the wet-coalesced than with the sintered coatings.

Surface Energy: Wet Coalescing Versus Sintering

The surface energy of wet-coalesced coatings, high- T_g coatings dried at room temperature, and sintered coatings was estimated from the measured contact angle over a wide range of pigmentation (40–90% PVC). The initial con-

tact angles of three different liquids, water, methylene iodide, and formamide, were measured for each case with the technique described by Al-Turaif et al.⁵ The surface energy was estimated from Kaelble's approach.^{6,7} Here, the total surface energy was estimated from the dispersive (γ^d) and polar (γ^p) components. Tables I–IV represent the surface energy and its polar and dispersive components as estimated from Kaelble's approach for wet-coalesced coatings, high- T_g coatings dried at room temperature, and sintered coatings at 40, 54, 80, and 90% PVC, respectively.

The effect of heat treatment of the high- T_g coating dried at room temperature on the estimated surface energy values was clear. In all cases, the sintered coatings showed a lower surface energy than the high- T_g coatings dried at room temperature. The decrease of the surface energy for the sintered coatings was accompanied by a sharp decrease in polar components but without a significant change in the dispersive components. This behavior of the sintered coatings after latex coalescence was the same as that found for conventional wet coalescence after latex coalescence. These phenomena could be caused by the change in the surfactant sites as a result of competitive sorption–desorption processes at the pigment and latex surfaces during the consolidation.³

A comparison between the surface energy at sintered coatings and wet-coalesced coatings in-

Table IV Surface Energy on Wet Coalesced and Sintered Coatings from Kaelble Equation (90% PVC), Where γ is the Total Surface Energy

Coating	γ^d (mJ/m ²)	γ^p (mJ/m ²)	γ (mJ/m ²)	Coefficient of Determination (R^2)
Wet coalesced	29.9	23.9	53.9	0.97
High T_g , dried at room temperature	30.3	34.4	64.7	0.98
Sintered	30.7	23.1	53.8	0.94

licated that two behaviors could be obtained. At 40 and 54% PVC (Tables I and II), the wet-coalesced coatings surface energy and polar components were higher than that of the sintered coatings. On the other hand, above the CPVC, at 80 and 90% PVC (Tables III and IV), no differences between the wet-coalesced and sintered coatings surface energy were obtained. At these two pigmentation levels (above the CPVC), no change in the surface composition was found.

CONCLUSION

Drying in the presence of water (wet coalescing) was compared to drying in the absence of water (sintering) for coatings containing latices with high levels of crosslinking caused by the presence of a chain-transfer agent. This is also valid for latex particle structure, morphology, and melt flows relevant to latices made by a batch process. Even though sintered coatings were more porous and had higher gloss, no significant difference was found in the SB/clay ratio at the surface or in

the surface energy above the CPVC. However, at and below the CPVC, the sintering process yielded a higher SB content at the surface and a lower surface energy than the wet-coalescing process.

This research was supported, in part, by the industrial sponsors of the Paper Surface Science Program at the University of Maine.

REFERENCES

1. Watanabe, J.; LePoutre, P. *J Appl Polym Sci* 1982, 27, 4207.
2. LePoutre, P.; Alince, B. *J Appl Polym Sci* 1981, 26, 791.
3. Al-Turaif, H. A.; LePoutre, P. *Prog Org Coat* 2000, 38, 43.
4. LePoutre, P.; Rezanowich, A. *Tappi J* 1977, 60, 86.
5. Al-Turaif, H. A.; Unertl, W. N.; LePoutre, P. *J Adhes Sci Technol* 1995, 9, 801.
6. Owens, D. K.; Wendt, R. C. *J Appl Polym Sci* 1969, 13, 1741.
7. Kaelble, D. H. *J Adhes* 1970, 2, 66.