

Theoretical Phase Domain Sizes in IPNs And Related Materials

INTRODUCTION

One of the more interesting and important questions in multipolymer materials relates to the size of the domains developed by various synthetic techniques.¹⁻⁶ For interpenetrating polymer networks (IPNs), an equation was recently derived by Donatelli et al.⁷ which expressed the domain diameter of polymer II, D_2 , in terms of the crosslink density of polymer I, ν_1 , the weight fraction of polymer II, W_2 , and the interfacial tension, γ . This equation can be written

$$\left(\frac{\nu_1}{CK_1}\right)^2 \left(\frac{1}{1-W_2} + \frac{2}{M_1\nu_1}\right) D_2^3 + \left(\frac{W_2}{M_2} - \frac{\nu_1}{2}\right) D_2 = \frac{2\gamma W_2}{RT} \quad (1)$$

where M_1 and M_2 are the molecular weights of polymers I and II, respectively, which go to infinity for a full IPN; $K_1 = r_{1,0}/M_1^{1/2}$, a constant relating the end-to-end distance $r_{1,0}$ to the molecular weight (for polymer I); C is roughly a constant taken as $\sqrt{2}$; and RT represents the universal gas constant multiplied by the absolute temperature.

Equation (1) has been tested several times,⁸⁻¹¹ yielding reasonable agreement with experiment under a variety of conditions. The purpose of this note is to illustrate the predictions of eq. (1) under different limiting conditions or assumptions.

In the following, unit density will be assumed so that, as a first approximation, the volume fraction v equals the weight fraction W . For cases far from this assumption, $(\rho/\rho_a) W_a = v_a$, where a takes the value of 1 or 2, and ρ is the density of the total system. Also assumed, except where stated otherwise, are spherical domains, which restricts W_2 to less than a critical value, sharp phase boundaries (implicitly), and thermodynamic equilibrium.

SIMPLIFICATION OF EQUATION (1)

In the original article⁷ two assumptions were made. First,

$$\left(\frac{r_1}{r_{1,0}}\right)^2 = \alpha^2 = \frac{1}{(1-W_2)^{2/3}} \quad (2)$$

where r_1 is the root-mean-square end-to-end distance of the polymer I chains in the IPN, and $r_{1,0}$ is the corresponding distance in the homopolymer network. Secondly,

$$\nu_1 = \frac{1-W_2}{M_{c,1}} \quad (3)$$

where $M_{c,1}$ is the segmental molecular weight between crosslinks in polymer I. Equation (3) means that the crosslink density of polymer I, calculated on the basis of the whole sample, depends on its weight fraction in the IPN.

These assumptions, together with other substitutions,⁷ leads to* for a full IPN:

$$D_2 = \frac{2\gamma W_2}{RT\nu_1 \left[\left(\frac{1}{1-W_2}\right)^{2/3} - \frac{1}{2} \right]} \quad (4)$$

which is a significant simplification of the cubic form in eq. (1). On the other hand, if

$$(r_1/r_{1,0})^2 = 1 \quad (5)$$

and

$$\nu_1 M_{c,1} = 1 \quad (6)$$

which obviates the sequential IPN swelling assumptions and/or assumes that W_2 is small, the form¹⁰

$$D_2 = \frac{2\gamma W_2}{RT\nu_1 \left(\frac{1}{1-W_2} - \frac{1}{2} \right)} \quad (7)$$

*See note added in proof.

is obtained. The derivation of eq. (7) is summarized in Appendix A.

NEWTON'S ALGORITHM

Rather than using eq. (4) or eq. (7), sometimes it is more useful to solve eq. (1) directly. While substitution solutions are available for equations in cubic form,¹² a more elegant approach uses Newton's algorithm.¹³ Also, it is easy to show via the method of identification of constants that eq. (1) has only one positive real root, except where $W_2 = 0$ or $\gamma = 0$.

$$W_2 = 0 \text{ and/or } \gamma = 0$$

Several special solutions of eq. (1) are also of interest. If $W_2 = 0$, D_2 equals either zero or 100 Å. Siegfried et al.,⁹ for example, found values of zero or 85 Å for $\gamma = 0$ and $W_2 = 0.5$. A fine structure of 50–100 Å was obtained via transmission electron microscopy, suggesting that the 85 Å value was correct. However, it should be noted that both eqs. (4) and (7) predict that D_2 equals zero only. Because of the form of eqs. (1), (4), and (7), similar results are obtained in the limit of W_2 or γ approaching zero.

THE CASE OF $\nu_1 = 0$

As the crosslink density of polymer I approaches zero, the structure and morphology of a graft copolymer is approached. In this case, eq. (1) yields

$$D_2 = 2\gamma M_2/RT \quad (8)$$

For $\gamma = 3 \text{ erg/cm}^2$ and $M_2 = 2 \times 10^5 \text{ g/mole}$, a domain diameter of the order of 4000–5000 Å is obtained. Note that eq. (8) does not have a dependence on W_2 . This value compares well with the cellular structures within the rubber particles in HiPS, for example.⁶

Equation (8) may be of interest to the field of colloid science, setting a lower limit on the domain size that can be obtained with oligomeric and polymeric dispersions.

THE CASE OF $W_2 = 1$

When W_2 approaches unity (100% polymer II), eqs. (1) and (4) predict that D_2 goes to infinity, but eq. (7) predicts that D_2 goes to zero. (As the pure phase, polymer II must have infinite bounds.)

Interestingly, the case of $\nu_1 = 0$, W_2 near unity and polymer II crosslinked (a semi-II IPN of nearly all polymer II) was studied by Donatelli et al.⁸ They confirmed the size of the polymer II domain increases as W_2 approached unity.

ON THE "CONSTANT" C

Originally, C was taken as the square root of 2, which was based on the best estimate of the average number of crosslinked chain segments needed to circumnavigate a domain. For a final equation without arbitrary constants, this assumption was the most important.

Instead of taking $C = \sqrt{2}$, a variable quantity may be assumed. For example,

$$C = 1/\sqrt{1 - W_2} \quad (9)$$

tends to modify eq. (1) for an IPN. (Note that for $W_2 = 0.5$, $C = \sqrt{2}$, still.) Equation (9) follows from an analysis that C probably increases as W_2 increases, but is otherwise arbitrary.

If $\gamma = 0$ eq. (1) yields

$$D_2^2 = \frac{C^2 K_1^2 (1 - W_2)}{2\nu_1} \quad (10)$$

Substituting eq. (3) into eq. (10) yields

$$D_2^2 = C^2 K_1^2 M_{c,1}/2 \quad (11)$$

Then, from eqs. (9) and (11);

$$D_2 = K_1 \frac{M_{c,1}}{2(1 - W_2)} \quad (12)$$

which predicts that D_2 goes to infinity as W_2 goes to unity. For W_2 approaching zero, a finite value of the order of 100 Å is obtained for D_2 , depending on $M_{c,1}$. If C is taken as a constant ($\sqrt{2}$), then D_2 is a constant if γ is zero. Thus, for a homo-IPN, D_2 may be either a constant or a variable, depending upon the exact assumptions.

DISCUSSION

As mentioned above, the solution of eq. (1) for the case of $\gamma = 0$ yields values of D_2 of either zero or ~ 100 Å. For IPNs, the latter rather than the former has been experimentally verified.

For polymer blends, the evidence appears divided.¹ Recent neutron scattering studies^{14,15} suggest that true miscibility means an ordinary molecular solution, where both polymers are dispersed as random coils. Such behavior is predicted by eq. (8). On the other hand, some studies such as electron microscopy¹⁶ and dynamic mechanical spectroscopy¹⁷ sometimes suggest some aggregation on a supermolecular level even in materials thought to be miscible.

For the special case of IPNs, which may be considered to have infinite molecular weights, special problems in attaining molecular miscibility may arise. This leaves ample grounds for future definitive experiments.

CONCLUSIONS

Equation (1) can be solved for a number of special cases. For ν_1 approaching zero, values of interest to graft copolymer materials are reached. For the case of zero interfacial tension, D_2 domains of the order of 100 Å are attained. Limiting cases of $W_2 = 1$ and $W_2 = 0$ yield reasonable values. In all cases where domain sizes are known experimentally for sequential IPNs, eq. (1) and its several simplified forms predict realistic domain diameters.

APPENDIX A

SIMPLIFICATION OF DONATELLI EQUATION

Starting with the original Donatelli equation, and assuming M_1 and M_2 large, $2/M_1 = 0$ and $W_2/M_2 = 0$, and factoring out D_2 and combining terms;

$$D_2 \left[D_2^2 \left(\frac{\nu_1^2}{C^2 K_1^2 (1 - W_2)} \right) - \frac{\nu_1}{2} \right] = \frac{2\gamma W_2}{RT} \quad (\text{A-1})$$

From Donatelli et al.,⁷

$$D_2 = Cr_1 \quad (\text{A-2})$$

and

$$r_{1,0} = K(\bar{M}_1)^{1/2} \quad (\text{A-3})$$

Substituting eqs. (A-2) and (A-3) into (A-1) yields

$$D_2 \left[(C^2 r_1^2) \left(\frac{\nu_1^2 \bar{M}_1}{C^2 r_{1,0}^2 (1 - W_2)} \right) - \frac{\nu_1}{2} \right] = \frac{2\gamma W_2}{RT} \quad (\text{A-4})$$

By assuming that the root-mean-square end-to-end distance for the unperturbed molecule for polymer I (r_0) is approached by the rms distance between crosslinks for polymer I (r_1), eq. (A-4) can be simplified to

$$D_2 \left[\frac{\nu_1^2 \bar{M}_1}{1 - W_2} - \frac{\nu_1}{2} \right] = \frac{2\gamma W_2}{RT} \quad (\text{A-5})$$

Factoring out ν_1 , and rearranging,

$$D_2 \left[\frac{\nu_1 \bar{M}_1}{1 - W_2} - \frac{1}{2} \right] = \frac{2\gamma W_2}{\nu_1 RT} \quad (\text{A-6})$$

Assuming

$$\frac{1}{M_{c,1}} = \nu_1 \quad (\text{A-7})$$

and also that

$$\bar{M}_1 = M_{c,1} \quad (\text{A-8})$$

since the value of interest is actually the segment molecular weight between crosslinks.

Substituting (A-6) and (A-7) into eq. (A-6) and rearranging,

$$D_2 = \frac{2\gamma W_2}{\nu_1 RT \left[\frac{1}{1 - W_2} - \frac{1}{2} \right]} \quad (\text{A-9})$$

Equation (A-9) yields the values expected for small W_2 .

Note added in proof: If ν_1 is redefined so that it refers to the crosslink density of the homopolymer network I, an easier-to-interpret equation emerges:

$$D_2 = \frac{2\gamma W_2}{RT \nu_1 W_1 \left[\left(\frac{1}{W_1} \right)^{2/3} + \frac{W_2}{W_1} \frac{1}{\nu_1 M_2} - \frac{1}{2} \right]} \quad (4a)$$

As in eq. (4), the term $(W_2/W_1)(1/\nu M_2)$ drops out for a full IPN, i.e., M_2 is considered infinite.

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J. MICHEL
S. C. HARGEST
L. H. SPERLING

Materials Research Center
Lehigh University
Bethlehem, Pennsylvania 18015

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