

Theoretical Development Of a Graphical Analysis Technique To Optimize the Particle Size Distribution Of Pigments in Paints and Coatings

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INTRODUCTION

As new paints and coatings with improved properties are developed for consumer applications, the importance of new techniques to control physical properties have taken on greater importance. Consequently, efforts to improve our theoretical understanding of how particulate additives influence such properties as viscosity,¹⁻¹⁰ modulus,¹¹⁻²² and impact²²⁻²⁷ have received increased attention in the literature. In a recent review, Liang et al.²³ indicated that there is a need to improve our understanding of the influence that the dispersed-phase particle size distribution has on some of these properties.

Several attempts have been made to elucidate both the theoretical²⁸⁻³¹ and the experimental^{5-7,32} influence of particle size distribution on viscosity or oil absorption in particulate suspensions or particulate mixtures. A new understanding of the influence of particle size, particle size distribution, and particle/matrix interaction on the viscosity of particulate suspensions and the modulus of particulate composites has also recently been initiated as a result of the derivation and development of a new generalized viscosity/modulus model.⁸⁻¹² This new generalized viscosity/modulus equation has been particularly effective in elucidating the separate influence of particle size from that of particle size distribution on the viscosity and modulus of particulate composites.

The packing fraction, ϕ_n , using this new generalized viscosity/modulus equation, has been found⁹⁻¹⁰ to depend on the particle size distribution as indicated by \bar{D}_5/\bar{D}_1 which is the ratio of the 5th moment, \bar{D}_5 , and the 1st moment, \bar{D}_1 , average particle sizes. When the ratio of these particle size averages, \bar{D}_5/\bar{D}_1 , goes through a maximum, ϕ_n goes through a maximum, but the viscosity goes through a minimum at this condition. In addition, for multimodal mixtures of monodisperse particles it has also been shown^{9,28} theoretically that a maximum in the ratio of \bar{D}_5/\bar{D}_1 is predicted by this new model when

The new analytical expression introduced in this study shows that a plot of the accumulated volume fraction of pigment particles vs. the square root of particle size should be a straight line for the theoretically preferred particle size distribution. This linear theoretical model was also found to be consistent with the experimentally developed linear model proposed by Kaeuffer. However, Kaeuffer proposed that his straight line went through the origin, but the analytical model developed in this paper has shown that this intercept is not zero. Thus, Kaeuffer's experimental model is only partially correct.

Starting with this new linear model for the theoretically preferred particle size distribution, another simplified analytical expression was also derived to calculate the xth moment average particle size, \bar{D}_x . The desired xth moment average particle size was found to depend primarily on the physical property to be predicted. Finally, the simplified calculation of the various \bar{D}_x particle size averages for this same square root particle size distribution should be useful in predicting the maximum packing fraction, maximum impact, and/or the minimum viscosity for pigments in most paint and coating applications.

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the volume fraction of the monomodal particles is proportional to the square root of the particle diameter.

Interestingly, Kaeuffer³¹ also proposed from experimental considerations that the maximum packing fraction for a particle mixture could be achieved when the accumulated volume fraction for the distribution was directly proportional to the square root of the particle diameter. In other words, according to Kaeuffer, the accumulated volume fraction should be a straight line function of the square root of the particle diameter. While Kaeuffer never offered any theoretical justification for this relationship, this approach appears to be useful as a tool to optimize particle size distributions involving blends of particles.

One of the objectives of this study was to address whether Kaeuffer's experimental observation could be developed theoretically from the author's previously published model.

GENERALIZED VISCOSITY/EQUATION ADDRESSING THE INFLUENCE OF PARTICLE SIZE DISTRIBUTION ON SUSPENSIONS AND PARTICULATE COMPOSITES

The complete generalized viscosity/modulus equation addressing particulate suspensions and composites has been developed over time and presented in a series of articles.^{8-12,28,33} However, the complete set of equations making up this model was introduced primarily in the first three articles⁸⁻¹⁰ of this series. The introduction of the fundamental equation describing this generalized viscosity model⁸ was generated from the Einstein limiting equations³⁴⁻³⁵ for spherical suspensions at very dilute concentrations. The packing fraction, ϕ_n , was then shown theoretically⁹ to have a strong dependence on particle size distribution as indicated by \bar{D}_5/\bar{D}_1 , which is the ratio of the 5th moment, \bar{D}_5 , and the 1st moment, \bar{D}_1 , average particle sizes. Finally, a new form of the interaction coefficient, σ , was shown¹⁰ to be significantly influenced by the number average particle size, \bar{D}_1 , in multiparticle latexes. The complete set of equations introduced in these first three introductory articles⁸⁻¹⁰ included the following:

$$\ln(\eta/\eta_0) = \left(\frac{[\eta]\phi_n}{\sigma - 1} \right) \left\{ \left(\frac{\phi_n - \phi}{\phi_n} \right)^{1-\sigma} - 1 \right\} \text{ for } \sigma \neq 1 \quad (1)$$

$$\sigma = \frac{\lambda_{PC}}{D_1} + \sigma_s \quad (2)$$

$$\phi_{\text{mult}} = 1 - (1 - \phi_m)^n \quad (3)$$

$$\phi_n = \phi_{\text{mult}} - (\phi_{\text{mult}} - \phi_m) e^{\alpha(1 - (\bar{D}_5/\bar{D}_1))} \quad (4)$$

$$\bar{D}_5 = \frac{\sum_{i=1}^n N_i D_i^5}{\sum_{i=1}^n N_i D_i^4} \quad \bar{D}_1 = \frac{\sum_{i=1}^n N_i D_i}{\sum_{i=1}^n N_i} \quad (5)$$

where, η = suspension viscosity; η_0 = viscosity of suspending medium, $[\eta]$ = intrinsic viscosity; σ = interaction coefficient; λ_{PC} = particle-particle constant part of the component of the interaction coefficient; σ_s = solvent-particle component of the interaction coefficient; ϕ = particle volume concentration; ϕ_n = particle packing fraction; ϕ_{mult} = ultimate particle packing fraction; ϕ_m = monodisperse particle packing; α = particle size distribution constant = 0.268; \bar{D}_1 = number average particle size or the 1st moment average particle size; \bar{D}_5 = 5th moment average particle size; N_i = number of particles of the *i*th particle size; n = number of different particle sizes in mixture; and D_i = diameter of the *i*th particle size.

First, it should be noted that equations (1-5) could easily be combined explicitly and incorporated into one equation that would be very cumbersome, to say the least. Consequently, with the advent of the computer it is very easy to work with each of these equations separately until they need to be combined in stages. While different considerations regarding this model have been described in more detail elsewhere,^{8-12,28,33} some important observations can be made regarding this model. First, consider some important observations regarding σ .

(1) The interaction coefficient, σ , in this model has been shown³³ to be directly proportional to and has the same sign as the interaction coefficient from Huggins and Kramer's equations for solutions. Since equation (1) has been shown elsewhere³³ to reduce directly to both Huggins and Kramer's equations for solutions, the correlation of the interaction coefficients was a simple but direct result.

(2) Consequently, when $\sigma \geq 1$ the mixture would be a well defined suspension or composite. When the interaction coefficient is $0 \leq \sigma < 1$ the mixture formed would be somewhere between a solution and a suspension (i.e., plastisizer). Finally, when the interaction coefficient is $\sigma < 0$ the particle/solute forms a solution with the matrix or solvent.

(3) In addition, by simply changing the magnitude of the interaction coefficient, the generalized viscosity model described primarily by equation (1) was also found to reduce to several other well known suspension equations. For example, when the interaction coefficient $\sigma = 0$ the Arrhenius equation³⁶ results, when $\sigma = 1$ the Krieger-Dougherty equation³⁷ results, and when $\sigma = 2$ the Mooney equation³⁸ results.

(4) The particle-particle component of σ has also been found to be an inverse function of particle size as indicated by \bar{D}_1 . In particular, as the number average particle size decreases the interaction coefficient increases and vice-versa.

Extended discussions of the full utilization of the interaction coefficient have been presented elsewhere.^{8,10,33}

The packing fraction, ϕ_n , is also an extremely important variable associated with the generalized viscosity/modulus model. Some important observations regarding ϕ_n as discussed previously⁹⁻¹⁰ would include:

(1) The packing fraction, ϕ_n , is primarily a function of the particle size distribution as indicated by the ratio,

\bar{D}_5/\bar{D}_1 . This means that as the ratio of \bar{D}_5/\bar{D}_1 increases the packing fraction increases.

(2) When the particle size distribution as indicated by the ratio, \bar{D}_5/\bar{D}_1 , of particle size averages goes through a maximum, ϕ_n , as indicated in equation (4) also goes through a maximum. As the packing fraction goes through a maximum, a MacLaurin series expansion of equation (1) can be easily shown to yield a minimum in viscosity or modulus using the generalized viscosity model as has been shown elsewhere.⁹

An extended analysis of ϕ_n for several applications has been addressed in some detail elsewhere.^{9,10,12,28}

As indicated above, this model described by equations (1-5) can be significantly influenced both by the number average particle size, \bar{D}_1 , in the interaction coefficient, σ , and influence of the particle size distribution, \bar{D}_5/\bar{D}_1 , on the packing fraction, ϕ_n , simultaneously for selected applications. This consideration would be particularly important, for example, when the viscosity of a preferred blend of two broad latex particle size distributions might need to be addressed.

As already discussed, when the ratio of \bar{D}_5/\bar{D}_1 goes through a maximum, ϕ_n as indicated in equation (4) also goes through a maximum. It has also been shown experimentally, as discussed previously,⁸⁻¹⁰ that the minimum viscosity for blends of multiple particles typically occurs when the value of the ratio of \bar{D}_5/\bar{D}_1 is at a maximum. It has also been shown²⁸ that at the maximum value of \bar{D}_5/\bar{D}_1 for blends of multiple particles results when the individual volume fraction, f_i , for each particle size can be described as:

$$f_i = \frac{\sqrt{D_i}}{\sum_{i=1}^{i=n} \sqrt{D_i}} \quad (6)$$

Equation (6) can then be expanded to define an accumulated volume fraction, $f_{\Sigma\beta}$ as

$$f_{\Sigma\beta} = \sum_{i=1}^{i=\beta} f_i = \frac{\sum_{i=1}^{i=\beta} \sqrt{D_i}}{\sum_{i=1}^{i=n} \sqrt{D_i}} \quad (7)$$

In the next section it will be shown that a linear relationship can be developed utilizing equations (6) and (7).

DEVELOPMENT OF THE STRAIGHT LINE ANALYSIS OF THE THEORETICALLY PREFERRED DISTRIBUTION

Based on experimental considerations, Kaeuffer³² suggested that the optimum particle size distribution for a pigment in a paint would be achieved when the accumulated volume fraction for the distribution was directly proportional to the square root of the particle diameter. In other words, according to Kaeuffer, the accumulated volume fraction from the smallest particle size up to the largest particle size considered, D_{β} , as was assumed to be dependent on the square root of the particle diameter as:

$$\sum_{i=1}^{i=\beta} f_i = a\sqrt{D_{\beta}} \quad (8)$$

Kaeuffer based this relationship primarily on oil absorption analysis measurements and did not offer any theoretical justification nor any additional verification that this was indeed a description of an optimum particle size distribution.

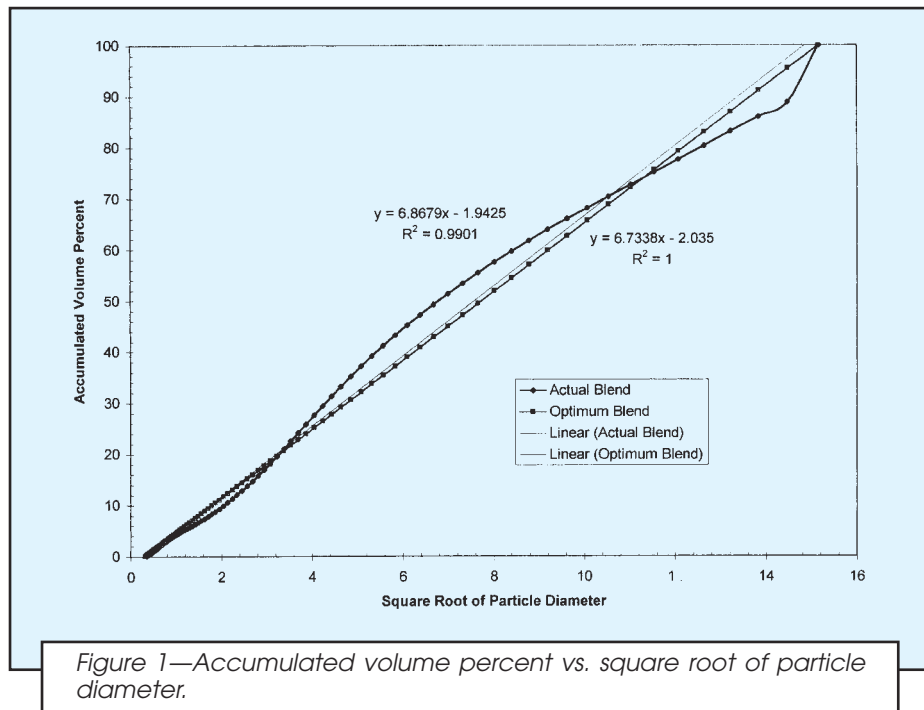


Figure 1—Accumulated volume percent vs. square root of particle diameter.

As already indicated, the theoretically preferred particle size distribution described by equation (6) was found to result^{9,28} when the particle size distribution has been mathematically manipulated to maximize the ratio of \bar{D}_5/\bar{D}_1 . However, it was of interest to see whether equations (6) and (7) could then be developed into an equation of the type described by Kaeuffer as indicated by equation (8).

If equation (8) had described the general equation for a straight line then it would have been more appropriately written as:

$$\sum_{i=1}^{i=\beta} f_i = a\sqrt{D_\beta} + b \quad (9)$$

Values for a and b in equation (9) can be directly calculated based on the following two boundary conditions.

For n = 1 then

$$D_\beta = D_1 \quad \text{and} \quad f_{\Sigma 1} = \sum_{i=1}^{i=1} f_i = f_i = \frac{\sqrt{D_1}}{\sum_{i=1}^{i=n} \sqrt{D_i}} \quad (10)$$

For n = β then

$$D_\beta = D_\beta \quad \text{and} \quad f_{\Sigma \beta} = \sum_{i=1}^{i=\beta} f_i = \frac{\sum_{i=1}^{i=\beta} \sqrt{D_i}}{\sum_{i=1}^{i=n} \sqrt{D_i}} \quad (11)$$

Substituting the conditions of equations (10) and (11) into equation (9) and solving gives

$$a = \frac{\sum_{i=1}^{\beta} \sqrt{D_i} - \sqrt{D_1}}{(\sqrt{D_\beta} - \sqrt{D_1}) \sum_{i=1}^n \sqrt{D_i}} \quad b = \frac{\sqrt{D_1} \left(\sqrt{D_\beta} - \sum_{i=1}^{\beta} \sqrt{D_i} \right)}{(\sqrt{D_\beta} - \sqrt{D_1}) \sum_{i=1}^n \sqrt{D_i}} \quad (12)$$

If equation (9) is in fact a straight line, then it must be shown that the values for a and b must be constants. To accomplish this objective, first note that many particle size analyzers (i.e., the LS 130 Coulter Counter) maintain a constant ratio between successive particle sizes analyzed, Z, such that for this Coulter Counter Z = 1.095329 that can be described as

$$D_i = Z^{i-1} D_1 \quad (\text{where in general } Z > 1) \quad (13)$$

Note that the maximum range of particles that can be indicated using the LS 130 Coulter Counter is from 0.1 to 899.9 microns. It can easily be shown using equation (13) that the maximum number of different particle size groups that can be analyzed with this machine is n = 101. With such a relationship as indicated by equation (13) it can easily be shown that

$$\sum_{i=1}^{i=n} \sqrt{D_i} = \left(\sqrt{D_1} \right) \left(\frac{\sqrt{Z^n} - 1}{\sqrt{Z} - 1} \right) \quad (14)$$

Substituting equations (13) and (14) into equation (12) gives

$$a = \left(\frac{1}{\sqrt{D_1}} \right) \left(\frac{\sqrt{Z}}{\sqrt{Z^n} - 1} \right) \quad b = \left(\frac{1}{1 - \sqrt{Z^n}} \right) \quad (15)$$

Since the values for the smallest particle size in the distribution (D_1), the ratio between consecutive particle sizes analyzed (Z), and the number of different sized particles in the distribution (n), are all constants for the theoretically preferred particle size distribution, then the values for a and b in equation (9) are indeed constants. Thus, the theoretically preferred particle size distribution as defined by equation (6) also implies that this same particle size distribution would form a straight line between the accumulated volume fraction and the square root of the particle diameter. These results also indicate that the intercept constant b is clearly not zero as was suggested by Kaeuffer and that the equation proposed by Kaeuffer is only partially correct.

An example of this straight line relationship between the accumulated volume fraction and the square root of the particle diameter is illustrated in Figure 1. Note that the maximum particle size analyzed in Figure 1 is 229.6 microns, which makes the maximum number of particle size groups to be n = 86. The straight line in Figure 1 has been defined by equations (9) and (15) for the theoretically preferred particle size distribution. The objective then of the blends of particle size distributions is to approach as close as possible to the theoretically preferred particle size distribution straight line as shown in Figure 1. Also shown in Figure 1 is an example of the optimal blend of three different but typical particle size distributions that might be available commercially to best match the theoretically preferred particle size distribution. Such blends as indicated in Figure 1 can be used to tune the pigment particle size distributions in paints and coatings as required to meet a specific physical property and/or to potentially develop a balance between physical properties (i.e., viscosity and impact) such as discussed elsewhere.²⁷

SIMPLIFIED AVERAGE PARTICLE SIZE ANALYSIS OF THE THEORETICALLY PREFERRED PARTICLE SIZE DISTRIBUTION

Two important average particle diameters of particle size distributions as indicated by \bar{D}_1 and \bar{D}_5 can be defined as:

$$\bar{D}_1 = \frac{\sum_{i=1}^n N_i D_i}{\sum_{i=1}^n N_i} \quad \bar{D}_5 = \frac{\sum_{i=1}^n N_i D_i^5}{\sum_{i=1}^n N_i D_i^4} \quad (5)$$

Such that in general

$$\bar{D}_x = \frac{\sum_{i=1}^n N_i D_i^x}{\sum_{i=1}^n N_i D_i^{x-1}} \quad (16)$$

Based on simplifying considerations introduced in the last section, an analytical description of the general average particle size, \bar{D}_x , described by equation (16) can be developed for the theoretically preferred particle size distribution. However, to achieve this further simplification, a relationship for the value of the number of each

particle size, N_i , needs to be evaluated. By definition, the volume fraction of a particle size distribution is normally defined as

$$f_{oi} = \frac{N_i D_i^3}{\sum_{i=1}^n N_i D_i^3} \quad (17)$$

Recalling that the volume fraction for the theoretically preferred particle size distribution as developed by the Sudduth Model^{8,9,28} can also be defined as

$$f_{oi} = \frac{\sqrt{D_i}}{\sum_{i=1}^n \sqrt{D_i}} \quad (6)$$

Combining equations (17) and (6) for the ratio of the volume fraction for two different particles sizes i and j and then setting these ratios equal to each other gives

$$N_i = \left(\frac{\sqrt{D_i}}{D_i^3} \right) \left(\frac{D_j^3}{\sqrt{D_j}} \right) N_j = \left(\frac{D_j^{2.5}}{D_i^{2.5}} \right) N_j \quad (18)$$

Then combining equations (13), (16), and (18) yields

$$\bar{D}_x = D_1 \frac{\sum_{i=1}^n Z^{(x-2.5)(i-1)}}{\sum_{i=1}^n Z^{(x-3.5)(i-1)}} \quad (19)$$

Equation (19) can then be further simplified to give

$$\bar{D}_x = \frac{\sum_{i=1}^n N_i D_i^x}{\sum_{i=1}^n N_i D_i^{x-1}} = \left(\frac{Z^{(x-3.5)} - 1}{Z^{(x-2.5)} - 1} \right) \left(\frac{Z^{(x-2.5)n} - 1}{Z^{(x-3.5)n} - 1} \right) D_1 \quad (20)$$

Thus, if the ratio Z for the LS 130 Coulter Counter is equal to $Z = 1.095329$, and $D_1 = 0.1$ microns, then the dif-

ferent weighted particle size averages can be calculated for the different numbers of particles, n , in the blend as indicated in Figure 2. Note that if the magnitude of a specific \bar{D}_x average is known, then the values for n and D_1 can be estimated using equation (20) or Figure 2. As a result, the straight line constants a and b as indicated by equation (15) for the theoretically preferred particle size distribution can then be determined from known values for the D_1 , Z , and n .

As $n \rightarrow \infty$ then equation (20) reduces to

$$\bar{D}_x = \left(\frac{Z^{(x-3.5)} - 1}{Z^{(x-2.5)} - 1} \right) Z^n D_1 \quad (\text{where } x \geq 4.0) \quad (21)$$

The simplification error in going from equation (20) to equation (21) is normally very small if the number of particles is greater than 60 or $n \geq 60$. However, calculation of the x th moment using both equations (20) and (21) is the most direct way to determine if the number of particles in a specific application is large enough to accept the simplification of equation (21).

But

$$D_{\text{Maximum}} = Z^{n-1} D_1 \quad (13)$$

Thus equation (21) becomes

$$\bar{D}_x = \left(\frac{Z^{(x-3.5)} - 1}{Z^{(x-2.5)} - 1} \right) Z D_{\text{Maximum}} \quad (22)$$

If the ratio Z for the LS 130 Coulter Counter is equal to $Z = 1.095329$ and $X = 4$, then

$$\frac{\bar{D}_4}{D_{\text{Maximum}}} = \frac{Z^{0.5} - 1}{Z^{1.5} - 1} \quad Z = 0.34861898 \quad (23)$$

Thus, if the maximum diameter in the particle size distribution, D_{Maximum} , is known, the limiting 4th moment average particle size, \bar{D}_4 , can readily be calculated.

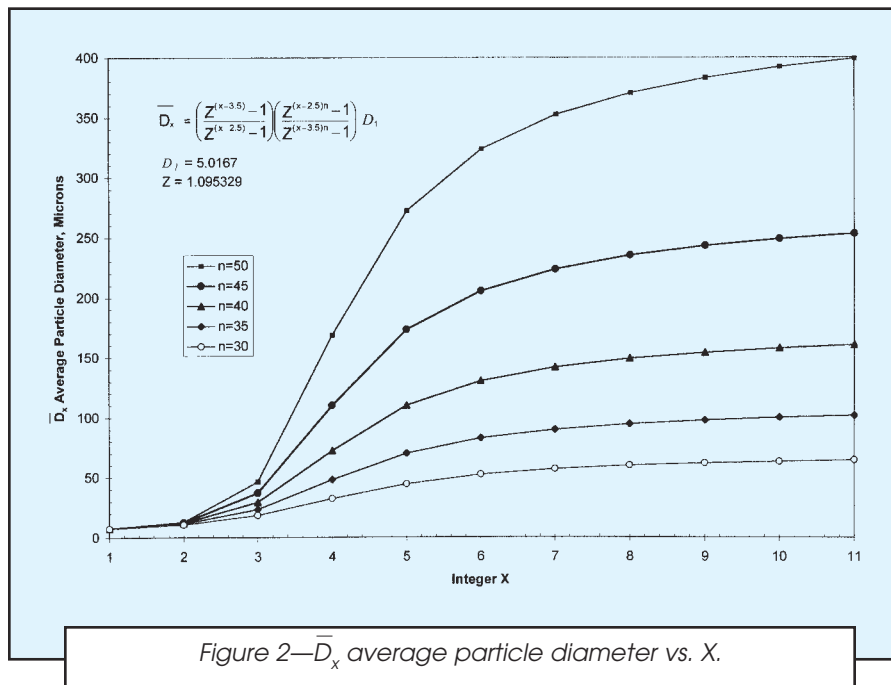
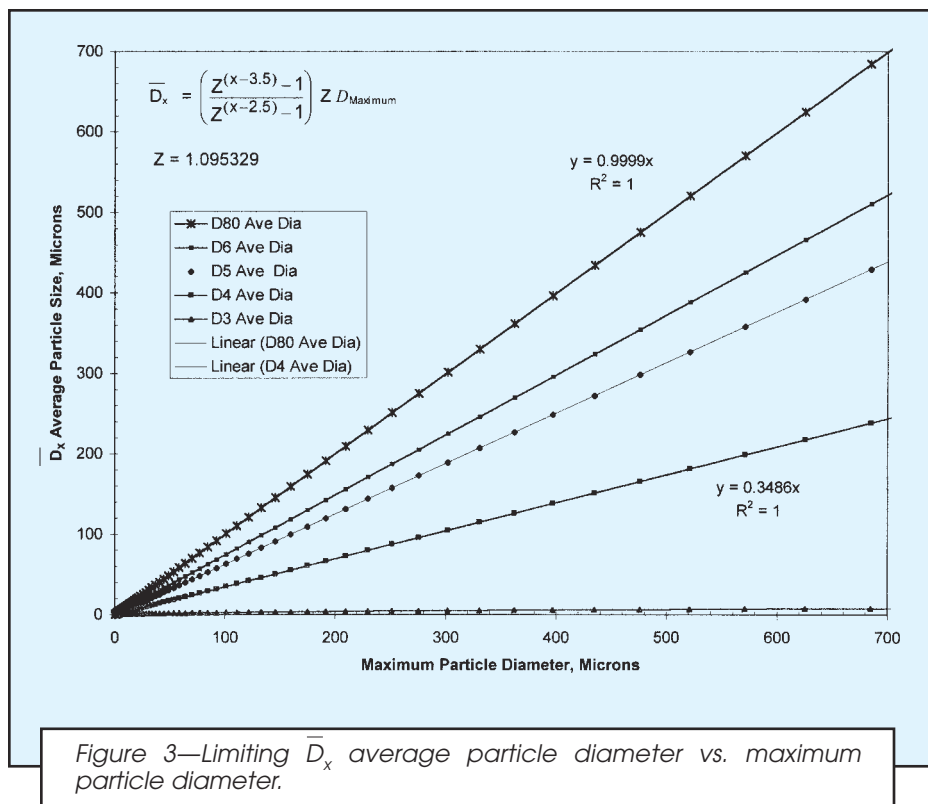


Figure 2— \bar{D}_x average particle diameter vs. X .



Again, assuming that $Z = 1.095329$ and assuming that the number of particles in the mixture is large enough to be able to simplify equation (20) to equation (21), then the limiting \bar{D}_x averages can be calculated using equation (22) as illustrated in Figure 3 for the theoretically preferred particle size distribution. Note particularly for \bar{D}_x average particle sizes calculated using equation (22) that it is not necessary to know the exact number of particle sizes, n , in the mixture. It is only necessary to know the x th moment desired, the value for ratio between particle size measurements Z and the largest particle size in the mixture, D_{Maximum} , as indicated in Figure 3. Equation (22) can also sometimes be particularly desirable to use when you may want to work backward to estimate the number of particle sizes, n , that need to be in the mixture if you know the desirable D_{Maximum} , and the desirable magnitude of the \bar{D}_x particle size average. In addition, once the number of particles that are needed in the blend are known, then it is possible to calculate the slope and intercept of the theoretically preferred particle size distribution as indicated by equation (15).

Which limiting \bar{D}_x particle size average would be of interest depends primarily on which physical property is desired to be predicted. For example, it has already been indicated that to predict the viscosity⁸⁻¹⁰ and/or modulus¹¹ then both the 1st moment or number average particle size, \bar{D}_1 , and the 5th moment average particle size, \bar{D}_5 , would be need to be evaluated. However, to predict the impact performance^{26,27} then the surface average particle size, \bar{D}_3 , would be of interest and could readily be calculated using either equation (20), (21), or (22).

It has also recently been found²⁷ that these average particle sizes can be particularly important when trying

to balance simultaneously several physical properties such as viscosity and impact. If three or more particle sizes have been utilized in the distribution, then the optimum particle size distribution utilized can apparently be characterized using the square root distribution described by equation (6) independent of the magnitude of the particle-particle component, λ_{pc} , of σ . This same square root particle size distribution should be able to satisfactorily predict the maximum packing fraction and/or the minimum viscosity for most paint and coating applications. However, it has also been found²⁷ that when balancing physical properties for binary particle size distributions, the influence of the preferred particle size distribution as determined using a square root distribution does not necessarily predict the most desirable particle size distribution. This is apparently particularly true²⁷ for binary particle size distributions if the λ_{pc} of the interaction coefficient, σ , is too high. However, since most common practical particle size distributions are rarely binary and usually consist of particle size distributions with considerably more than three particle sizes, the new approach described in this study to predict the various \bar{D}_x particle size averages can be invaluable. This is particularly true when trying to optimize and/or balance one or more physical properties based primarily on particle size distributions.

CONCLUSION

Based on simplifying considerations introduced in this study, it has been shown that a new theoretical analytical expression can be derived for a straight line between the accumulated volume fraction of particles and the square root of particle size. The derivation of this new linear relationship evolved from an extension of the generalized viscosity/modulus model for suspensions/composites published earlier by this author. Kaeuffer also suggested from experimental considerations that an optimum particle size distribution for a pigment in a paint would be achieved when the accumulated volume fraction for the distribution was directly proportional to the square root of the particle diameter. However, the importance of the non-zero intercept in the correct straight line relationship was not identified by Kaeuffer. Thus, the equation proposed by Kaeuffer from experimental considerations is only partially correct. The application simplicity of this new straight line analysis was also illustrated using a blend of three different particle size distributions.

Using this same theoretically preferred particle size distribution, it was also shown that an analytical description can also be derived for the general x th moment average particle size, \bar{D}_x . The analytical expression for \bar{D}_x uses only the value for the smallest particle size in the distribution (D_1), the ratio between consecutive particle sizes analyzed (Z), and the number of different sized particles in the distribution (n), to calculate the x th moment average particle size \bar{D}_x . Which x th moment average particle size that would be of interest was found to depend primarily on the physical property rest to be evaluated. For viscosity or modulus, both the 5th moment average particle size, \bar{D}_5 , and the 1st moment or number average particle size, \bar{D}_1 , would be of interest. However, to predict impact performance the 3rd moment or surface average particle size, \bar{D}_3 , would be of interest.

In a companion study²⁷ it has been found that these average particle sizes can be particularly important when trying to balance simultaneously several physical properties such as viscosity and impact. For binary particle size distributions, the influence of the preferred particle size distribution as determined using a square root distribution does not necessarily predict the most desirable particle size distribution since the interaction coefficient can also significantly influence the resulting physical properties. However, if three or more particles have been utilized in the distribution, then the theoretically preferred particle size distribution can normally be characterized using the square root analysis approach independent of the magnitude of the particle-particle component, of the interaction coefficient. Since most practical particle size distributions are rarely binary and usually consist of particle size distributions with considerably more than three particle sizes, the new approach introduced in this study to predict any of the x th moment average particle sizes, \bar{D}_x , can be invaluable. This is particularly true when trying to balance one or more physical properties based primarily on pigment particle size distributions.

References

- Vand, V., *J. Phys. Colloid Chem.*, 52, 277 (1948).
- Ackermann, N.L. and Shen, H.T., "Rheological Characteristics of Solid-Liquid Mixtures," *AIChE Journal*, 25, 327 (1972).
- Jinescu, V.V., "Rheology of Suspension," *Int. Chem. Eng.*, 14, 397 (1974).
- Eckersley, S.T. and Helmer, B.J., "Mechanistic Considerations of Particle Size Effects on Film Properties of Hard/Soft Latex Blends," *JOURNAL OF COATINGS TECHNOLOGY*, 69, No. 864, 97 (1997).
- Chong, J.S., Christiansen, E.B., and Baer, A.D., "Rheology of Concentrated Suspensions," *J. Appl. Polym. Sci.*, 15, 2007 (1971).
- Parkinson, C., Matsumoto, S., and Sherman, P., "The Influence of Particle Size Distribution on the Apparent Viscosity of Non Newtonian Dispersed Systems," *J. Colloid Interface Sci.*, 33, 150 (1970).
- Luckham, P.F. and Ukeje, M.A., "Effect of Particle Size Distribution on the Rheology of Dispersed Systems," *J. Colloid Interface Sci.*, 220, No. 2, 347-356 (1999).
- Sudduth, R.D., "A Generalized Model to Predict the Viscosity of Solutions with Suspended Particles. I," *J. Appl. Polym. Sci.*, 48, 25 (1993).
- Sudduth, R.D., "A New Method to Predict the Maximum Packing Fraction and the Viscosity of Solutions with a Size Distribution of Suspended Particles II," *J. Appl. Polym. Sci.*, 48, 37 (1993).
- Sudduth, R.D., "A Generalized Model to Predict the Viscosity of Solutions with Suspended Particles, Part III," *J. Appl. Polym. Sci.*, 50, 123-147 (1993).
- Sudduth, R.D., "Modulus Evaluation of Particulate Composites Using Generalized Viscosity Model for Solutions with Suspended Particles," *J. Appl. Polym. Sci.*, 54, 1243 (1994).
- Sudduth, R.D., "A Generalized Model to Predict the Effect of Voids on Modulus in Ceramics," *J. Mater. Sci.*, 30, 4451 (1995).
- Kausch, H.H., Beguelin, P., and Fisher, M., "Failure of Particulate Reinforced Polymers," *Mech. Compos. Mater.*, 36, No. 3, 177 (2000).
- Schwarzl, F.R., Bree, H.W., Nederveen, C.J., Schwippert, G.A., Struik, L.C.E., and Van der Wal, C.W., "Behavior of Unfilled and Filled Rubbers in Shear in the Glass Transition Region," *Rubber Reviews*, 42, No. 1, 557 (1969).
- Hashin, Z., "Extremum Principals for Elastic Heterogenous Media with Imperfect Interfaces and Their Application to Bounding of Effective Moduli," *J. Mech. Phys. Solids*, 40, No. 4, 767 (1992).
- Dutta, N.K. and Tripathy, D.K., "Effects of Types of Fillers on the Molecular Relaxation Characteristics, Dynamic Mechanical, and Physical Properties of Rubber Vulcanizates," *J. Appl. Polym. Sci.*, 44, 1635 (1992).
- Lewis, T.B. and Nielsen, L.E., "Dynamic Mechanical Properties of Particulate-Filled Composites," *J. Appl. Polym. Sci.*, 14, 1449 (1970).
- Bartczak, Z., Argon, A.S., Cohen, R.E., and Weinberg, M., "Toughness Mechanism in Semi-Crystalline Polymer Blends: II High-Density Polyethylene Toughened with Calcium-Carbonate Filler Particles," *Polymer*, 40, No. 9, 2347 (1999).
- Wei, G.X., Sue, H.J., Chu, J., Huang, C., and Gong, K., "Toughening and Strengthening of Polypropylene Using the Rigid-Rigid Polymer Toughening Concept Part I. Morphology and Mechanical Property Investigations," *Polymer*, 41, No. 8, 2947 (2000).
- Nakamura, Y., Yamaguchi, M., Masayoshi, and Matsumoto, T., "Effects of Particle Size on Mechanical and Impact Properties of Epoxy Resin Filled with Spherical Silica," *J. Appl. Polym. Sci.*, 45, 1281 (1992).
- Cigna, G., Lomelli, P., and Merlotti, M., "Impact Thermoplastics: Combined Role of Rubbery Phase Volume and Particle Size on Toughening Efficiency," *J. Appl. Polym. Sci.*, 37, 1527 (1989).
- Bucknall, C.B., Rizzieri, R., and Moore, D.R., "Detection of Incipient Rubber Particle Cavitation in Toughened PMMA Using Dynamic Mechanical Tests," *Polymer*, 41, No. 11, 4149 (2000).
- Liang, J.Z. and Li, R.K.Y., "Rubber Toughening in Polypropylene: A Review," *J. Appl. Polym. Sci.*, 77, No. 2, 409 (2000).
- Smit, R.J.M., Brekelmans, W.A.M., and Meijer, H.E.H., "Predictive Modeling of the Properties and Toughness of Polymeric Materials, Part II: Effect of Microstructural Properties on the Macroscopic Response of Rubber Modified Polymers," *J. Mater. Sci.*, 35, 2869 (2000).
- Bucknall, C.B., Karpodinis, A., and Zhang, X.C., "A Model for Particle Cavitation in Rubber-Toughened Plastics," *J. Mater. Sci.*, 29, 3377 (1994).
- Sudduth, R.D., "A Theoretical Development of the Relationship Between Grafting and Particle Size on Impact in Two Phase Plastics," *J. Appl. Polym. Sci.*, 22, No. 9, 2427 (1978).
- Sudduth, R.D., "Optimizing the Balance Between Viscosity/Modulus and Impact in Particulate Composites," *J. Appl. Polym. Sci.*, 83, 291 (2002).
- Sudduth, R.D., "A Generalized Model to Predict the Viscosity of Solutions with Suspended Particles, Part IV—Determination of Optimum Particle to Particle Volume Fractions," *J. Appl. Polym. Sci.*, 52, 985 (1994).
- Hoy, K.L., "The Effect of Particle-Size Distribution on the Rheology and Film Formation of Latex Coatings," in *Organic Coatings and Science and Technology*, Vol. 5, Parfitt, G.D. and Patis, A.V. (Eds.), Dekker, New York, 1983.
- Lee, D.L., *JOURNAL OF PAINT TECHNOLOGY*, 42 No. 550, 513 (1961).
- Farris, R.J., "Prediction of the Viscosity of Multimodal Suspensions from Unimodal Viscosity Data," *Transactions of the Society of Rheology*, 12:2, 281 (1968).
- Kaeuffer, J.L., "Determination of the Optimum Granulometric Packing and Some Related Properties," *Double Liaison-Chim. Peint.*, 22, 239-240, 343 (1972).
- Sudduth, R.D., "Development of Huggins' and Kraemer's Equations for Polymer Solution Evaluations from the Generalized Viscosity Model for Suspensions," *J. Appl. Polym. Sci.*, 66, 2319 (1997).
- Einstein, A., *Ann. Phys.*, 19, 289 (1906).
- Einstein, A., *Ann. Phys.*, 34, 591 (1911).
- Arrhenius, *Biochem.*, 1, 11, 112 (1917).
- Krieger, I.M. and Dougherty, T.J., *Trans. Soc. Rheol.*, 3, 137 (1959).
- Mooney, M., *J. Colloid Sci.*, 6, 2, 162 (1952).