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Influence of particle dispersion on the matrix ligament thickness of polymer blends. 1. The configuration of well-dispersed particles *versus* simple cubic lattice

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The relations among the morphological parameters of binary polymer blends with the morphology of well-dispersed particles are quantitatively studied to correct the error from the simple cubic (sc) lattice assumption made in previous works. A new morphological parameter, the particle spatial distribution parameter ξ, is defined. A new equation for correlating the spatial distribution with other morphological parameters is derived. The relationships among them are discussed. The values of the spatial distribution parameter for poly(vinyl chloride)/nitrile rubber, polypropylene (PP)/EPDM and PP/EVA blends appear to be a constant. The errors stemming from the sc lattice assumption for these blends are analysed. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: equation; morphological parameter; morphology of well-dispersed particles)

Introduction

The average matrix ligament thickness (T, average surface to surface interparticle distance) is a morphological parameter which can be correlated with some physical and mechanical properties of multiphase materials. For example, plastics can be toughened by the incorporation of rubber particles, and there is a critical value (T_c) of T at which a brittle–ductile transition takes place, i.e. a blend is brittle when $T>T_c$, and is tough when $T<T_c$[1–11]. Particle dispersion also has a marked influence on the impact toughness of polymer blends[12–18]. It has been well known that the agglomeration of particles results in a brittle blend. Compared with the morphology of agglomerated particles, the morphology of well-dispersed particles will considerably increase the toughening efficiency. Furthermore, the toughening efficiency for the blends with the pseudonetwork morphology is much higher than that for blends with the morphology of well-dispersed particles[17,18].

A simple equation for relating T to particle size (d) and particle volume fraction (ϕ) is usually used to correlate impact toughness with T[1–9]. In some cases the toughness–T relation does not give a brittle–ductile transition master curve for $T < T_c$, for instance, nylon/rubber blends[1,3,4] and high density polyethylene (HDPE)/$CaCO_3$ composites[7,8]. Recently we derived a new equation for correlating T to d, particle size distribution (σ) and ϕ[19]. We pointed out that the equation is generally applicable to binary polymer blends with a log-normal distribution of particle size and a configuration of well-dispersed particles in a polymer matrix. The new equation has been successfully employed to interpret the splitting of the brittle–ductile transition master curve of HDPE/$CaCO_3$ composites for $T < T_c$. The splitting has been attributed to the neglect of the influence of σ on T in the above simple equation. This example shows that the choice of an appropriate equation is important. This importance will be seen further in our work published elsewhere.

In fact, the configuration of well-dispersed particles was simulated by a simple cubic (sc) lattice in previous work[1–19]. This assumption has introduced the configurational error. Accordingly, it is the purpose of this paper to improve on our earlier equation by the introduction of a particle spatial distribution based on the sc lattice. The configurational errors originating from the sc lattice assumption for poly(vinyl chloride) (PVC)/nitrile rubber (NBR), polypropylene (PP)/EPDM and PP/EVA blends were underestimated in our previous paper and will be corrected in this work.

Evaluation of the average centre-to-centre interparticle distance

The definition of particle size distribution. The log-normal distribution has been shown to be suitable for describing the feature of particle size distribution in many polymer blend systems[4,6–22]. The probability density $f(d_i)$ of a particle size d_i is thus defined by [23]

$$f(d_i)=\frac{1}{\sqrt{2\pi}\,\ln\sigma}\exp\left[\frac{-(\ln d_i-\ln d)^2}{2\ln^2\sigma}\right] \tag{1}$$

where d and σ are given by[23]

$$\ln d=\frac{\sum_{i=1}^{N} n_i\ln d_i}{\sum_{i=1}^{N} n_i} \tag{2}$$

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and

$$\ln\sigma = \sqrt{\frac{\sum_{i=1}^{N} n_i(\ln d_i - \ln d)^2}{\sum_{i=1}^{N} n_i}} \tag{3}$$

In the case of monodispersity, $\sigma = 1$; and $\sigma > 1$ when there is polydispersity.

The average centre-to-centre interparticle distance. The average centre-to-centre interparticle distance (L) is a key factor in relating the particle spatial distribution to T, as will be shown in the next section of this paper. We do not set any limit to the particle spatial distribution parameter in the derivation of a universal equation for evaluating L. The centre-to-centre interparticle distance (L_k) of two neighbouring hard spheres i and j is

$$L_k = T_k + \tfrac{1}{2}(d_i + d_j) \tag{4}$$

where T_k is the matrix ligament thickness of the two adjacent spheres. The word 'hard' is emphasised to avoid sphere overlapping. The sum of equation (4) gives

$$\sum_{k=1}^{N} n_k L_k = \sum_{k=1}^{N} n_k T_k + \tfrac{1}{2}\left(\sum_{i=1}^{N} n_i d_i + \sum_{j=1}^{N} n_j d_j\right) \tag{5}$$

The average values L and T are the arithmetic means according to equation (5). Thereafter

$$\sum_{k=1}^{N} n_k L_k = L \sum_{k=1}^{N} n_k \tag{6}$$

and

$$\sum_{k=1}^{N} n_k T_k = T \sum_{k=1}^{N} n_k \tag{7}$$

Because the particles obey log-normal distribution and the blend system has only one d value, we have[23]

$$\sum_{i=1}^{N} n_i d_i = \sum_{j=1}^{N} n_j d_j = \exp(\ln d + 0.5\ln^2\sigma)\sum_{i=1}^{N} n_i \tag{8}$$

One can easily find that

$$\sum_{k=1}^{N} n_k = \sum_{i=1}^{N} n_i \tag{9}$$

Insertion of equations (6)–(9) into equation (5) yields

$$L = T + d\exp(0.5\ln^2\sigma) \tag{10}$$

Equation (10) gives the exact relation of L to T, d and σ for hard spheres fitting the log-normal distribution and occupying any lattice.

The definition of particle spatial distribution. The other two factors governing the result of equation (10) are the particle dispersion state and the neighbouring number considered in addition to d, σ and ϕ. Clearly the L value for the nearest two particles in the blend system where particles occupy the random lattice is the smallest. If the second neighbour is included, the L increases, and so on. Therefore L increases with the neighbouring number considered. So does the value of T.

For the sc lattice, we have

$$L_{\mathrm{sc}} = T_{\mathrm{sc}} + d\exp(0.5\ln^2\sigma) \tag{11}$$

In the case of the same d, σ and ϕ, we define the particle spatial distribution parameter (ξ) for the morphology of well-dispersed particles as

$$\xi = \frac{L}{L_{\mathrm{sc}}} = \frac{T + d\exp(0.5\ln^2\sigma)}{T_{\mathrm{sc}} + d\exp(0.5\ln^2\sigma)} \tag{12}$$

The geometric significance of ξ, as defined by equation (12), is the ratio of L for the configuration of well-dispersed particles to L_{sc} when d, σ and ϕ are identical.

Two particle configurations, the sc lattice and the morphology of well-dispersed particles, are of interest here. *Figure 1* schematically displays the two configurations in order that the value of ξ can be estimated. The coordination number for the sc lattice is 6 (*Figure 1a*). The configuration of well-dispersed particles is shown in *Figure 1b*. We fix the neighbouring number for the configuration of well-dispersed particles at 6 to eliminate its influence on L. Powell[24] constructed a lattice for random close packing whose mean coordination is 6. The volume restriction for the morphology of well-dispersed particles is much less rigorous than that for random close packing. So, the neighbouring number (6) for the morphology of well-dispersed particles is a very reasonable value.

The lines connecting the centres of particles in *Figure 1a* would be straight, while the lines connecting the centres of particles in *Figure 1b* would be zigzag. We judge the ξ for the morphology of well-dispersed particles to be ≥ 1 from the basic knowledge that the straight line connecting two points is shorter than any other line. $\xi = 1$ when the morphology of well-dispersed particles is transformed into the sc lattice.

The relationship between ξ and other morphological parameters

The average matrix ligament thickness for the sc lattice (T_{sc}) can be exactly calculated by[19]

$$T_{\mathrm{sc}} = d\left[\left(\frac{\pi}{6\phi}\right)^{1/3}\exp(1.5\ln^2\sigma) - \exp(0.5\ln^2\sigma)\right] \tag{13}$$

Rearrangement of equation (13) gives

$$T_{\mathrm{sc}} + d\exp(0.5\ln^2\sigma) = d\left(\frac{\pi}{6\phi}\right)^{1/3}\exp(1.5\ln^2\sigma) \tag{14}$$

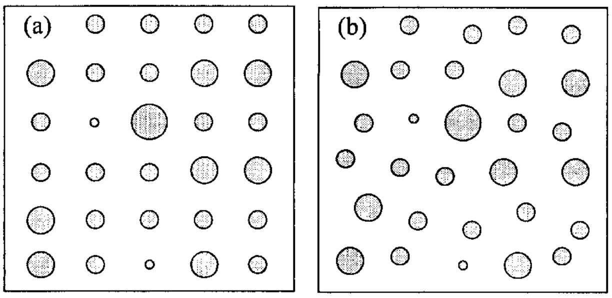

Figure 1 Schematic representations of (*a*) the simple cubic lattice and (*b*) the morphology of well-dispersed particles. The filled symbols represent the dispersed particles

Combination of equation (12) and equation (14) yields

$$T = d\left[\xi\left(\frac{\pi}{6\phi}\right)^{1/3}\exp(1.5\ln^2\sigma) - \exp(0.5\ln^2\sigma)\right] \qquad (15)$$

In general, equation (15) can be used to exactly calculate T for binary polymer blends with the morphology of well-dispersed particles.

In the case of the same d, σ and ϕ, the normalised T is given by

$$\frac{T}{T_{sc}} = \frac{\xi\left(\frac{\pi}{6\phi}\right)^{1/3}\exp(1.5\ln^2\sigma) - \exp(0.5\ln^2\sigma)}{\left(\frac{\pi}{6\phi}\right)^{1/3}\exp(1.5\ln^2\sigma) - \exp(0.5\ln^2\sigma)} \qquad (16)$$

The influence of ξ on T can be analysed using equation (16). T/T_{sc} is plotted *versus* σ, as shown in *Figure 2*. It is seen that for a constant ξ, e.g. 1.1, T/T_{sc} decreases with σ for a given ϕ and that the higher the ϕ, the larger the T/T_{sc}. It is clear that the T/T_{sc} increases with ξ at constant σ and ϕ.

Now we re-evaluate the experimental T values in our earlier work[19] and estimate the ξ values for the PVC/NBR, PP/EPDM and PP/EVA blends. The T values approximately fit the log-normal distribution. The experimental T given in Ref. 19 is the value at the probability of 50%, which is labeled as T_e here. The distribution of T is described by the parameter σ_T. An arithmetic mean value T is defined throughout our work. Thus, the relation between T, T_e and σ_T is[23]

$$T = \exp(\ln T_e + 0.5\ln^2\sigma_T) \qquad (17)$$

To correct the errors in T calculated from previous equations, the other two equations reported in literature are cited as follows. Assumimg $\xi = 1$, Wu[1] obtained

$$T = d\left[\left(\frac{\pi}{6\phi}\right)^{1/3} - 1\right] \qquad (18)$$

To account for the effect of σ on T, Wu[4] proposed

$$T = d\left[\left(\frac{\pi}{6\phi}\right)^{1/3} - 1\right]\exp(\ln^2\sigma) \qquad (19)$$

Using the data in Ref. 19 we obtain the T and ξ values for the PVC/NBR, PP/EPDM and PP/EVA blends, which are listed in *Table 1*. The T value for the PVC/NBR blend is 0.109 μm. The values calculated from equation (13), equation (18) and equation (19) are 0.076, 0.051 and 0.041 μm, respectively. The corresponding errors are 30, 53 and 62%, rather than 5, 36 and 49% reported in Ref. 19. Equation (13) gives the smallest error, which arises from the sc lattice assumption. However, the errors for equation (18) and equation (19) are much greater and have been mentioned in Ref. 19. The same conclusion can be reached from the data for the PP/EPDM and PP/EVA blends in *Table 1*. We are able to calculate the ξ values for PVC/NBR, PP/EPDM and PP/EVA blends using equation (15) and the experimental data. The values are 1.21, 1.18 and 1.16, and are greater than 1. These values seem a constant, though other morphological parameters are dramatically different.

It is very difficult to obtain the three-dimensional value of T. Two-dimensional scanning electron microscopy pictures were used to measure T[19]. The scalene triangles for connecting centres of dispersed particles, as described by Chan[25], were drawn in that work. However, the mean neighbouring number for the above measurements on T has not yet been evaluated. It may be around 12, and is, thus, larger than the neighbouring number 6 required by this work. Therefore, the above experimental ξ values greater

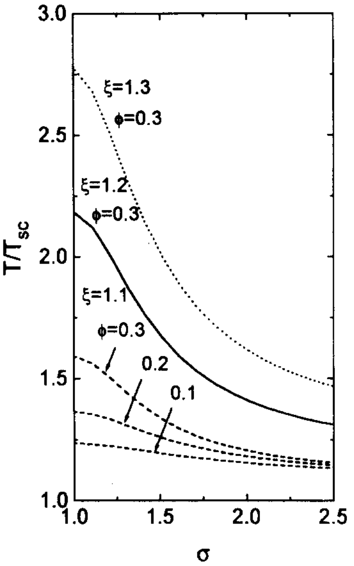

Figure 2 Calculated variations of T/T_{sc} with σ at varying ξ and ϕ for the binary polymer blends with the morphology of well-dispersed particles

Table 1 The ξ values for PVC/NBR, PP/EPDM and PP/EVA blends with the morphology of well-dispersed particles

Morphological parameters	Blends		
	PVC/NBR	PP/EPDM	PP/EVA
d (μm)	0.073	0.51	0.32
σ	1.58	2.31	1.59
ϕ	0.136	0.243	0.243
σ_T	2.20	1.90	1.90
T_e (μm)	0.080	1.22	0.250
T (μm)	0.109	1.50	0.307
T_{sc} (from equation (13)) (μm)	0.076	1.16	0.210
Error[a] (%)	30(5)[b]	23(5)	32(16)
T_1 (from equation (18)) (μm)	0.051	0.30	0.12
Error (%)	53(36)	80(75)	61(52)
T_2 (from equation (19)) (μm)	0.041	0.15	0.093
Error (%)	62(49)	90(88)	70(63)
ξ (from equation (15))	1.21	1.18	1.16

[a] The error is defined as $|T_c - T| \times 100/T$, where T_c is the value calculated from equations (13), (18) and (19).

[b] The data in the parentheses are those reported in Ref. 19

than 1 are slightly larger than those measured based on the neighbouring number 6.

Conclusions

A new equation for calculating the average centre-to-centre interparticle distance (L) of hard spheres fitting log-normal distribution (see equation (10)) is derived with no restriction on the type of configuration. The equation is exact and generalised.

A new morphological parameter, the particle spatial distribution parameter (ξ), is defined by equation (12). In this work, it denotes the ratio of the L for the morphology of well-dispersed particles to the L_{sc} for the simple cubic (sc) lattice when the particle size (d), particle size distribution parameter (σ) and particle volume fraction (ϕ) are identical. ξ is related to d, σ, ϕ and the average matrix ligament thickness (T) by equation (15). The greater the value of ξ, the more rapid the T decreases with σ. Moreover, the higher the ϕ, the more significant the influence of σ on T. The experimental ξ values for the PVC/NBR, PP/EPDM and PP/EVA blends are 1.21, 1.18 and 1.16, and appear to be constant. These ξ values greater than 1 indicate that the particles in the above blends occupy a random lattice rather than an sc lattice.

The errors in T stemming from the sc lattice assumption have been corrected in this paper and are greater than those reported in Ref. 19.

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References

1. Wu, S., *Polymer*, 1985, **26**, 1855.
2. Flexman, E. A., *Mod. Plast.*, 1985, **Feb.**, 72.
3. Wu, S., *Polym. Eng. Sci.*, 1990, **30**, 753.
4. Wu, S., *J. Appl. Polym. Sci.*, 1988, **35**, 549.
5. Jancar, J., DiAnselmo, A. and DiBenedetto, A. T., *Polym. Commun.*, 1991, **32**, 367.
6. Wu, X., Zhu, X. and Qi, Z., in *Proceedings of the 8th International Conference on Deformation, Yield and Fracture of Polymers*. London, 1991, 78/1.
7. Liu, C. X., M.S. thesis. Chengdu University of Science and Technology, Chengdu, 1992.
8. Fu, Q., Wang, G. and Shen, J., *J. Appl. Polym. Sci.*, 1993, **49**, 673.
9. Gloaguen, J. M., Steer, P., Gailland, P., Wrotecki, C. and Lefebver, J. M., *Polym. Eng. Sci.*, 1993, **33**, 748.
10. Liu, Z. H., Zhu, X. G., Zhang, X. D., Qi, Z. N., Choy, C. L. and Wang, F. S., *Acta Polymerica Sinica*, 1996, **4**, 468.
11. Liu, Z. H., Zhu, X. G., Li, Q., Qi, Z. N. and Wang, F. S., *Polymer* (in press).
12. Haaf, F., Breuer, H. and Stabenow, J., *Angew. Macromol. Chem. (Vol. 58–59)*, 248, 1977.
13. Breuer, H., Haaf, F. and Stabenow, J., *J. Macromol. Sci. Phys.*, 1977, **B14**, 387.
14. Keskkula, H., Kim, H. and Paul, D. R., *Polym. Eng. Sci.*, 1990, **30**, 1373.
15. Kim, H., Keskkula, H. and Paul, D. R., *Polymer*, 1990, **31**, 870.
16. Majumdar, B., Keskkula, H. and Paul, D. R., *Polymer*, 1994, **35**, 5453.
17. Liu, Z. H., PhD thesis. Institute of Chemistry, Academia Sinica, Beijing, P.R. China, 1994.
18. Liu, Z. H., Zhu, X. G., Zhang, X. D., Qi, Z. N., Choy, C. L. and Wang, F. S., *Acta Polymerica Sinica* (in press).
19. Liu, Z. H., Zhang, X. D., Zhu, X. G., Qi, Z. N. and Wang, F. S., *Polymer*, 1997, **38**, 5267.
20. Wu, S., *Polym. Eng. Sci.*, 1987, **27**, 335.
21. Serpe, G., Jarrin, J. and Dawans, F., *Polym. Eng. Sci.*, 1990, **30**, 553.
22. Favis, B. D., *J. Appl. Polym. Sci.*, 1990, **39**, 285.
23. Irani, R. R. and Callis, C. F., *Particle Size: Measurement, Interpretation, and Application*. Wiley, New York, 1963.
24. Powell, M. J., *Phys. Rev. B*, 1979, **20**, 4194.
25. Chan, S. L., in *Fractography and failure Mechanisms of Polymers and Composites*, ed. A. C. Roulin-Moloney. Elsevier Science Publishers, London, 1989, p. 172.