

The use of hollow sphere pigments as strength additives in paper and paperboard coatings—Part 1: The predictive nature of packing models on coating properties

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ABSTRACT: Hollow sphere pigments (HSPs) are widely used at low levels in coated paper to increase coating bulk and to provide gloss to the final sheet. However, HSPs also provide an ideal system through which one can examine the effect of pigment size and particle packing within a coating due to their unimodal and tunable particle sizes.

The work presented in Part 1 and Part 2 of this study will discuss the use of blends of traditional inorganic pigments and HSPs in coating formulations across a variety of applications for improved coating strength. Part 1 of this study focuses on the theory of bimodal spherical packing and demonstrates the predictive nature of packing models on the properties of coating systems containing HSPs of two different sizes.

This study also examines conditions where the model fails by examining the effect of particle size on coating strength in systems like thermal paper basecoats where the non-HSP component has a broad particle size distribution, and how these surprising trends can be used to generate better-than-expected thermal printing performance in systems with low HSP/clay ratios.

Part 2 of this study focuses on the incorporation of HSPs of different particle sizes into paperboard formulations to affect coating strength and opacity.

Application: This study focuses on the theory of bimodal spherical packing and demonstrates the predictive nature of packing models on the properties of coating systems. It uses this model to inform real world formulations designed for improved coating strength in thermal paper applications.

Coatings are regularly applied to paper and paperboard to provide properties that the substrate would not have otherwise. These coatings consist primarily of pigments, such as clays and carbonates, and synthetic polymer binders that hold pigments together. The ratios of these materials can be altered to provide a wide array of properties to the substrate for any number of desired applications. In the case of coated paper and paperboard, these properties include smoothness, brightness, surface gloss, printability, etc. Alternatively, thermal paper basecoats use similar materials to improve smoothness and thermal insulation. While these applications are disparate, the formulation spaces for these coatings are similar. Namely, both coatings regularly have high pigment volume concentration (PVC), and, for the most part, are above the critical PVC (CPVC) where the binder phase is no longer continuous.

Because the binder in systems above CPVC is no longer continuous, a significant portion of the properties of the coating come from the pigments from which the coating is composed and the air voids between the pigment par-

ticles, which contribute directly to properties such as brightness and thermal insulation. Furthermore, coatings for paper, paperboard, and thermal paper regularly contain more than one pigment. As such, it is imperative to have a fundamental understanding of the random close packing that exists after the coating is applied and how this formation might change when multiple pigments are blended together.

This report will examine one method to model coating properties, including coating strength and thermal insulation, and will examine the model's ability to correctly predict coating performance. As will be described, blends of hollow sphere pigments (HSPs) are an ideal system by which to test the robustness of the model due to their monodisperse and tailorable particle sizes. Moreover, the lessons from these modeling efforts will be extended to a thermal paper system with a blend of HSPs and calcined clays to demonstrate the ways by which designing a coating around improved particle packing allows for additional benefits to be gained beyond the properties dictated by the individual pigments themselves.

COATING ADDITIVES

EXPERIMENTAL METHODS

Pre-coat formulation

The formulations as described in **Tables 1-3** were mixed with an overhead blade mixer and diluted with deionized water to the same solids.

Image layer formulation

Image layer materials and formulations were formulated to 20% solids and contained the following materials by dry weight %: 24.76% of precipitated calcium carbonate (PCC), 20.64% of silica dioxide, 0.83% of polyvinyl alcohol 203 (PVA-203) buffer, 24.76% of D-8 developer (4-Hydroxy-4'-isopropoxydiphenylsulfone), 4.13% of sensitizer (2-benzyl-oxy-napthalene), 8.25% of PVA-117 binder, 6.19% of zinc

stearate lubricant, and 10.32% of dye (2-Anilino-6-(dibutylamino)-3-methylfluoran). The materials were added to the water in this order and mixed with an overhead blade mixer.

Coating preparation

Freesheet paper with a basis weight of 60 g/m² was cut to 19 cm x 24 cm, with the long side in the machine direction, and weighed to get an initial base weight of the paper. The paper was taped using masking tape to a piece of copy paper clipped to the drawdown machine. A wire wound rod was attached to the drawdown machine above the tape. Then, a bead of pre-coat formulation was pipetted onto the masking tape above the freesheet. The wire wound rod was

	Formulation 1	Formulation 2	Formulation 3
Large HSP	100.0	50.0	
Small HSP		50.0	100.0
Binder	20.0	20.0	20.0
Total Parts	120.0	120.0	120.0

I. Example formulations for binary hollow sphere pigment (HSP) blends.

	Small HSP	Medium HSP	Large HSP
HSP	46.0	37.5	29.2
Calcined clay	46.8	46.8	46.8
Latex binder	19.0	19.0	19.0
PVOH	5.0	5.0	5.0
Total Parts	116.8	108.3	100.0
HSP/clay size ratio	0.53	1.33	2.0
Clay volume fraction	0.24	0.24	0.24
Total PVC	0.83	0.83	0.83

HSP = hollow sphere pigment; PVOH = polyvinyl alcohol; PVC = pigment volume concentration.

II. Example thermal paper basecoat formulations for model testing.

	Small HSP	Medium HSP	Large HSP
HSP	29.2	29.2	29.2
Calcined clay	46.8	46.8	46.8
Latex binder	19.0	19.0	19.0
PVOH	5.0	5.0	5.0
Total Parts	100.0	100.0	100.0

HSP = hollow sphere pigment; PVOH = polyvinyl alcohol; PVC = pigment volume concentration.

III. Example thermal paper pre-coat formulations.

moved down over the strip of pre-coat formulation and across the paper so that the paper would be coated evenly. The paper was then dried in an oven at 80°C for 1 min.

After drying, the paper was conditioned in a controlled temperature room (72°F and 50% humidity) for at least 2 h. After conditioning, the freesheet was cut from the copy paper and the coat weight was determined. All samples in this study had a pre-coat coat weight of approximately 5 g/m². This pre-coated paper was then coated with image layer via the aforementioned procedure. All samples in this study had an image layer coat weight of approximately 4 g/m².

Measuring coat weights

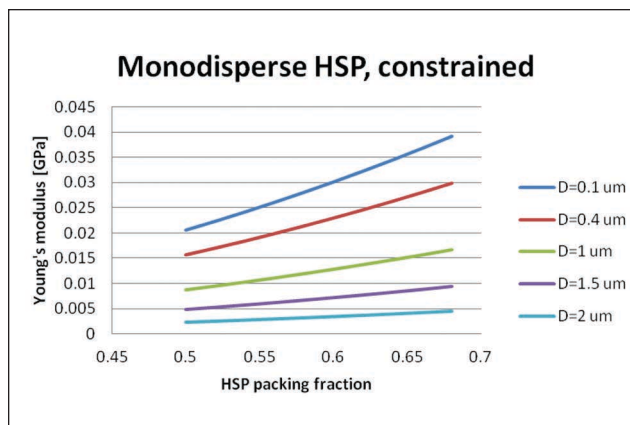
Uncoated freesheet was cut to 19 cm x 24 cm using a metal die as a template. This sheet was then weighed on an analytical balance, and the mass was multiplied by (0.0456 m²) to attain the basis weight of the sheet of paper in units of grams per square meter (g/m²). Pre-coated sheets were cut to 19 cm x 20.5 cm using a metal die as a template. The sheet was then weighed on an analytical balance. The mass was multiplied by (0.0390 m²) to attain the weight of the pre-coated sheet in g/m². The basis weight of the uncoated sheet was then subtracted from the weight of the pre-coated sheet to determine the coat weight of the pre-coat in g/m². Sheets coated with image layer were cut to 16.5 cm x 16.5 cm using a metal die as a template. The sheet was then weighed on an analytical balance. The mass was multiplied by (0.0272 m²) to attain the weight of the fully coated sheet in g/m². The weight of the pre-coated sheet was then subtracted from the weight of the fully coated sheet to determine the coat weight of the image layer in g/m².

IGT dry pick measurement

IGT dry pick measurement was carried out using IGT AIC 2-5 unit (IGT Testing Systems; Almere, The Netherlands). Coated paperboard samples were cut into 1.5 in. x 12 in. size and mounted onto the equipment using a WestVaco wheel. IGT was measured according to the IGT WestVaco pick test W38, and three readings were taken to get an averaged value of IGT pick strength. IGT measurements were performed in machine direction, and typically medium viscosity ink from IGT (IGT Pick Test Ink Nr. 2, medium tack, 404.800.002) was used for measurements.

Instron tape pull

A 1.5 in. x 3 in. piece of thermal paper basecoat was cut with the long axis in the machine direction. This strip was then attached to a metal support with the coating facing out via double-stick tape. Using masking tape, a tab was placed on the end of a strip of Tesa Tape (Tesa Tape Inc.; Charlotte, NC, USA). The Tesa Tape was then applied to the supported coating, with the tab facing down, using two passes of a 1-kg roller. The support was then placed in an



1. Calculated Young's modulus of a coating (E) as a function of hollow sphere pigment (HSP) packing fraction for HSPs with a particle size of 0.1 μm (dark blue), 0.4 μm (red), 1 μm (green), 1.5 μm (purple), and 2 μm (light blue). (D = particle size.)

Instron 5565 tensile testing machine (Instron; Norwood, MA, USA), and the tabbed side of the tape was attached to the top Instron clamp in the geometry of a 180° peel test. The tape was then pulled upward at 40 in./min. The geometry of the test can be seen in **Fig. 1**.

Dynamic sensitivity

Fully coated paper was cut in the machine direction into two strips that were 2.5-in. wide. These two strips were then taped end to end, and printed using an Atlantek Paper Tester Model 200 (Global Media Instruments LLC; Milpitas, CA, USA). The printing conditions were set to the following values: the sequence dot pulse duration was 0.8 ms, and the full cycle time was $T_{\text{cycle}} = 5.0$ ms. The print head resistance was 583 ohms with an applied voltage of 20.6 V. A 50% 80 x 80 checkerboard pattern was printed with print energies of 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, and 0.50 mJ/dot. The optical density (OD) of three boxes of each print energy was measured using a handheld X-Rite 428 spectrodensitometer (X-Rite; Grand Rapids, MI, USA).

RESULTS AND DISCUSSION

Modeling a coating of hollow sphere pigments

The mechanical response of a coating is a critical fundamental property that has a direct relation to application-specific properties such as dry pick strength and glueability. Typically, the binder of the system is seen as the primary source of added coating strength. However, through modeling efforts, one can demonstrate that the pigment packing within the coating can also affect the coating's mechanical response. To model this, one can calculate the Young's modulus, a measure of coating stiffness, for a given system. Since HSPs have been chosen as a model experimental system, the Young's modulus can be calculated for a single HSP by relating the modulus of the particle to the shell material, shell thickness, and particle size, as seen in Eq. 1 [1,2]:

$$E_p = \frac{4E_{shell}h^2}{\pi D^2\sqrt{3}(1-\nu^2)} \quad (1)$$

where E_{shell} is the modulus of the shell material, h is the shell thickness, D is the particle size, and ν is the Poisson ratio. This can then be extended to represent the modulus of an HSP coating by modeling the coating as a collection of particles with a variable packing fraction, as seen in Eq. 2 [3]:

$$E = E_p \left[1 - \frac{(1-\phi)}{P_c} \right]^n \quad (2)$$

where E_p is the effective modulus of a single particle, ϕ is the HSP packing fraction, P_c is the critical coating porosity (void space between HSPs) at which the coating would be expected to fall apart, and n is a critical exponent for a 3D cluster [3]. Figure 1 shows the calculated Young's modulus as a function of HSP packing fraction for HSPs of various particle sizes where the void fraction of the HSP has been constrained by the particle diameter.

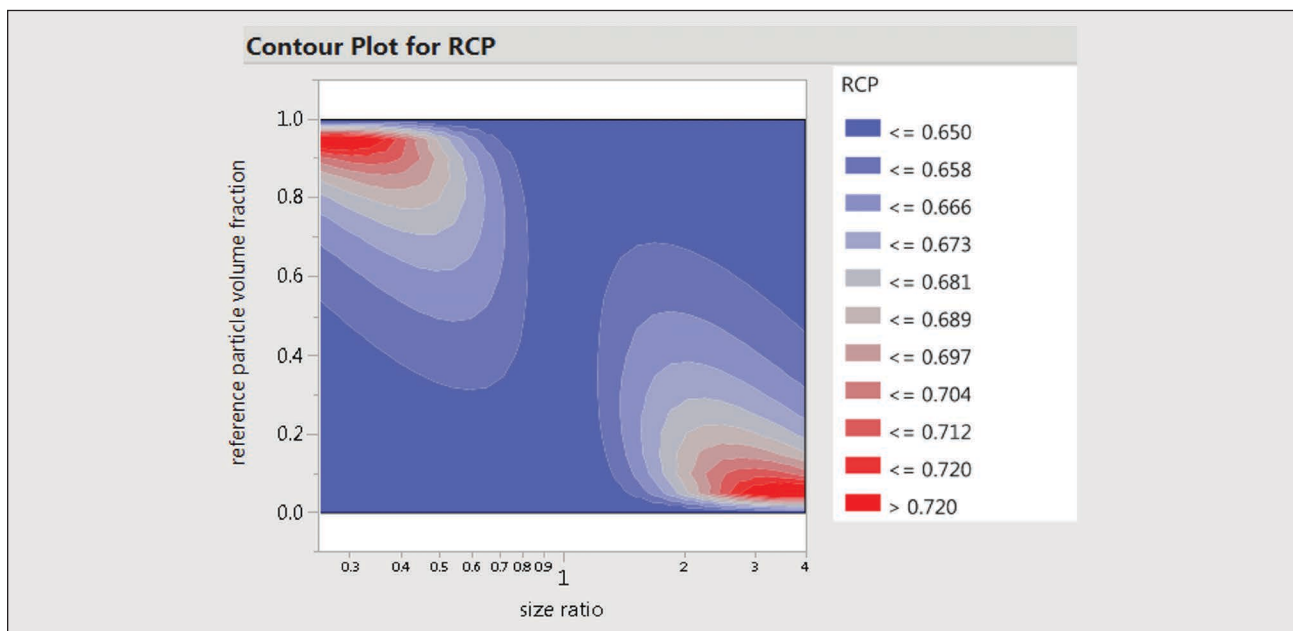
Figure 1 shows that in coatings of monodispersed HSPs, the Young's modulus increases when the void fraction of the particles is low and the packing fraction of the coating is high. While neither of these results is particularly surprising, it affirms the hypothesis that finding ways to formulate densely packed coating structures is one way to improve the mechanical stability of the coating. Furthermore, the data in Fig. 1 suggests that if one understands the packing behavior of a given coating system, the calculated packing fraction should provide a directional predictor for the mechanical strength of the coating.

One way to improve the packing efficiency of a coating is to use blends of pigments with different particle sizes. For modeling simplicity, binary blends were chosen for this study. On one hand, such a system can be thought of in pure geometric terms where hard spheres are packed and are always in contact with their nearest neighbors [4]. However, such a treatment overestimates the degree of random close packing. Instead, the coating can be treated as a simplified [5] jammed colloidal system where the final configuration follows the infinite pressure limit of hard sphere glasses [6]. The simplified equation for the random closed packing density of a binary blend can be seen in Eq. 3:

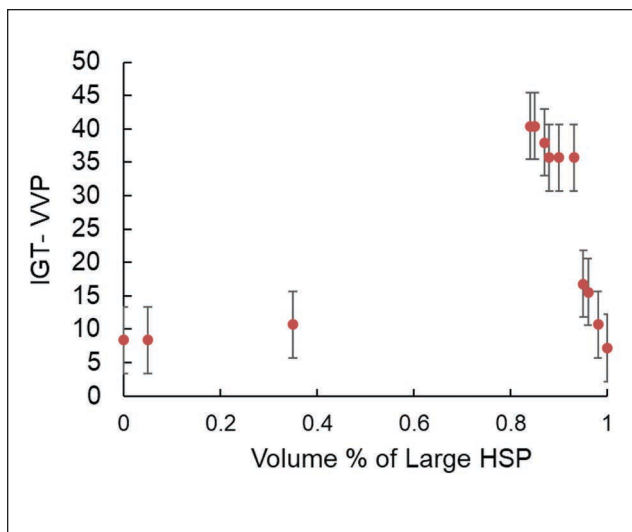
$$RCP = RCP_{monodisperse} + \frac{4}{3}\beta \times RCP_{monodisperse} (1 - RCP_{monodisperse})(1 - X_l)X_l(r^3 - 1) \quad (3)$$

where $RCP_{monodisperse} = 0.64$, $\beta = 0.2$ and is a fit parameter, X_l is the number fraction of the reference particle, and r is the size ratio of the variable particle to the reference particle. This equation can be used to calculate the packing density of binary blends where the variable particle ranges from 0.25 to 4 times the size of a reference particle. The results from the calculation can be found in **Fig. 2**.

Figure 2 shows that it is possible to drastically improve the packing fraction of a coating by using a binary blend of pigment particles, provided there is sufficient difference in the size of the two particles and the volume fraction of the smaller particle is low. Conceptually, this makes sense, as both conditions would mean that the majority of the coating volume is filled by large particles,



2. Random close packing (RCP) density as a function of size ratio and reference particle volume fraction.



3. IGT viscosity-velocity product (IGT-VVP) as a function of the volume percentage of the large HSP in a blended system with a size ratio of 0.27.

while the interstitial voids between them can be filled with small particles.

Relating models of binary blends to the properties of laboratory produced coatings

HSPs provide an ideal system to empirically test the results of the models described previously because of their monodisperse and tailorable particle sizes. To test the hypothesis that improving the packing density of a coating will improve the mechanical strength of a coating, an HSP blend was chosen with a size ratio of 0.27 (the large particle in this case is the reference particle) and formulated with various volume fractions of the two HSPs. This size ratio was chosen because Fig. 2 predicts that particles with this size ratio should see a drastic increase in the packing density, and thus it is hypothesized that such a system would see a strength improvement when the large particle volume fraction is large. Example formulations can be seen in Table I.

These formulations were coated on freesheet paper via hand drawdown with a wire wound rod to a coat weight of 8 g/m². Coating strength was measured via IGT dry-pick according to TAPPI Standard Test Method T 499 “Surface strength of paper (IGT tester),” and the results are presented in viscosity-velocity product (VVP) in **Fig. 3**.

Figure 3 shows that the strength of the coating increases significantly when the volume fraction of the large HSP increases to 80%–90% before decreasing again as the system returns to functioning more as a coating of mono-dispersed large HSPs. Not only does this result support the hypothesis, but the volume fractions where the experimental system observes a peak in coating strength agrees with that predicted by the model in Fig. 2.

Particle packing to improve thermal paper coatings: Testing the model

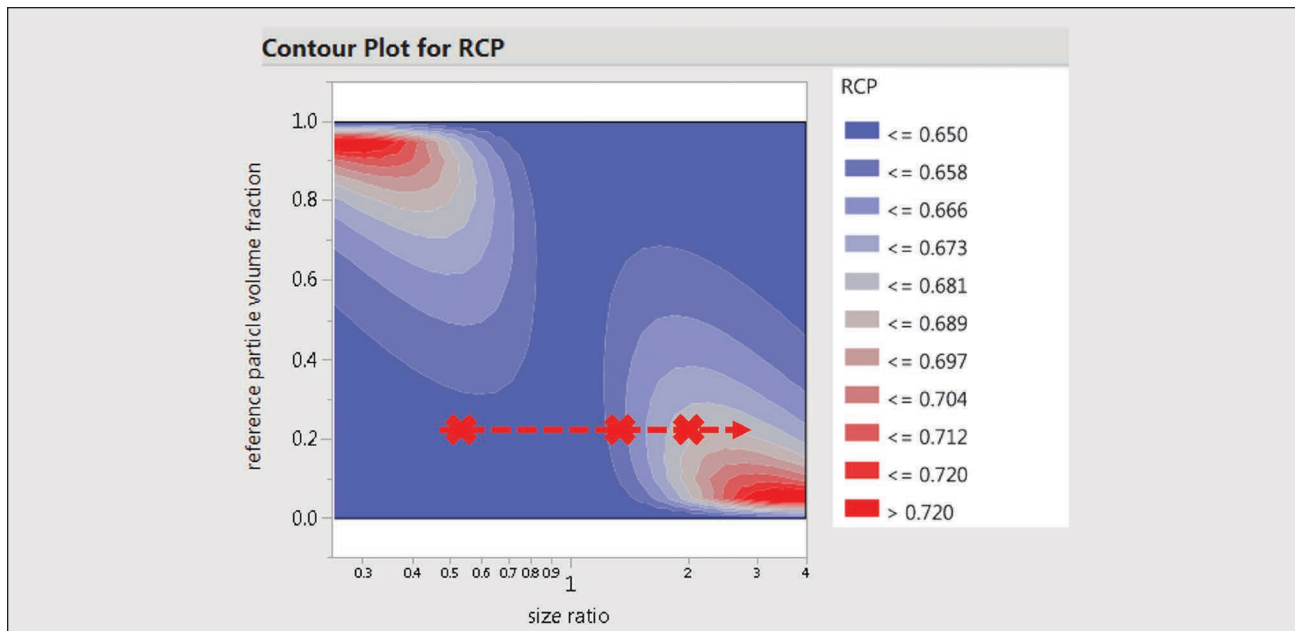
Thermal paper pre-coats are a natural extension for this work to a practical application because these coatings typically contain a blend of calcined clay and an HSP. Basecoats for thermal paper provide smoothness and thermal insulation to the paper such that the paper maintains contact with the thermal printhead and the heat applied by the print head is localized near the imaging chemicals, both of which improve the print performance of thermal paper. In this case, the internal voids provided by both the calcined clay and the HSP provide insulation by adding more air into the coating than would naturally occur through the interstitial voids of the coating.

When comparing thermal paper coatings to the model described here, assumptions must be made. Primarily, the model accounts for discrete bimodal spherical packing. Adding a particle size distribution makes the model far more complex, so for this report, calcined clay will be assumed to be a spherical pigment with a particle size of 755 nm [7]. Despite this assumption, we can account for the real-world coating structure by calculating the volume fraction of the clay through its dry density. Since HSPs are far less dense than calcined clay due to their large internal voids, they take a larger proportion of the final coating volume than might be assumed purely from their particle size. Moreover, the HSP/clay ratio required to maximize the packing density according to Fig. 2 uses far less HSP than is practical due to the restrictions of sufficient thermal insulation. Therefore, the following data will use a more practical HSP/clay ratio, with the hypothesis that the general trends of disparate particle sizes and larger volume percentages of the large species in the coating promote coating strength.

To test the effectiveness of our packing model to predict the strength behavior of thermal paper coatings, a set of formulations were made (Table II) with equal PVC to hold the binder concentration constant throughout the study. This is an important consideration, because the densities of the HSPs in this study change as the particle size changes. As a result, if one were to formulate on a traditional dry parts replacement, there would be far fewer particles present in the small HSP case, and thus that system would be overbound, potentially hiding any packing effects that might exist.

The hypothesized theoretical packing fractions of the coatings from Table II are plotted in **Fig. 4** as overlay data points on the topographical packing map from Fig. 2. Based on the clay volume fraction within the coating and the HSP/clay size ratios, one would hypothesize that the estimated packing fractions would lead to the coating that included large HSPs and would be the strongest, followed by the medium HSP, and with the small HSP producing the weakest coating.

Coating strength for this part of the study was per-

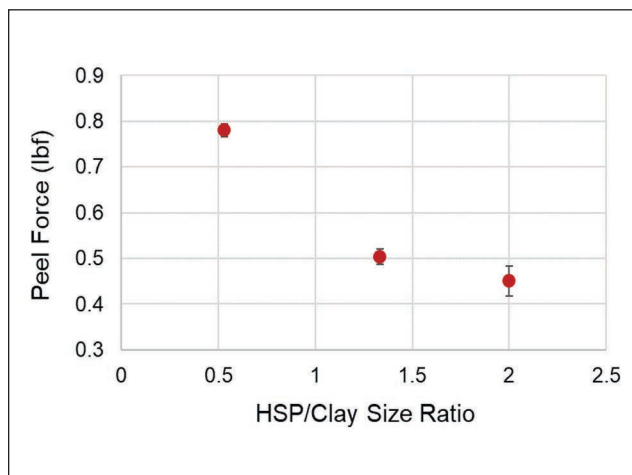


4. RCP density as a function of size ratio and reference particle volume fraction. The red symbols represent each of the three formulations in this experiment. The red dashed line shows the estimated densification that is predicted as the HSP increases in size.

formed using a 180° peel test where Tesa Tape is pulled off the coating via an Instron. The tape, in each case, was applied to the coating using a 1-kg roller to ensure that the pressure sensitive adhesive was attached with the same pressure. In all cases, the point of failure is cohesive within the coating. Furthermore, previous work in our group has shown that in high PVC formulations, the failure point is between the binder and pigments, where the coating fracture occurs around an HSP. In this test, the higher the average pull force as registered by the Instron, the stronger the coating. Coating strength vs. HSP/clay size ratio is shown in **Fig. 5**.

The data in Fig. 5 demonstrate that the strength of thermal paper coatings with equal PVC decreases when the HSP/clay Size ratio increases at the HSP level tested for this study. This is the opposite of the trend expected by the presented model, and it is useful to undergo the thought exercise as to why the model might fail in this example.

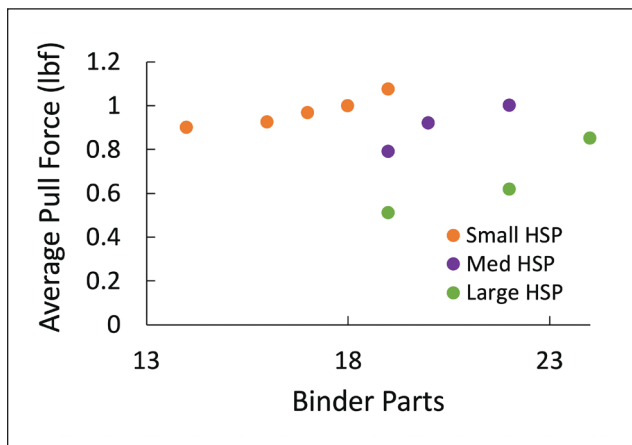
The primary difference between this example and the condition of bimodal blends of HSP is that the calcined clay used in this study has a broad particle size distribution. It is clear, then, that the assumption that calcined clay could be modeled as a particle of uniform size is not sufficient to describe the system, and that the model would apply best in systems with particles of discrete size. While this helps with the understanding of how one might apply this model, it is reasonable to consider the deeper question of why small HSP/clay size ratios provide such a marked improvement in coating strength in this system when the binder concentration was held constant. A particle number argument might apply; however, small



5. Coating strength as a function of HSP/clay size ratio.

HSPs take up less volume than large HSPs, and thus more small HSP particles must be used to achieve the same volume concentration as large HSPs. This would suggest that the small HSP case would be weaker, because there are a greater number of particles that must be bound, but the data clearly show that this is not the case. In fact, the trends in coating strength are the direct opposite.

One potential explanation for the surprising trend in coating strength lies in the particle size distribution of the calcined clay. It is possible that while the median particle size of the calcined clay is 755 nm, the majority of the volume of the calcined clay is taken up by particles larger than that. In this case, it is possible that adding the small HSPs into the formulation fill in space in the coating in the same way the small HSP did in the bimodal



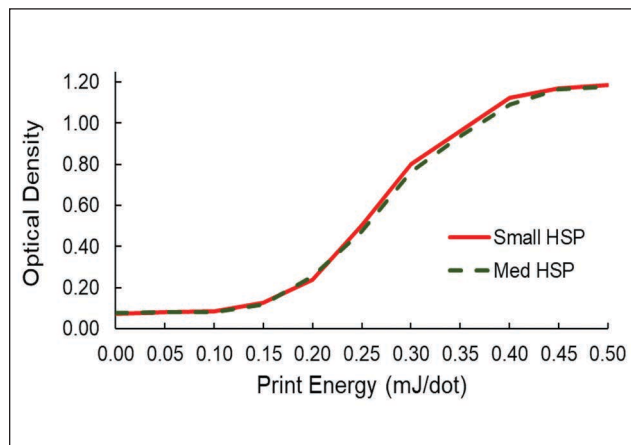
6. Average pull force as a function of binder parts for the HSP/clay ratios represented in Table III for small HSPs (orange), medium HSPs (purple), and large HSPs (green).

HSP blend case, building coating strength through improved packing density. Another potential explanation for the observed coating strength trends involves changes in binding efficiency. Calcined clay is known to require higher binder levels than other clays due to its internal porosity and rough surface topology. HSPs, on the other hand, are uniform in shape and surface topology and therefore would require less binder to hold together. As mentioned earlier, the small HSP case requires more HSP particles to fill the same volume than the large HSP case, and therefore the number of HSP/HSP points of contact should increase. This could allow the binder in the system to work more efficiently, and therefore lead to an increase in coating strength as the HSP particle size decreases.

Using coating strength to improve thermal printing

While the previous example did not fit with the designed packing model, the surprising coating strength improvement when using small particle size HSPs suggests that this effect could be used in more practical formulation spaces. While it worked to test the robustness of the model, one would never compare a thermal paper coating using small HSPs to one using large HSPs based on equivalent dry coating volume, because the coating containing small HSPs would be much more expensive. Instead, one must examine more practical formulation spaces.

The formulation space of thermal paper pre-coats varies greatly from customer to customer. Many use a blend of HSPs and calcined clay. For the customers that use large amounts of HSP, large HSPs with high void fractions tend to be preferable due the thermal insulation that those void fractions provide. However, the data in Fig. 5 suggests that there might be ways to formulate small HSPs into basecoat formulations that use low HSP/clay ratios such that they improve the insulation of that coating by taking advantage



7. Dynamic sensitivity of the coatings in Table II containing small (solid red line) and medium (dashed green line) HSPs at equal coating strength.

of the strength improvement when using small HSPs to remove binder and add air to the final coating. Example formulations for this work are shown in Table III.

Coating strength for this part of the study was again performed using a 180° peel test where Tesa Tape is pulled off the coating via an Instron. In this test, stronger coatings have higher average pull forces as registered by the Instron. The results of this study for many additional binder levels are shown in **Fig. 6**.

The formulations for this study use an equal dry parts replacement for the HSP level. This means that the number of particles in the system increases as the particle size of the HSPs increases, since the dry density of each individual HSP decreases with increasing particle size. This trend, as observed in Fig. 6, accentuates the difference in coating strength as observed in the equal PVC case.

Figure 7 shows the dynamic sensitivity of coatings at equal strength containing small and medium HSPs with the HSP/clay ratio depicted in Table II. In this case, binder has been removed from the small HSP coating to account for the strength improvement. As observed in Fig. 5, when this strength adjustment is made, the interstitial voids brought to the coating from binder reduction improves the print performance of the small HSP such that it equals that of the medium HSP with a higher void fraction. Such a conclusion is interesting for two reasons:

1. Such a formulary change could help thermal paper producers who are dryer limited despite low HSP/clay ratios, as the lower particle size HSPs have higher solids.
2. It suggests that these HSP particle size effects could be used to design systems with improved strength for other applications, and the resulting binder reduction could improve secondary properties in those applications. This topic is the focus of Part 2 of this paper from Einsla et al. [8].

SUMMARY

The following is a summary of findings from Part 1 of this study:

- Improving the strength of a coating is of critical importance to many paper, paperboard, and thermal paper applications. In addition to binder choice, models of coating packing demonstrate that choosing a pigment system that maximizes the packing density of the coating can have a significant impact on the mechanical response of the coating.
- Such a system can be obtained by creating a bimodal system through the use of HSPs. The HSP can be chosen based on the size ratio and used at levels that can be predicted to maximize the packing density of the resulting coating.
- This paper demonstrates that these results are not only theoretical but extend to empirical systems. Using bimodal HSPs, one can observe an increase in coating strength not by changing the binder system or level, but simply by altering the volume fractions of the HSPs.

ABOUT THIS PAPER

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- While the model breaks down in systems where an HSP is replacing a pigment with a broad particle size distribution, there are many other pigment systems that have more discrete particle sizes where this model could be more useful.
- Moreover, an examination of the strength improvements exhibited by small particle size HSPs from this

ABOUT THE AUTHORS

We studied this topic because attaining a fundamental understanding of the way different pigments pack within a paper coating and how that correlates to the strength properties of the coating could allow us to strategically design coatings for optimized strength of other secondary properties.

Structure/property relationships of pigment choice and coating strength have been studied extensively in the past, but relating pigment choice back to fundamentals of particle packing and modeling of various coating properties builds on the previous work.

The most difficult aspect of this research was picking the correct systems and formulations to make direct comparisons on the model. This is always challenging, but particularly so in the world of paper coatings. Hollow sphere pigments proved to be a great model system, and it allowed us to relate the models to real-world properties in thermal paper coatings.

We discovered that the properties of thermal

paper coatings could be predicted based on models. The results in real-world thermal paper pre-coats were most interesting and proved that the principals we learned from the model system could still be applied to real world formulations to take advantage of improved coating strength to improve thermal insulation.

Mills could benefit from this information by using the predictive nature of particle packing to strategically design their coatings for coating strength. An example of this can be seen in Part 2 of this manuscript from Einsla et al. [8].

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study demonstrate how creative formulating can be advantageous in thermal paper applications when other constraints, such as cost or drying capacity, limit one's access to certain raw materials.

- In addition to the work described previously, one can extend this work to other systems where HSPs could be useful, including paperboard applications where HSPs could be used to replace titanium dioxide as a method to improve coating brightness. **TJ**

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