Optimizing the Balance Between Viscosity/Modulus and Impact in Particulate Composites

RICHARD D. SUDDUTH

Chemical Engineering Department, University of Louisiana at Lafayette, Box 44130, Lafayette, Louisiana 70504-4130

Received 25 August 2000; accepted 25 January 2001

ABSTRACT: The objective of this study was to develop some new concepts of importance when trying to optimize the viscosity/modulus and impact relative to the particle-size distribution in suspensions and particulate composites. The results of this study appear to indicate that, conceptually, it is possible to significantly improve the viscosity versus the impact balance for material formulations by optimizing the particle-size distribution. For binary particle-size distributions, the influence of the preferred particle-size distribution, as determined using a square-root distribution, did not yield the most desirable particle-size distribution if the particle-to-particle component of the interaction coefficient was high. However, if three or more particles were utilized in the distribution, then the optimum particle-size distribution utilized can apparently be characterized using the square-root distribution even when the particle–particle component, σ_{pc}, of the interaction coefficient, σ, was found to be quite high . In addition, this same square-root particle-size distribution can also satisfactorily predict a probability of impact that can remain consistently high as long as the particles utilized are well chosen and not too close in size. Thus, this preferred particle-size distribution can be utilized to predict at least one of the preferred distributions to optimize the balance of properties between impact and the viscosity/modulus. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 291–304, 2002

Key words: viscosity; suspension; modulus; particle size distribution; interaction coefficient; particulate composite

INTRODUCTION

As new materials with improved properties are developed for consumer applications, the importance of new techniques to control such physical properties as viscosity, modulus, impact, etc., has taken on new importance. This is particularly true for products with consumer potential that could involve, for example, the viscosity of particulate suspensions and/or the modulus as well as the impact for particulate/polymer compounds and composites. Consequently, a better theoretical understanding of how particulate additives influence such properties as viscosity,[1–7] modulus,[7–13] and impact[13–19] has received increased attention in the literature.

Recent reviews by Liang and Li,[18] Smit et al.,[20] and Bucknall et al.[21,22] addressed several of the currently accepted mechanisms of rubber toughening in polymers that, in some instances, were extensions of models by previous authors. Some of these mechanisms for rubber toughening include multiple crazing and damage competition theory,[23,24] rubber particle energy absorption,[25] shear band formation and shear-yielding theory,[26,27] dilatation,[28] and cavitation theories.[21,22] Liang and Li[18] also pointed out that there is a major need for a better description of these rubber-toughening theories in quantitative terms—particularly with regard to the need to improve the understanding of the distribution of the dispersed-phase particle size and suitable filler size.

One additional rubber-toughening theory involves the probability of a crack hitting a particle during the impact failure process. Fortunately, this last rubber-toughening concept has been able to generate some initial quantitative understanding of the influence of the particle size, particle-size distribution, and grafting on rubber-toughened polymers. The theory of impact toughening based on the probability of a crack hitting a particle was addressed by several authors.[19,29,30] Bragaw's model[29] attempted to consider the statistics of one-crack branching at a rubber particle which resulted in two new cracks, which, in turn, caused two new cracks as each crack hit another rubber particle. This model, however, did not indicate clearly why two new cracks were generated as a propagating crack hit a rubber particle instead of simply propagating the same crack or by propagating more than two new cracks. In addition, this model gave limited understanding of the influence of the particle size and particle-size distribution on impact.

The rubber-toughening probability model of Dinges and Schuster[30] did not consider multiple branching. Instead, this model considered the probability of a single crack hitting rubber particles as it propagated through the sample. Dinges and Schuster[30] considered only a monodisperse particle-size distribution in their probability model derivation. Consequently, their model was only able to empirically introduce the particle-size distribution and the volume fraction of rubber in their analysis and they were not able to effectively introduce the concept of grafting into their model. Several of the shortcomings of the Bragaw and the Dinges and Schuster models were overcome in the probability model developed by this author in an earlier publication.[19] This more extensive probability model[19] was able to show explicitly that the surface-average particle size, D_s, effectively characterizes both the average particle size and the particle-size distribution in rubber-toughened plastics. In addition, this probability model was also able to effectively introduce grafting, which, in turn, led to a well-defined impact maximum as a function of the particle size. An outline of the details of this model will be briefly reviewed in the next section of this article.

A new understanding of the influence of the particle size, particle-size distribution, and particle/matrix interaction on the viscosity of particulate suspensions and the modulus of particulate composites was also recently initiated as a result of the derivation and development of a new generalized viscosity/modulus equation.[31–38] This new generalized viscosity/modulus equation has been particularly effective in elucidating separately the influence of the particle size from that of the particle-size distribution on the viscosity and modulus of particulate composites.

One specific variable introduced in this new generalized viscosity/modulus equation is the packing fraction, ϕ_n, which has been found to depend primarily on the particle-size distribution as indicated by the ratio, D_5/D_1, of two well-defined particle-size averages D_5 and D_1. When the ratio of these particle-size averages, D_5/D_1, goes through a maximum, the packing fraction, ϕ_n, also goes through a maximum, *but* the viscosity goes through a minimum at this condition. It has also been shown theoretically that the value of the ratio of these two particle-size averages, D_5/D_1, goes through a maximum at a very specific volume fraction that can be determined from a knowledge of all the diameters of each of the groups of mondisperse particles in the mixture.

Another new variable introduced in this new generalized viscosity/modulus equation is the interaction coefficient, σ. This new interaction coefficient, σ, describes the interaction between the particle and the matrix and is partially dependent on the number-average particle size, D_1.

From other considerations, it has been suggested that the calculated particle-size distribution giving a minimum viscosity using the generalized viscosity/modulus model could very well also yield a maximum impact condition. Such a particle-size distribution condition could possibly result from an increase in the probability of hitting a particle for a crack propagating through a rubber- or particulate-toughened material. Therefore, it appears that by combining the viscosity model and the impact model it may be possible to optimize the properties of impact and viscosity simultaneously. Surprisingly, the potential for an optimum viscosity/modulus and impact balance by combining these models based primarily on the particle-size distribution has not yet been addressed in the literature. The objective of this study, then, was to develop some new concepts of consideration when trying to optimize these two

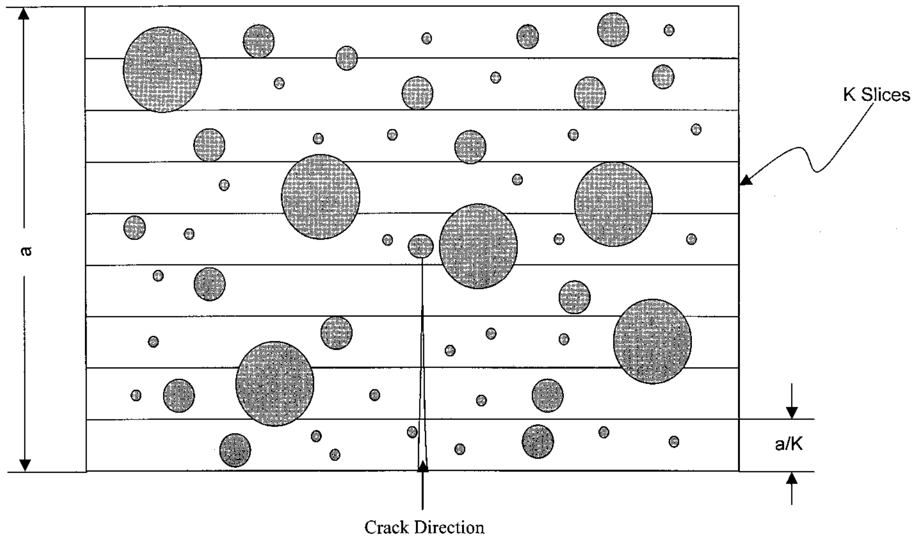

Figure 1 Model for the probability of a crack hitting a particle.

properties relative to the particle-size distribution.

PROBABILITY IMPACT MODEL ADDRESSING THE INFLUENCE OF PARTICLE-SIZE DISTRIBUTION

The probability model to be reviewed here was originally derived in a earlier article.[19] This model began by assuming that the rubber-modified polymer consisted of a rectangular specimen which has a propagating crack that will eventually reach a length **a** as indicated in Figure 1. If such a specimen as illustrated in Figure 1 is considered to be split into K slices, then the total cross-sectional area A_i of the i^{th} particle-size population in the K^{th} slice will be

$$A_i = (\pi/4)n_i D_i^2(1/K) \tag{1}$$

where n_i is the total number of particles in the sample of the i^{th} diameter, and D_i, the diameter of the i^{th} particle-size population.

The cross-sectional area A_{xs} exposed to the crack tip will then be

$$A_{\text{xs}} = V_T/a \tag{2}$$

where V_T is the total volume of the specimen, and a, the crack length. Thus, the probability of the crack tip hitting the i^{th} particle-size population in the K^{th} slice, P_i, is given as

$$P_i = \frac{(\pi/4)n_i D_i^2(1/K)}{(V_T/a)} \tag{3}$$

The total volume of the specimen is given as

$$V_T = \frac{(\pi/6)\sum n_i D_i^3}{f_{\text{RV}}} \tag{4}$$

where f_{RV} is the volume fraction of rubber in the sample. Substituting gives

$$P_i = \left(\frac{1}{K}\right)\left(\frac{(3/2)an_i D_i^2 f_{\text{RV}}}{\sum n_i D_i^3}\right) \tag{5}$$

Let P_{iK} be the probability of not hitting any of the particles in the i^{th} population in all of the K slices. Then,

$$P_{iK} = (1 - P_i)^K \tag{6a}$$

$$P_{iK} = \left[1 - \left(\frac{1}{K}\right)\left(\frac{(3/2)an_i D_i^2 f_{\text{RV}}}{\sum n_i D_i^3}\right)\right]^K \tag{6b}$$

Now, as K approaches infinity or $K \to \infty$,

$$P_{iK} \to \exp\left(\frac{-(3/2)an_i D_i^2 f_{\text{RV}}}{\sum n_i D_i^3}\right) \tag{7}$$

Now let $1 - P_T$ be the probability of missing all particles in all of the particle-size populations. Then,

$$1 - P_T = P_{1K}P_{2K}P_{3K}P_{4K}\cdots P_{nK} \quad (8a)$$

$$= \exp\left(\frac{-(3/2)a \sum n_i D_i^2 f_{\mathrm{RV}}}{\sum n_i D_i^3}\right) \quad (8b)$$

But

$$D_S = D_3 = \frac{\sum_{i=1}^{n} N_i D_i^3}{\sum_{i=1}^{n} N_i D_i^2} \quad (9)$$

where $D_s = D_3$ is the surface-average particle size. Hence,

$$P_T = 1 - \exp\left(\frac{-(3/2)af_{\mathrm{RV}}}{D_s}\right) \quad (10)$$

where P_T is the probability of hitting at least one particle in at least one of the particle-size populations in at least one of the K slices.

It is also apparent that eq. (10) applies only to ungrafted particles. Note in Figure 2 that if the modulus of the graft layer of thickness T is assumed to increase to the point that it is essentially equal to that of the matrix phase then the effective diameter of the low-modulus substrate after grafting, D_{EFF}, would be

$$D_{\mathrm{EFF}} = D_i - 2T$$

For the grafted particles as indicated in Figure 2, then as developed in an earlier article,[19] the grafted form of eq. (10) can be written as

$$P_T = 1 - \exp\left(\frac{-(3/2)aC_{\mathrm{GT}}f_{\mathrm{RV}}}{D_s}\right) \quad (11)$$

$$C_{\mathrm{GT}} = \frac{\sum_{i=1}^{n} N_i (D_i - 2T)^2}{\sum_{i=1}^{n} N_i D_i^2} \quad (12)$$

where T is the graft thickness, and C_{GT}, the correction factor for the graft thickness.

As indicated in Figure 3, a plot of eq. (11) as a function of the surface-average particle size, D_s,

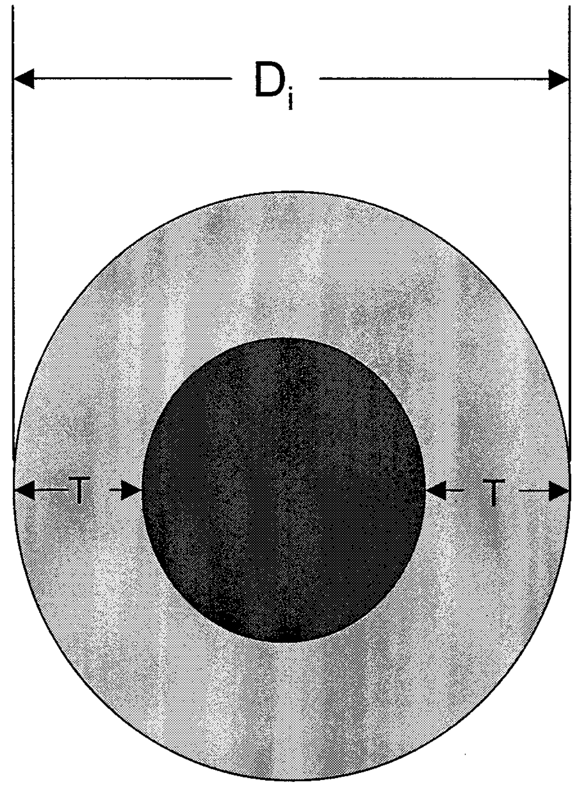

Figure 2 Model for a grafted rubber particle with graft thickness T.

shows that a maximum in impact is reached at a diameter that is equal to $D_s = 6T$. Such a maximum impact as a function of the particle size, as indicated in Figure 3, is well documented experimentally in the literature[16] for several different rubber-toughened polymers including nylon and polystyrene. However, for this study, only the ungrafted form of eq. (10) was utilized to address the optimum viscosity and impact combination as a function of particle size and particle-size distribution.

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 was developed over a series of articles.[31–38] The primary equation describing this generalized viscosity model was generated from the Einstein limiting equations[39,40] for spherical

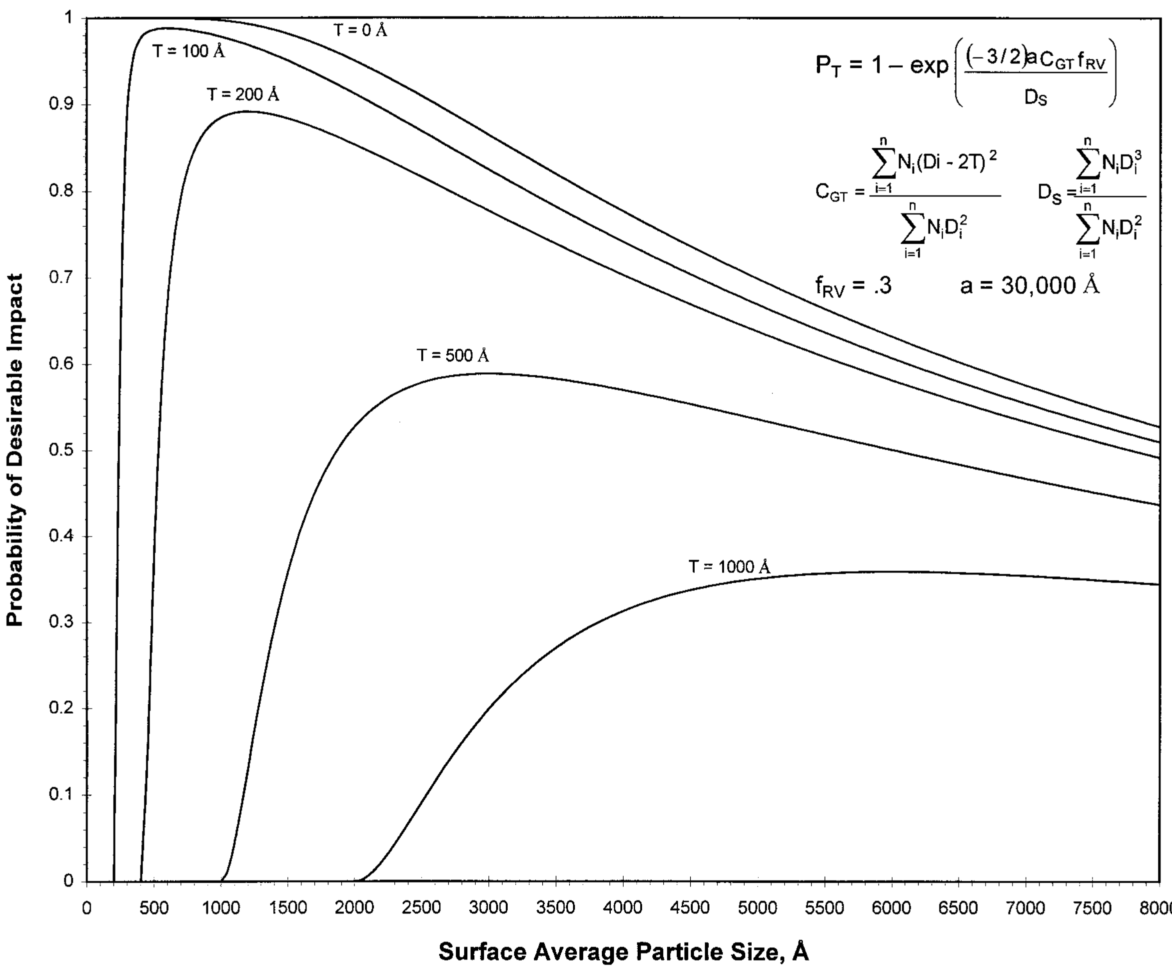

Figure 3 Probability of desirable impact versus particle size at different levels of grafting.

suspensions at very dilute concentrations in the series' first article.[31] This primary model introduced a packing fraction, ϕ_n, and a new form of an interaction coefficient, σ, as described by the following equations:

$$\ln(\eta/\eta_0) = \left(\frac{[\eta]\varphi_n}{\sigma - 1}\right)\left\{\left(\frac{\varphi_n - \varphi}{\varphi_n}\right)^{1-\sigma} - 1\right\} \quad \text{for } \sigma \neq 1 \tag{13}$$

$$\sigma = \frac{\sigma_{pc}}{D_1} + \sigma_s \tag{14}$$

where η is the concentrated viscosity; η_0, the viscosity of the suspending medium; $[\eta]$, the intrinsic viscosity; σ, the interaction coefficient; σ_{pc}, the particle–particle constant part of the component of the interaction coefficient; σ_s, the solvent–particle component of the interaction coefficient; ϕ, the particle volume concentration; ϕ_n, the particle packing fraction; and D_1, the number-average particle size.

This generalized viscosity model described by eq. (13) was found to reduce to several other well-known suspension equations by simply changing the magnitude of the interaction coefficient. When the interaction coefficient $\sigma = 0$, the Arrhenius equation[41] resulted; when $\sigma = 1$, the Krieger–Dougherty equation[42] resulted; and when $\sigma = 2$, the Mooney equation[43] resulted.

The second, third, and fourth articles[32–34] in this series addressed an extended analysis of the packing fraction, ϕ_n, to give the following equations:

$$\varphi_{\mathrm{nult}} = 1 - (1 - \varphi_m)^n \tag{15}$$

$$\varphi_n = \varphi_{\mathrm{nult}} - (\varphi_{\mathrm{nult}} - \varphi_m)e^{\alpha[1-(D_5/D_1)]} \tag{16}$$

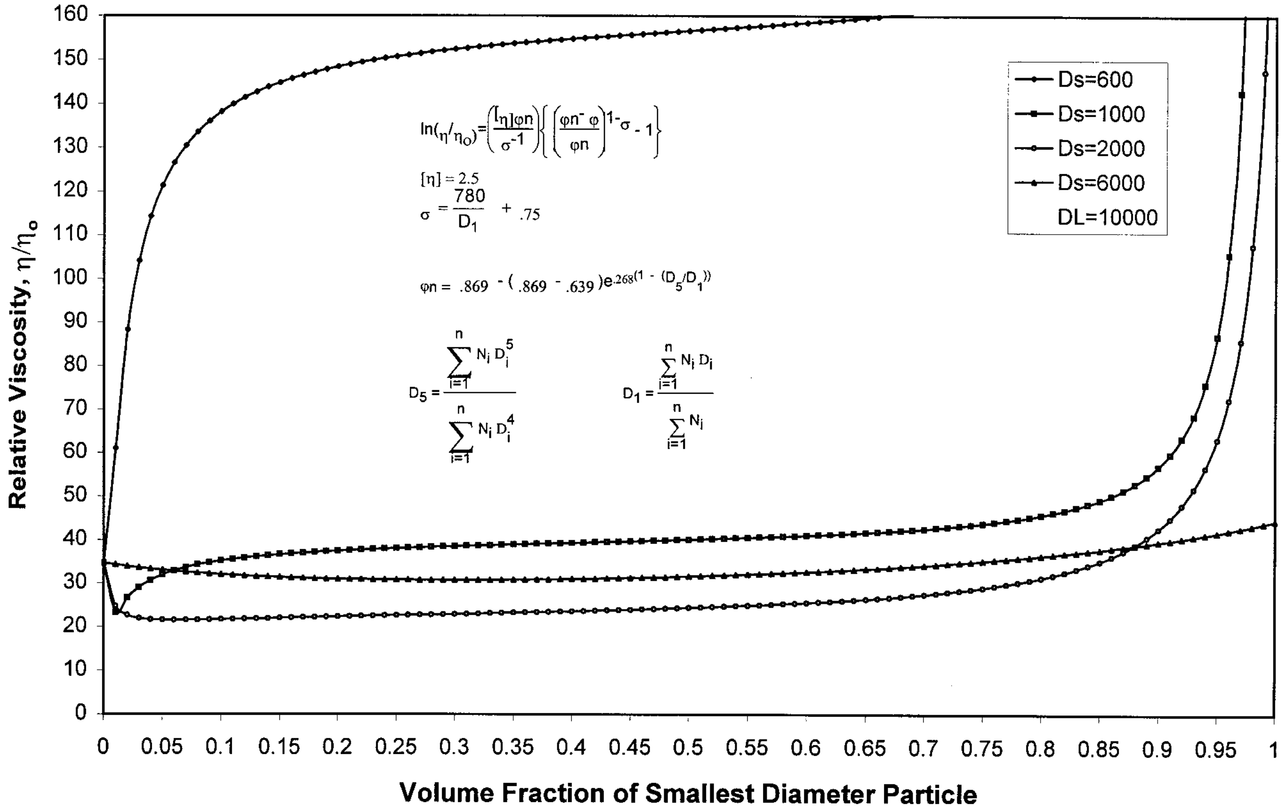

Figure 4 Viscosity and/or modulus as a function of particle-size distribution indicated by the volume fraction of the smallest diameter particle in a binary mixture of particles blended at 60 vol % ($\sigma_{pc} = 780$).

$$D_5 = \frac{\sum_{i=1}^{n} N_i D_i^5}{\sum_{i=1}^{n} N_i D_i^4} \qquad D_1 = \frac{\sum_{i=1}^{n} N_i D_i}{\sum_{i=1}^{n} N_i} \tag{17}$$

where ϕ_n is the particle packing fraction; ϕ_{nult}, the ultimate particle packing fraction; ϕ_m, the monodisperse particle packing fraction; n, the number of particles in the mixture; and D_i, the diameter of the i^{th} particle.

Note that the packing fraction, ϕ_n, was found to depend only on the ratio of the D_5 and D_1 particle-size averages. When the ratio of D_5/D_1 goes through a maximum, the packing fraction, as indicated in eq. (16), also goes through a maximum. In addition, it was shown previously[32–34] that the optimum/minimum viscosity for blends of multiple particles often occurs when the value of the ratio of D_5/D_1 is at an optimum/maximum. In addition, it has also been shown[34] that the optimum/maximum value of D_5/D_1 and the packing fraction, ϕ_n, for blends of multiple particles can be achieved when the volume fraction, f_i, is generated using the following formulation:

$$f_i = \frac{\sqrt{D_i}}{\sum_{i=1}^{i=n} \sqrt{D_i}} \tag{18}$$

Extended discussions of the full utilization of the interaction coefficient, σ, were addressed in the third and fifth articles in this series.[33–35] In general, it was found that, when the interaction coefficient was $\sigma < 0$, the particle/solute formed a solution with the matrix or solvent. When the interaction coefficient was $0 \leq \sigma < 1$, then the mixture was somewhere between a solution and a solvent, and, finally, when $\sigma \geq 1$, the mixture was a well-defined suspension or composite.

The sixth, seventh, and eighth articles in this series[36–38] showed that the model initially developed for the suspension viscosity applies equally

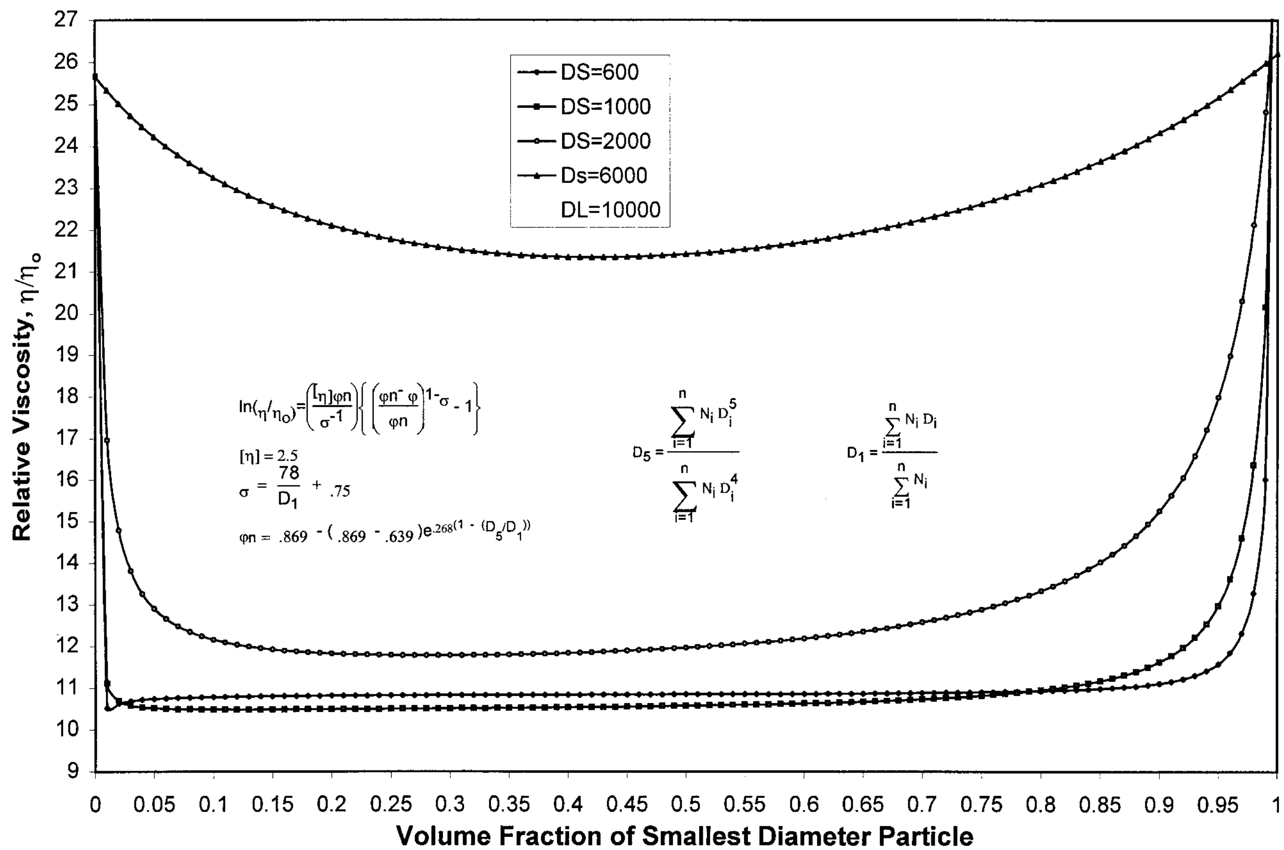

Figure 5 Viscosity and/or modulus as a function of particle-size distribution indicated by the volume fraction of the smallest-diameter particle in a binary mixture of particles blended at 60 vol % (σ_{pc} = 78).

well to the modulus of particulate composites. Interestingly, eqs. (13)–(18) were found to apply equally well to both the viscosity and the modulus. These then are the primary equations of interest in this study where the most important consideration was the influence on the viscosity.

COMBINED VISCOSITY AND IMPACT MODELS ADDRESSING THE INFLUENCE OF PARTICLE-SIZE DISTRIBUTION ON SUSPENSIONS AND PARTICULATE COMPOSITES

It is apparent that the above models involve different relationships to characterize the particle-size distribution to predict the viscosity/modulus, on the one hand, and the impact, on the other. Consequently, it was not immediately apparent that there was an optimum distribution that both minimizes the viscosity and maximizes the impact. In an effort to show conceptually that such a viscosity/impact property balance can be achieved, five different particles were chosen to develop some initial concepts to optimize these models. The first part of this study looked only at potential binary combinations or binary particle-size distributions of these five particles. This section of this study intended to show that such an optimum balance of viscosity and impact could exist, but it was not intended to establish the optimum particle-size distribution to use for all applications. The second phase of this study then looked at selected concepts to optimize all five particles in a mixture to evaluate a potential optimum distribution to achieve the desired balance between viscosity/modulus and impact.

BINARY PARTICLE-SIZE DISTRIBUTION INFLUENCE ON VISCOSITY AND IMPACT

The largest particle diameter used in these binary mixture calculations was maintained at a diame-

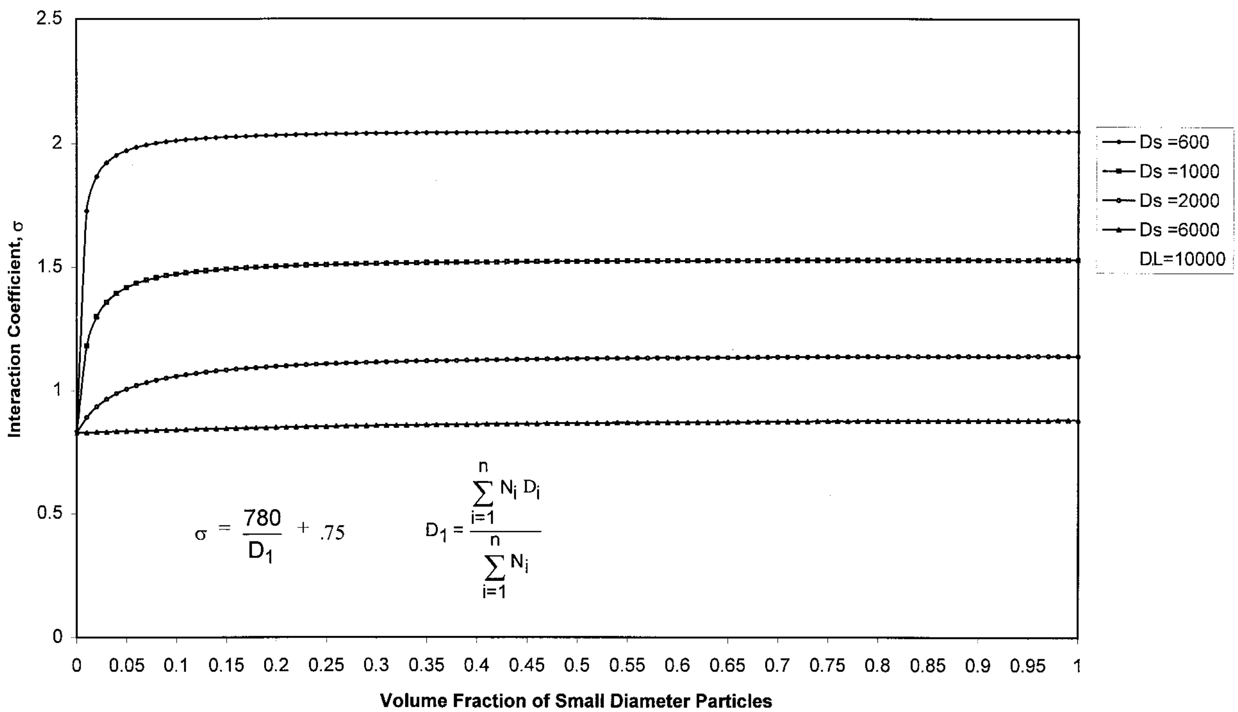

Figure 6 Interaction coefficient as a function of the binary mixture volume fraction of the smallest-diameter particle in a 60 vol % concentration composite (σ_{pc} = 780).

ter of 10,000 Å, while the smaller of the binary particle sizes included one of the following diameters: 6000, 2000, 1000, or 600 Å. These smaller particle sizes were blended from 0 to 100% by volume in the particle mixture and the particulate mixtures were then evaluated at a 60% concentration by volume in the suspension/particulate composite.

Two levels of the interaction coefficient, σ, were evaluated. Based on previously published latex data,[33] the two values chosen for the particle–particle interaction constant, σ_{pc}, of the particle interaction coefficient, σ, included either σ_{pc} = 780 Å or σ_{pc} = 78 Å. However, the solvent (matrix)/particle component, σ_s, of the interaction coefficient, σ, was maintained at $\sigma_s = 0.75$.

For this conceptual study, only a negligible graft thickness, T, at $T = 0$, was assumed for the impact model. A future publication will address the more extended influence of the graft thickness on the balance of the properties for viscosity and impact. A characteristic crack length of a = 30,000 Å was also assumed for the impact model evaluated in this study. The impact model was also evaluated at the same particle mixture volume concentration of $f_{RV} = 0.60$ as the viscosity/modulus characterization.

The results from the evaluation of these binary mixtures for σ_{pc} = 780 Å are summarized in Figure 4. For binary mixtures involving the 600-Å particles, it is apparent in Figure 4 that any increase in concentration of this particle size significantly increased the viscosity. While the 1000-Å particles did give a minimum in viscosity, it is apparent that this minimum was for only a very small concentration range. However, the nearly equivalent minimum viscosity for the 2000-Å particles was found to be very broad and easy to achieve in a practical sense. By contrast, for the case where σ_{pc} = 78 Å, a minimum viscosity did occur for the 600-Å particle binary mixture as indicated in Figure 5. However, again, the 1000-Å particle binary mixture gave almost the same relative minimum viscosity but a much broader minimum relative to concentration. Therefore, in a practical sense, the 1000-Å particles would be preferred over the 600-Å particles for the lower values of the interaction coefficient.

As indicated in Figure 6, the interaction coefficient, σ, ranged from 0.828 to 2.05 for the case where σ_{pc} = 780 Å and the range of particles addressed for the binary mixtures in Figure 4. By contrast, the interaction coefficient, σ, only ranged from 0.758 to 0.88 as indicated in Figure 7

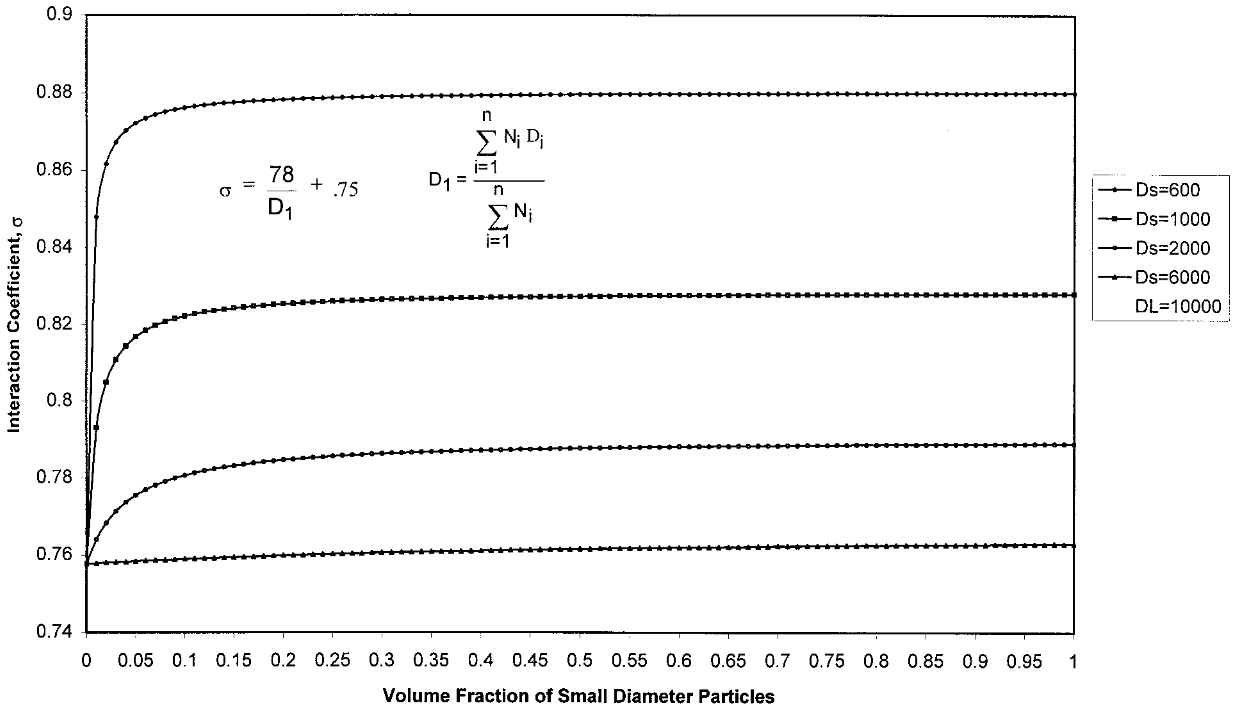

Figure 7 Interaction coefficient as a function of the binary mixture volume fraction of the smallest-diameter particle in a 60 vol % concentration composite (σ_{pc} = 78).

for these same binary mixtures when σ_{pc} = 78 Å. Therefore, the location of the minimum viscosity was strongly affected by the interaction coefficient, which, in turn, was a strong function of the number-average particle size.

As indicated in Figures 8 and 9, the location of the maximum values for the ratio of D_5/D_1 and the packing fraction, ϕ_n, did not necessarily predict the minimum viscosity for the larger particle–particle component of the interaction coefficient (σ_{pc} = 780 Å). This last result indicates that optimizing the packing fraction relative to the particle-size distribution does not always result in a minimum viscosity for binary mixtures when the particle–particle interaction coefficient, σ_{pc}, is strong or very significant.

The calculated impact evaluations for these same binary particle-size distributions are summarized in Figure 10. As indicated in Figure 10, the 600-Å mixture reached a probability of impact of P_T = 0.999 at approximately 10% concentration of the smaller-size particles. Similarly, the 1000-Å mixture reached a probability of impact of P_T = 0.999 at approximately 18%, and for the 2000-Å particle mixtures, at 39%. However, a probability of impact of P_T = 0.999 was not achieved for any of the 6000-Å particle binary mixtures.

Based on these binary particle combinations, the 2000-Å particle mixtures appeared to give the best balance between impact and flow for the higher particle–particle component of the interaction coefficient of σ_{pc} = 780 Å. Similarly, the 1000-Å particle mixtures appeared to give the best balance between impact and flow when σ_{pc} = 78 Å.

OPTIMUM VISCOSITY–IMPACT CALCULATIONS FOR FIVE PARTICLES

It was shown previously[34] that the optimum/minimum viscosity for blends of multiple particles often occurs when the value of the ratio of D_5/D_1 is at an optimum/maximum. In addition, it has also been shown[34] that the optimum/maximum value of D_5/D_1 and the packing fraction, ϕ_n, for blends of multiple particles can be achieved when the volume fraction, f_i, is generated using the following formulation:

$$f_i = \frac{\sqrt{D_i}}{\sum_{i=1}^{i=n} \sqrt{D_i}} \tag{18}$$

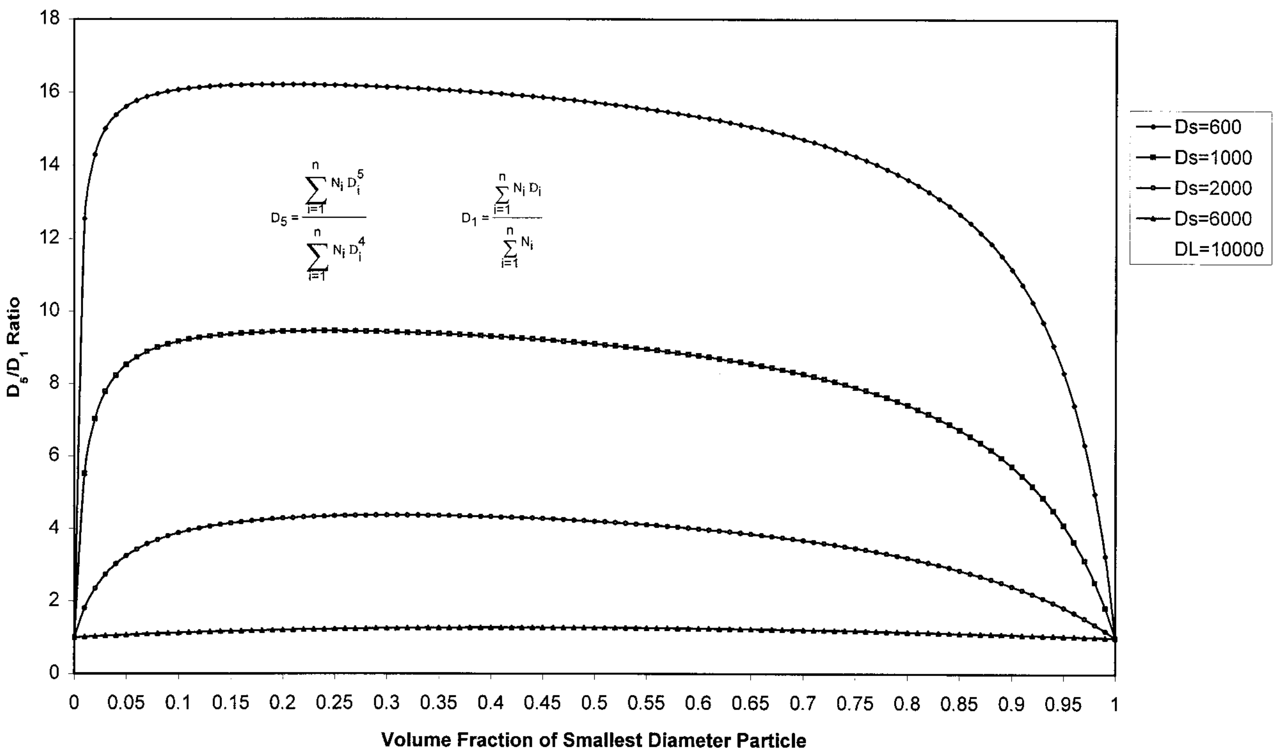

Figure 8 Particle-size distribution indicated by the D_5/D_1 ratio versus volume fraction smallest-diameter particle in a binary mixture of particles.

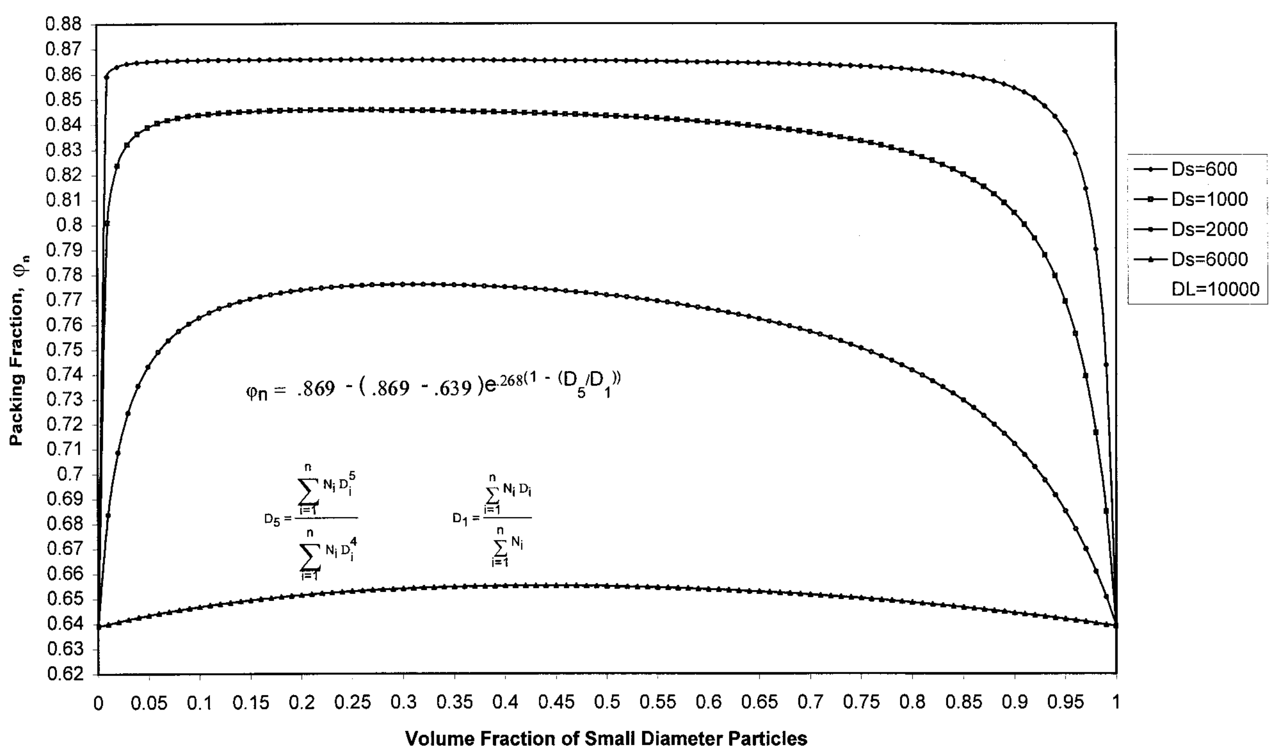

Figure 9 Packing fraction as a function of the volume fraction of the smallest-diameter particle in a binary mixture of particles.

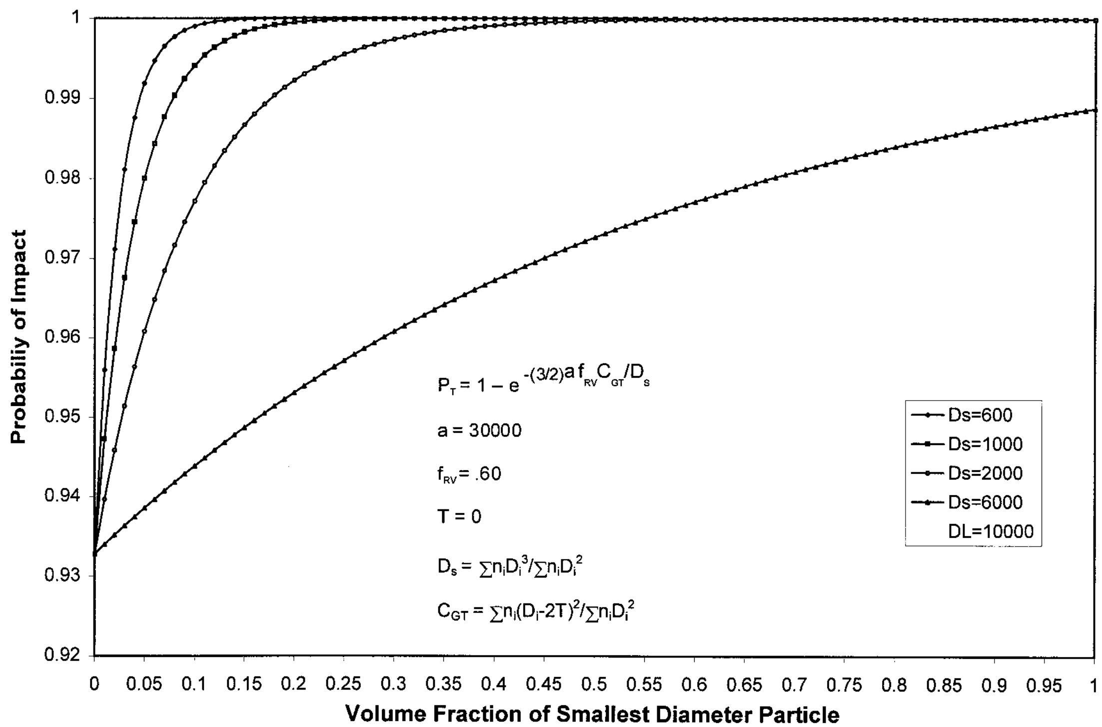

Figure 10 Probability of impact as a function of the binary mixture volume fraction of the smallest-diameter particle in a 60 vol % concentration composite.

Therefore, by mixing all five of the particles described in this study together in an appropriate mixture using eq. (18), it appears potentially possible to optimize/minimize the viscosity. A summary of these calculations appears in Tables I and II and are indicated graphically in Figures 11 and 12, respectively. As indicted in Figure 11, the optimum volume fraction of the smallest particle (600 Å), f_s, at which the optimum/minimum viscosity is achieved, significantly decreases as the number of particles in the mixture increases for the particle sizes considered in this study. Note that the calculated results in Table I and Figure 11 are independent of the interaction coefficient, σ.

However, the influence of the interaction coefficient is clearly indicated in Table II and Figure 12. The results in Figure 12 clearly indicate that optimizing the particle-size distribution can significantly reduce the optimum/minimum viscosity. This is particularly true when the particle-to-particle interaction component, σ_{pc}, of the interaction coefficient, σ, is high (i.e., when σ_{pc} = 780

Table I Particle-size Distributions Used to Evaluate the Optimum Volume Fraction, f_s, for the Smallest Particle in the Distribution

No. Particles	D_L	D_{IL}	D_{IM}	D_{IS}	D_S	f_s
5	10,000	6000	2000	1000	600	0.08801657
4	10,000	6000	2000		600	0.09929991
4	10,000	6000		1000	600	0.10486847
4	10,000		2000	1000	600	0.12196283
3	10,000	6000			600	0.12128915
3	10,000		2000		600	0.14475499
3	10,000			1000	600	0.15690022
2	10,000				600	0.196754
1					600	1.0

Table II Relative Viscosity and Probability of Impact for Various Particle-size Distributions in a 60 Vol % Concentration Composite

No. Particles	f_s	σ (σ_{pc} = 78)	η/η_0 (σ_{pc} = 78)	σ (σ_{pc} = 780)	η/η_0 (σ_{pc} = 780)	Impact Probability
5	0.08801657	0.85337	8.865113	1.783698	33.16278	0.999989
4	0.09929991	0.863109	8.990769	1.881092	40.89308	0.999919
4	0.10486847	0.860369	8.964006	1.853695	38.65062	0.999984
4	0.12196283	0.855108	8.908939	1.801083	34.72411	0.999999
3	0.12128915	0.874747	9.389281	1.997475	61.47713	0.999992
3	0.14475499	0.865794	9.301891	1.907942	49.9382	0.999999
3	0.15690022	0.862451	9.262646	1.874507	46.20397	0.999999
2	0.196754	0.87823	10.81423	2.0323	148.2748	0.999984
1	1.0	0.88	44.47396	2.05	6.17E + 11	1.00000

Å) as indicated in Figure 12. For this case, note that the calculated viscosity for the five-particle mixture was approximately 1/5 of the viscosity calculated for the simple 600-Å binary mixtures. Conversely, note that when the particle-to-particle interaction component, σ_{pc}, of the interaction coefficient, σ, is low (i.e., when σ_{pc} = 78 Å) that the influence of the particle-size distribution is not as dominant as it is when the particle-to-particle component is high.

It is also interesting to note in Table II that the probability of impact was found to be remarkably

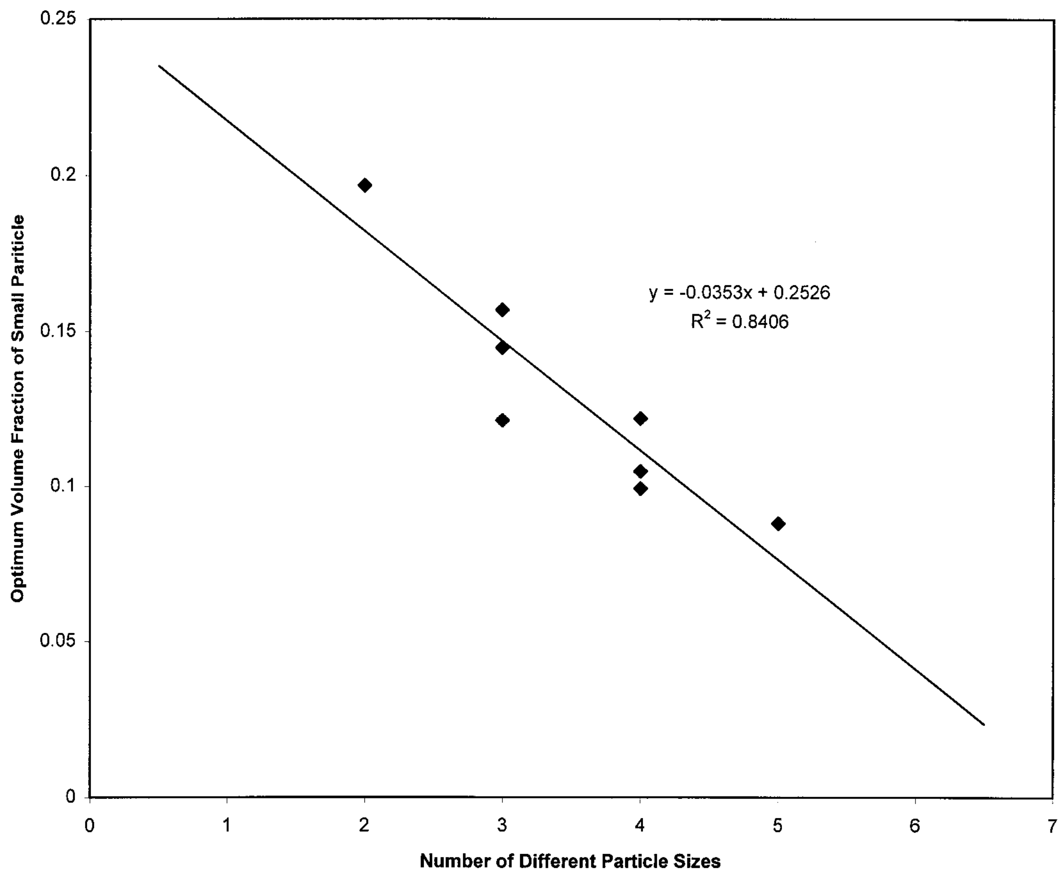

Figure 11 Optimum volume fraction of small particles versus number of monodisperse particles in mixture.

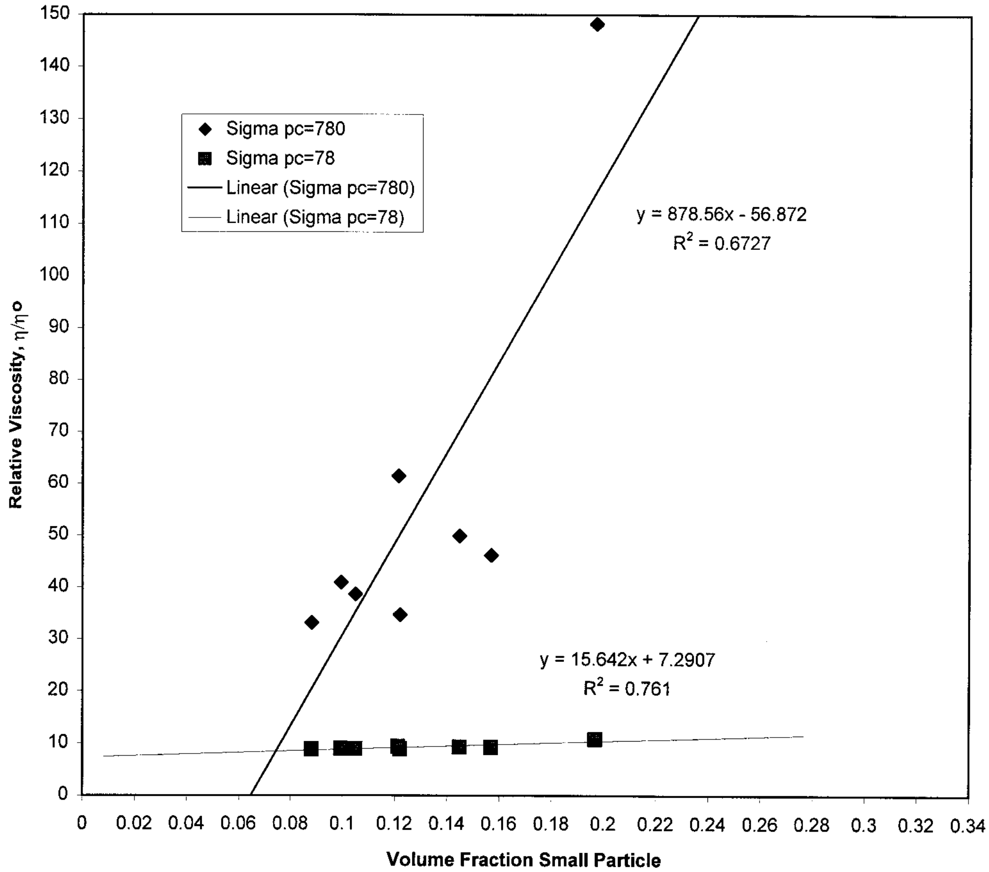

Figure 12 Relative viscosity versus optimum volume fraction of smallest-diameter particle in a 60 vol % concentration composite comparing two interaction coefficient levels.

constant at the optimum/maximum value of the ratio of D_5/D_1, which is characterized by the volume fraction calculations using eq. (18). Thus, if the optimum particle-size distribution is utilized as characterized using eq. (18), then the probability of impact can apparently remain relatively consistent as long as the particles utilized are well chosen and not too close in size.

CONCLUSIONS

The results of this study appear to indicate that, conceptually, it is possible to significantly improve the viscosity/impact balance for material formulations by optimizing the particle-size distribution. However, particularly for binary particle-size distributions, the influence of the preferred particle-size distribution as determined using eq. (18) may not yield the most desirable particle-size distribution if the particle-to-particle component of the interaction coefficient is high. However, if three or more particles are utilized in the distribution, then the optimum particle-size distribution utilized can be characterized using eq. (18). For more than binary particle-size distributions, then this preferred particle-size distribution can be utilized to predict at least one of the preferred distributions to optimize the balance of properties between impact and the viscosity/modulus. In addition, this same particle-size distribution can also predict the probability of an impact that can remain consistently high as long as the particles utilized are well chosen and not too close in size. Finally, this preferred particle-size distribution was found to be particularly significant when the particle–particle component, σ_{pc}, of the interaction coefficient, σ, was found to be very high.

It should also be pointed out, however, that the results from this study simply indicate that an optimized balance between impact and viscosity is possible from the preliminary data. However, complete verification has not yet been extensively proven experimentally. Perhaps one of the rubber-toughened polymer systems (i.e., nylon, polystyrene, ABS, etc.) could be used to extensively validate the results predicted in this study.

REFERENCES

1. Vand, V. J Phys Colloid Chem 1948, 52, 277.
2. Chong, J. S.; Christiansen, E. B.; Baer, A. D. J Appl Polym Sci 1971, 15, 2007–2021.
3. Ackermann, N. L.; Shen, H. T. AIChE J 1972, 25, 327–332.
4. Parkinson, C.; Matsumoto, S.; Sherman, P. J Colloid, Interf Sci 1970, 33, 150–160.
5. Jinescu, V. V. Int Chem Eng 1974, 14, 397–420.
6. Luckham, P. F.; Ukeje, M. A. J Colloid Interf Sci, 1999, 220, 347–356.
7. Eckersley, S. T.; Helmer, B. J. J Coat Technol 1997, 69(864), 97–107.
8. Kausch, H. H.; Beguelin, P.; Fisher, M. 2000, 36, 177–184.
9. Schwarzl, F. R.; Bree, H. W.; Nederveen, C. J.; Schwippert, G. A.; Struik, L. C. E.; Van der Wal, C. W. Rubb Rev 1969, 42, 557–564.
10. Hashin, Z. J Mech Phys Solids 1992, 40, 767–781.
11. Dutta, N. K.; Tripathy, D. K. J Appl Polym Sci 1992, 44, 1635–1648.
12. Lewis, T. B.; Nielsen, L. E. J Appl Polym Sci 1970, 14, 1449–1471.
13. Bartczak, Z.; Argon, A. S.; Cohen, R. E.; Weinberg, M. Polymer 1999, 40, 2347–2365.
14. Wei, G. X.; Sue, H. J.; Chu, J.; Huang, C.; Gong, K. Polymer 2000, 41, 2947–2960.
15. Nakamura, Y.; Yamaguchi, M.; Okubo, M.; Matsumoto, T. J Appl Polym Sci 1992, 45, 1281–1289.
16. Cigna, G.; Lomelli,, P.; Merlotti, M. J Appl Polym Sci 1989, 37, 1527–1540.
17. Bucknall, C. B.; Rizzieri, R.; Moore, D. R. Polymer, 2000, 41, 4149–4156.
18. Liang, J. Z.; Li, R. K. Y. J Appl Polym Sci 2000, 77, 409–417.
19. Sudduth, R. D. J Appl Polym Sci 1978, 22, 2427–2437.
20. Smit, R. J. M.; Brekelmans, W. A. M.; Meijer, H. E. H. J Mater Sci 2000, 35, 2869–2879.
21. Bucknall, C. B.; Karpodinis, A.; Zhang, X. C. J Mater Sci 1994, 29, 3377–3383.
22. Bucknall, C. B.; Rizzieri, R.; Moore, D. R. Polymer 2000, 41, 4149–4156.
23. Bragaw, C. G. Adv Chem Soc 1971, 99, 86.
24. Lyu, S. P.; Zhu, X. G.; Qi, Z. N. J Polym Res 1995, 2, 217.
25. Merz, E. H.; Claver, G. C.; Baer, M. J Appl Phys 1956, 22, 325.
26. Pearson, R. A.; Yee, A. F. J Mater Sci 1991, 26, 3838.
27. Sjoerdsma, S. D. Polym Commun 1989, 30, 106.
28. Newman, S.; Strellan, S. J Appl Polym Sci 1965, 9, 2297.
29. Bragaw, C. G. Adv Chem Soc 1971, 99, 86.
30. Dinges, K.; Schuster, H. Makromol Chem 1967, 101, 200.
31. Sudduth, R. D. J Appl Polym Sci 1993, 48, 25–36.
32. Sudduth, R. D. J Appl Polym Sci 1993, 48, 37–55.
33. Sudduth, R. D. J Appl Polym Sci 1993, 50, 123–147.
34. Sudduth, R. D. J Appl Polym Sci 1994, 52, 985–996.
35. Sudduth, R. D. J Appl Polym Sci 1997, 66, 2319–2332.
36. Sudduth, R. D. J Appl Polym Sci 1994, 54, 1243–1262.
37. Sudduth, R. D. J Mater Sci 1995, 30, 4451–4462.
38. Sudduth, R. D. J Appl Polym Sci 2000, 77, 1954–1963.
39. Einstein, A. Ann Phys 1906, 19, 289–306.
40. Einstein, A. Ann Phys 1911, 34, 591–592.
41. Arrhenius, S. Biochem J 1917, 11, 112.
42. Krieger, I. M.; Dougherty, T. J. Trans Soc Rheol 1959, 3, 137–152.
43. Mooney, M. J Colloid Sci 1952, 6, 162–170.