Theoretical prediction of domain sizes in IPN's and related materials

J. K. Yeo, L. H. Sperling and D. A. Thomas
Materials Research Center, Coxe Laboratory 32, Lehigh University, Bethlehem, PA 18015, USA

(Received 4 *January* 1982*)*

A series of new theoretical equations for predicting the domain size in interpenetrating polymer networks, IPN's, and related materials was derived. The equations are based on a domain formation process comprising the crosslinking density of each polymer, mixing and demixing thermodynamics, network swelling and elastic deformation of each polymer network, and the interfacial tension between two polymers. The new equations are applicable to both crosslinked and linear materials. The experimental variables required to determine the domain size include the volume fraction and crosslink level of each polymer (or molecular weight, if linear), the interfacial tension, and the temperature. The theory was applied to poly(n-butyl acrylate)/polystyrene IPN's and semi-IPN's. The results are also compared with the earlier theory of Donatelli *et al.*

Keywords Interpenetrating polymer networks; domains; theory; dimensions; crosslink density

INTRODUCTION

One of the most challenging areas today concerning phase separated multipolymer materials relates to the prediction of the domain sizes. Polymer blends, grafts, blocks and interpenetrating polymer networks, IPN's, yield very different dimensions[1–8]. Much theoretical work on domain size prediction has been done on block polymers[9–23], but not on other multipolymer systems.

For interpenetrating polymer networks, Donatelli *et al.*[24] recently derived an equation especially for semi-IPN's of the first kind (polymer I crosslinked, polymer II linear) and extended this to IPN'S by assuming that the molecular weight of polymer II is infinite. Michel *et al.*[25] solved the Donatelli equation considering several boundary cases, and reinterpreted the constants involved. However, because of the semiempirical nature of the Donatelli equation, its intrinsic shortcomings limit its applicability. A new set of theoretical equations is proposed herein which considers the domain diameters IPN's and semi-IPN's.

DERIVATION OF THE BASIC EQUATION FOR IPN DOMAIN DIAMETERS

Method of sequential IPN formation

An interpenetrating polymer network, IPN, is defined as a combination of two polymers in network form, at least one of which is synthesized and/or crosslinked in the immediate presence of the other. In forming a sequential IPN, the synthetic steps are taken in the following order:

(a) Polymer I is synthesized
(b) Polymer I is crosslinked
(c) Monomer II is swollen in
(d) Monomer II is polymerized (with crosslinking)
(e) Phase separation between I and II takes place.

In the above, (a) and (b) may be simultaneous in time, as with vinyl polymerizations using multifunctional crosslinkers. This is the case of the data to be analysed below. Step (e) is usually simultaneous with (d), but starts after (d) has proceeded to a certain extent.

A principal objective of this paper will be to predict the domain diameters formed during step (e).

Physical model

A working model of the domain structure in IPN's and related materials is depicted in *Figure 1*. Polymer II constitutes a spherical core and is in a contracted

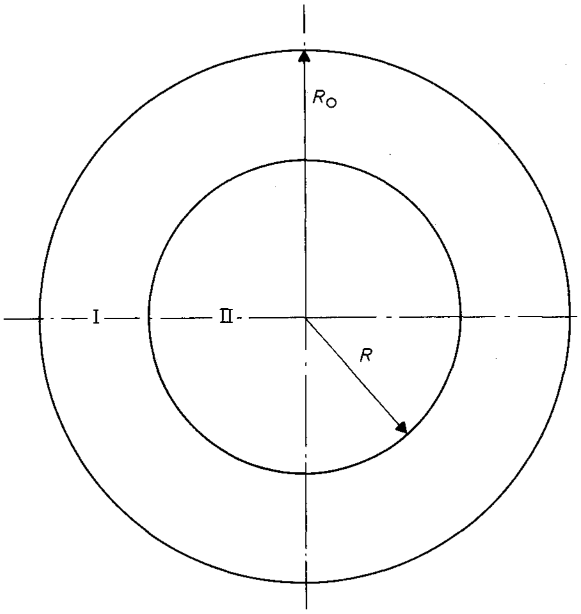

Figure 1 Working model of a domain. A spherical domain of polymer II surrounded by a shell of polymer I. R_0 = radius of an imaginary spherical region containing both polymers I and II. R = radius of a polymer II domain

0032–3861/83/030307–07$03.00

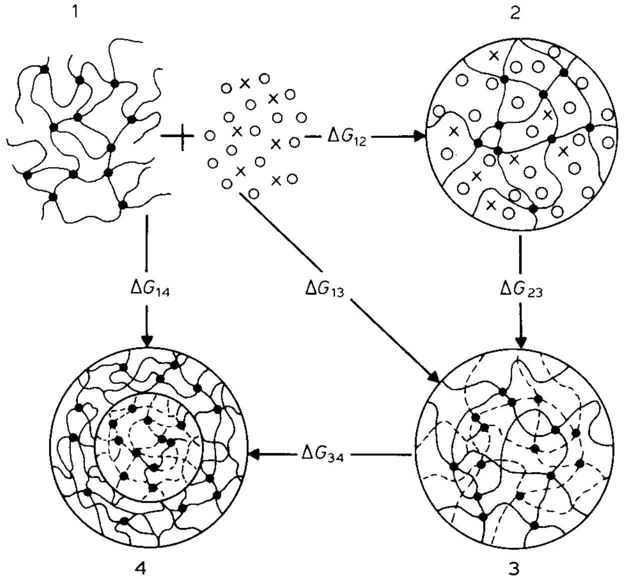

Figure 2 Simplified path of domain formation

(deformed) state, while polymer I surrounds the core and is in an expanded (deformed) state. While the model in *Figure 1* is over simplified, it describes the physical situation of a spherical domain. Related to this model, several essential relationships are evolved: Let φ_1 and φ_2 be the volume fractions of polymer I and II, and α the linear deformation ratio of polymer network I from swelling.

The following simple geometric constraints will be noted:

$$\varphi_1 + \varphi_2 = 1 \tag{1}$$

$$R^3 = (1-\varphi_1)R_0^3 = \varphi_2 R_0^3 \tag{2}$$

$$\alpha = \varphi_1^{-1/3} \tag{3}$$

Subscripts 1 and 2 denote polymer (or monomer) I and polymer (monomer) II, respectively, throughout, and R is the radius of a polymer II domain.

Process path

Several assumptions are made for the derivation:

(1) Thermodynamic equilibrium processes exist throughout the development of the domain formation.

(2) The domains have identical diameters with a spherical shape.

(3) The polymer networks obey Gaussian statistics.

(4) A sharp interfacial boundary exists between the two phases.

The process path of domain formation is illustrated in *Figure 2.* Initially, in state 1, network I is completely separated from monomer II (plus crosslinker). In state 2, polymer network I is swollen with the monomer II mixture. The path from state 1 to state 2 is accompanied by the mixing (dilution) between polymer I and monomer II, and mutual concomitant expansion of polymer I caused by swelling with monomer II mixture. The free energy of polymerization on going from state 2 to state 3 will be ignored, as it is not of interest to this problem. Also, the enthalpic 1, 2 contact energies between monomer II and polymer I will be assumed to be the same as the polymer II–polymer I enthapic contact energies.

State 3 is the hypothetical, mutually mixed state, where polymers I and II are mixed and mutually diluted. Network I is stretched in the Flory–Rehner mode[26], although maximum swelling (with excess monomer) is not assumed. Demixing (phase separation) between polymer I and polymer II, with concomitant deformation of polymer II with further deformation of polymer I into a shell leads to state 4.

State 4 shows a phase-separated state, with a spherical domain of polymer II forming as the core, surrounded by polymer I, deformed into a spherical shell. In reality, however, the core and shell are not sharply demarked, with some chains mechanically trapped in the wrong phase. Since the distance of diffusion required is less than 500 Å in most cases, this is of the same order as the dimensions of the chains themselves.

Referring to *Figure 2,* the molecular rearrangements taking place on transforming state 3 to state 4 requires amplification. Certainly no covalent bonds are broken during the process, as would be required from a literal interpretation of the model. Instead, phase separation ensues at an early stage of the polymerization of monomer II, when the free energy of mixing becomes positive and the second derivative of the free energy of mixing with respect to composition is negative. This is probably at or before the gel stage for many IPN systems. Thus, the molecular migration begins earlier than illustrated in the model, and hence state 3 is hypothetical, for calculation purposes only.

Thermodynamics of the process

For a closed system at constant pressure and temperature, the Gibbs free energy (hereafter free energy) change, ΔG, is given by

$$\Delta G = \Sigma(\Delta H_{i,i+1}) - T\Sigma(\Delta S_{i,i+1}) \quad (i=1,2,3) \tag{4}$$

where $\Delta H_{i,i+1}$, $\Delta S_{i,i+1}$ represent the enthalpy and entropy changes involved in the process from state i to state $i+1$, respectively; and T is the absolute temperature.

Extending equation (4) to the domain formation process, the free energy change for polymer II domain formation, ΔG_d, can be expressed as

$$\Delta G_d = \sum_{i=1}^{3}(\Delta H_{i,i+1}) - T\sum_{i=1}^{3}(\Delta S_{i,i+1}) + \Delta G_i \tag{5}$$

where ΔG_i represents the interfacial free energy change for domain formation.

The quantity ΔG_i is a thermodynamic property related to the process taking place from state 3 to state 4. *Figure 2* indicates that the path from state 1 to state 3 *via* state 2 can be replaced by the direct path from state 1 to 3. Therefore, equation (5) reduces to

$$\Delta G_d = \Delta H_{13} + \Delta H_{34} - T(\Delta S_{13} + \Delta S_{34}) + \Delta G_i \tag{6}$$

In fact, ΔH_{13} and ΔH_{34} are the heat of mixing and the heat of demixing (the negative heat of mixing) between polymers I and II, respectively, such that the sum of these two terms can be assumed to be zero. This, of course, is an approximation which assumes that the contact heats between monomer II and polymer I do not change on polymerization.

The phase separation from state 3 to state 4 involves configurational and conformational rearrangements which are not necessarily balanced by the transformation from state 1 to state 3. There will be an entropic component to each rearrangement and they will not necessarily cancel each other. (The free energies of polymerization are not considered.)

The quantity ΔS_{13} is equal to the sum of the entropy of mixing, ΔS_m, and the entropy change for the elastic deformation of polymer I being swollen with polymer II, $\Delta S^{\mathrm{I}}_{sw}$. The quantity ΔS_{34} is equal to the sum of the entropy change of demixing, ΔS_{dm}; the rearrangement entropy change for elastic deformation (contraction of the polymer II network upon deswelling, $\Delta S^{\mathrm{II}}_{dsw}$; and the entropy change for elastic deformation (biaxial inflation) of polymer I network, $\Delta S^{\mathrm{I}}_{df}$. Again, ΔS_m and ΔS_{dm} cancel each other, ending up zero. The interfacial free energy change, ΔG_i consists of the interfacial free energy change for quiescent domain formation, ΔG_i^0. A term for the entropy change on placing polymer I and II molecules in each domain, ΔS_p, must also be added. In summary, the free energy change for polymer II domain formation can be expressed as follows:

$$\Delta G_d = -T(\Delta S^{\mathrm{I}}_{sw} + \Delta S_p + \Delta S^{\mathrm{II}}_{dsw} + \Delta S^{\mathrm{I}}_{df}) + \Delta G_i^0 \qquad (7)$$

The superscripts I and II indicate changes for polymers I and II only.

In the following sections, each of the thermodynamic quantities in equation (7) will be developed.

Entropy change for the elastic deformation of polymer I by swelling with polymer II

Polymer network I undergoes an isotropic deformation by being swollen with polymer II, which gives rise to an entropy change. The entropy change upon affine elastic deformation is given by[26-30]

$$\Delta S^{\mathrm{I}}_{sw} = -\frac{v'_{\mathrm{I}}}{2}\mathbf{R}(3\alpha^2 - 3 - \ln\alpha^3) \qquad (8)$$

where v' is the number of moles of effective network chains, α represents the linear deformation ratio upon isotropic swelling, and $\mathbf{R}$ represents the gas constant.

Then, from equation (2) and *Figure 1*,

$$v'_1 = \frac{4}{3}\pi R_0^3 \varphi_1 v_1 = \frac{\pi}{6}\left(\frac{\varphi_1}{\varphi_2}\right) v_1 D_2^3 \qquad (9)$$

where D_2 is the diameter of the polymer II domain and v_1 is the number of effective network chains (in moles) of polymer I per unit volume of dry polymer I.

The quantity α is equal to $\varphi_1^{-1/3}$, as defined in equation (3). Therefore, $\Delta S^{\mathrm{I}}_{sw}$ is finally expressed as

$$\Delta S_{\mathrm{I}sw} = -\frac{\pi}{12}\left(\frac{\phi_1}{\phi_2}\right) v_1 \mathbf{R}(3\phi_1^{-2/3} - 3 + \ln\phi_1) D_2^3 \qquad (10)$$

Rearrangement entropy change

The thermodynamic probability, Ω, of placing N_1 polymer I linear molecules by N_2 polymer II linear molecules into the shell domain and its core could be expressed as

$$\Omega = {\varphi_1}^{N_1}{\varphi_2}^{N_2} \qquad (11)$$

where φ_1 and φ_2 represent the volume fraction of the shell and the core, respectively.

The entropy change, ΔS, and Ω are related by the Boltzmann equation

$$\Delta S = -k\ln\Omega \qquad (12)$$

where k is Boltzmann's constant.

Combining equations (11) and (12), the rearrangement entropy change, ΔS_p, of placing the polymers I and II in domains and expressing N_1 and N_2 in moles yields

$$\Delta S_p = -\mathbf{R}(N_1 \ln\varphi_1 + N_2 \ln\varphi_2) \qquad (13)$$

Then, referring to *Figure 1* and equation (2),

$$N_1 = \frac{4}{3}\pi(R_0^3 - R^3)\frac{\rho_1}{M_1} = \frac{\pi}{6}\left(\frac{\varphi_1}{\varphi_2}\right)\left(\frac{\rho_1}{M_1}\right)D_2^3 \qquad (14)$$

and

$$N_2 = \frac{4}{3}R^3\left(\frac{\rho_2}{M_2}\right) = \frac{\pi}{6}\left(\frac{\rho_2}{M_2}\right)D_2^3 \qquad (15)$$

where ρ_1 and ρ_2, and M_1 and M_2 represent the densities and molecular weights of polymers I and II, respectively.

Substituting equation (14) and equation (15) into equation (13), the rearrangement entropy is finally expressed as

$$\Delta S_p = -\frac{\pi}{6}\mathbf{R}\left(\frac{\phi_1}{\phi_2}\frac{\rho_1}{M_1}\ln\phi_1 + \frac{\rho_2}{M_2}\ln\phi_2\right)D_2^3 \qquad (16)$$

Entropy change for elastic deformation of polymer II

Polymer II is polymerized in the presence of polymer I such that polymer II is in a swollen state. The swollen polymer II then deswells into the spherical core, which constitutes an isotropic contraction type of deformation. Therefore, again from equation (9) and equation (2),

$$v'_2 = \frac{4}{3}\pi R_0^3 \varphi_2 v_2 = \frac{\pi}{6} v_2 D_2^3 \qquad (17)$$

where v'_2 is the number of moles of elastically effective polymer II network chains, not considering the total volume. The polymer II linear contraction is given by

$$\alpha = \left(\frac{\varphi_2}{\varphi_1 + \varphi_2}\right)^{1/3} = \varphi_2^{1/3} \qquad (18)$$

such that

$$\Delta S^{\mathrm{II}}_{dsw} = -\frac{\pi}{12} v_2 \mathbf{R}(3\varphi_2^{2/3} - 3 - \ln\varphi_2)D_2^3 \qquad (19)$$

Entropy change for biaxial elastic deformation (inflation of polymer I)

As the domain model in *Figure 1* indicates, polymer I is biaxially deformed into a spherical shell. The deformation entropy change, $\Delta S^{\mathrm{I}}_{df}$, is related to different strains in different directions and hence could be represented in terms of λ_x, λ_y and λ_z. Evaluation of $\Delta S^{\mathrm{I}}_{df}$ is achieved by working out the geometry of biaxial deformation. As

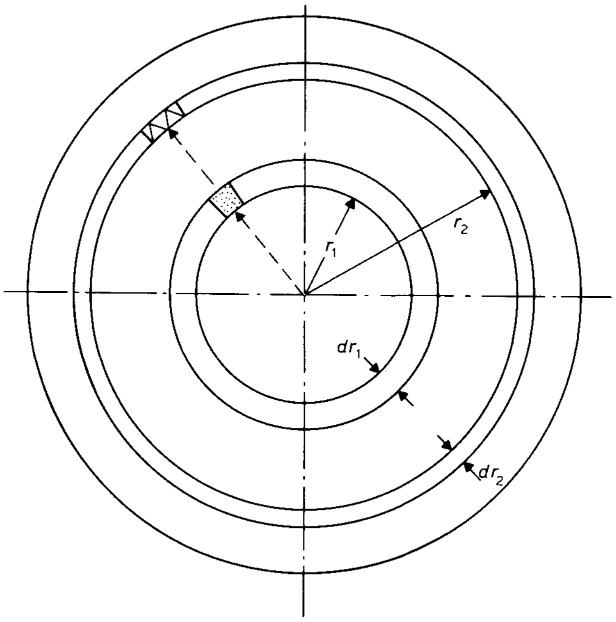

Figure 3 Working geometry for biaxial deformation — I

depicted in *Figure 3*, an element in a sphere of the swollen network ends up strained and in a new location in the spherical shell. The volume of the isotropically swollen element, ΔV_1, equals $\Delta X_1 \Delta Y_1 \Delta Z_1$.

Upon demixing and moving to r_2, its volume becomes $V_2 = \phi_2\ \Delta X_2 \Delta Y_2 \Delta Z_2 = \phi_1 \Delta X_2^2 \Delta Z_2$ (i.e. biaxially deformed).

The entire shell at r_1 moves to r_2 upon demixing and is strained such that

$$\varphi_1 = \frac{4\pi r_2^2 dr_2}{4\pi r_1^2 dr_1} \tag{20}$$

i.e.

$$dr_2 = \varphi_1 \left(\frac{r_1^2}{r_2^2} \right) dr_1 \tag{21}$$

Let α_{zs} be the strain ratio in radial direction, then

$$\alpha_{zs} = \frac{dr_2}{dr_1} = \varphi_1 \frac{r_1^2}{r_2^2} \tag{22}$$

The area ratio of the shells at r_2 and r_1 is $4\pi r_2^2 / 4\pi r_1^2 = r_2^2 / r_1^2$ such that the strain ratio in x direction is expressed as

$$\alpha_{xs} = \left(\frac{r_2^2}{r_1^2} \right)^{1/2} = \frac{r_2}{r_1} \tag{23}$$

Since the deformation is biaxial,

$$\alpha_{ys} = \left(\frac{r_2^2}{r_1^2} \right)^{1/2} = \frac{t_2}{r_1} \tag{24}$$

Now it is necessary to find r_2 in terms of r_1 and φ_1. After phase separation, the material which was inside r_1 resides in a spherical shell between R (*Figure 1*) and r_2, as deformed (see *Figure 4*), where R is the final value for r_2 after phase domain formation is complete. Then:

$$\frac{4}{3}\pi r_1^3 \varphi_1 = \frac{4}{3}\pi (r_2^3 - R^3) \tag{25}$$

such that

$$r_2 = (R^3 + \varphi_1 r_1^3)^{1/3} \tag{26}$$

Substituting equation (2) into equation 26),

$$r_2 = \{R_0^3 (1 - \varphi_1) + \varphi_1 r_1^3\}^{1/3} \tag{27}$$

Recognizing that $\lambda_x = \alpha\, \alpha_{xs}$, equations (3), (23) and (27) can be combined to give

$$\lambda_x = \varphi_1^{-1/3} \{R_0^3 (1 - \varphi_1) + \varphi_1 r_1^3\}^{1/3} / r_1 \tag{28}$$

Let r_1 equal $f R_0$, such that f represents a fractional radius position going from 0 to 1 over the sphere. Then,

$$\lambda_x = \lambda_y = \varphi_1^{-1/3} \{R_0^3 (1 - \varphi_1) + \varphi_1 f^3 R_0^3\}^{1/3} (f R_0)^{-1} \tag{29}$$

$$\lambda_x = \lambda_y = \left\{ 1 + \frac{\varphi_2}{\varphi_1} f^{-3} \right\}^{1/3} \tag{30}$$

Likewise, from λ_z equalling α times α_{zs}, and equations (3), (22) and (27),

$$\lambda_z = \varphi_1^{-1/3} \varphi_1 r_1^2 \{R_0^3 (1 - \varphi_1) + \varphi_1 r_1^3\}^{-2/3} \tag{31}$$

$$\lambda_z = \left\{ 1 + \left(\frac{\varphi_2}{\varphi_1} \right) f^{-3} \right\}^{-2/3} \tag{31a}$$

For a spherical shell of radius r_1 and thickness dr_1, its volume is $4\pi r_1^2 dr_1$ which contains $v_1 \phi_1 (4\pi r_1^2) dr_1$ elastically effective network chains.

From a consideration of the entropy change on affine deformation *via* swelling[26–29].

$$\mathrm{d}(\Delta \mathrm{S}_{df}^{\mathrm{I}}) = \frac{v_1}{2} \mathbf{R} \varphi_1 (4\pi r_1^2)(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3 - \ln \lambda_x \lambda_y \lambda_z) dr_1 \tag{32}$$

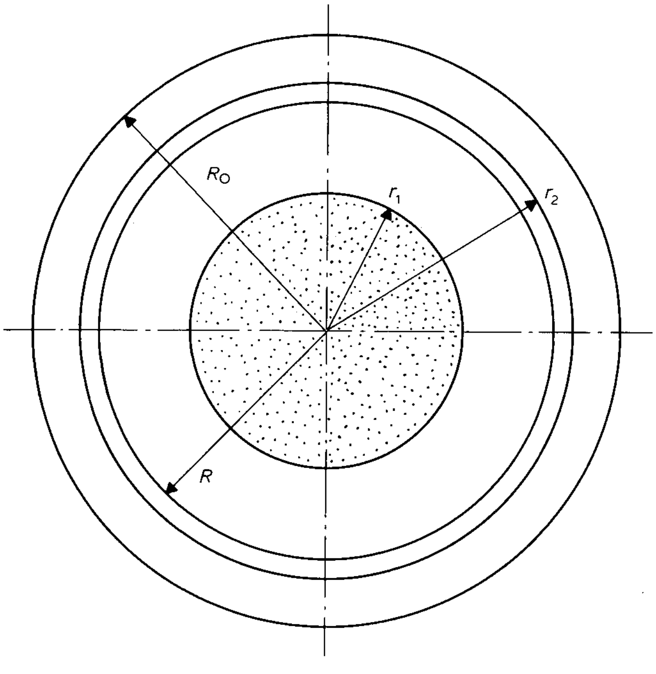

Figure 4 Working geometry for biaxial deformation — II

The quantity ln $\lambda_x\lambda_y\lambda_z$ is seen to equal zero.

$$+\left(1+\frac{\phi_2}{\phi_1}f^{-3}\right)^{-4/3}-3\Bigg\}f^2df \tag{32a}$$

$$d(\Delta S^{\mathrm{I}}_{df})=\frac{\pi}{4}v_1\left(\frac{\phi_1}{\phi_2}\right)\mathbf{R}D_2^3\Bigg\{2f^2\left(1+\frac{\phi_2}{\phi_1}f^{-3}\right)^{2/3}$$

$$d(\Delta S^{\mathrm{I}}_{df})=\frac{\pi}{4}v_1\left(\frac{\varphi_1}{\varphi_2}\right)\mathbf{W}D_2^3\Bigg\{2f^2\left(1+\frac{\varphi_2}{\varphi_1}f^{-3}\right)^{2/3}$$

$$+f^2\left(1+\frac{\varphi_2}{\varphi_1}f^{-3}\right)^{-4/3}-3f^2\Bigg\}df \tag{32b}$$

Integrating equation (32b) from $f=0$ to $f=1^{30}$, the entropy change for biaxial elastic deformation of polymer I is finally expressed as

$$\Delta S^{\mathrm{I}}_{df}=\frac{\pi}{4}v_1\mathbf{R}\left(\frac{1}{\phi_2}\right)(2\phi_1^{1/3}-\phi_1^{4/3}-\phi_1)D_2^3 \tag{33}$$

Interfacial free energy change for domain formation

The interfacial free energy change for domain formation is brought about from the intrinsic interfacial tension between the two polymers, γ^0. This can be expressed as

$$\Delta G_i^0=\pi\gamma^0D_2^2 \tag{34}$$

for spheres.

Now, the free energy change for domain formation, ΔG_d, can be expressed by substituting equations (10), (16), (19), (33) and (34) into equation (7). After appropriate manipulation and rearrangement, ΔG is given by

$$\Delta G_d=-\frac{\pi}{6}\mathbf{R}T\Bigg[-\left\{\frac{\phi_1}{\phi_2}\frac{\rho_1}{M_1}\ln\phi_1+\frac{\rho_2}{\mathrm{M}_2}\ln\varphi_2\right\}$$

$$+\frac{v_1}{2}\left(\frac{1}{\varphi_2}\right)(3\varphi_1^{1/3}-3\varphi_1^{4/3}-\varphi_1\ln\varphi_1)$$

$$-\frac{v_2}{2}(3\varphi_2^{2/3}-3-\ln\varphi_2)\Bigg]D_2^3+\pi\gamma^0D_2^2 \tag{35}$$

In order to determine the domain size, D_2, which gives a minimum in the free energy, the first partial derivative of equation (36) with respect to D_2, $\partial(\Delta G_d)/\partial D_2$, is equated to zero and solved for D_2, i.e.

$$\frac{\partial(\Delta G_d)}{\partial D_2}=-\frac{\pi}{2}\mathbf{R}T\Bigg[-\left\{\frac{\varphi_1}{\varphi_2}\frac{\rho_1}{M_1}\ln\varphi_1+\frac{\rho_2}{M_2}\ln\phi_2\right\}$$

$$+\frac{v_1}{2}\left(\frac{1}{\varphi_2}\right)(3\varphi_1^{1/3}-3\varphi_1^{4/3}-\varphi_1\ln\varphi_1)$$

$$-\frac{v_2}{2}(3\varphi_2^{2/3}-3-\ln\varphi_2)\Bigg]D_2^2+2\pi\gamma^0D_2=0 \tag{36}$$

Thus solving for D_2

$$D_2=4\gamma^0[\mathbf{R}T(Av_1+Bv_3-C)]^{-1} \tag{37}$$

where

$$A=\frac{1}{2}\left(\frac{1}{\phi_2}\right)(3\phi_1^{1/3}-3\phi_1^{4/3}-\phi_1\ln\phi_1) \tag{38}$$

$$B=\frac{1}{2}(\ln\phi_2-3\phi_2^{2/3}+3) \tag{39}$$

$$C=\frac{\phi_1}{\phi_2}\frac{\rho_1}{M_1}\ln\phi_1+\frac{\rho_2}{M_2}\ln\phi_2 \tag{40}$$

Thus, equation (37) provides D_2 in terms of the volume fraction and crosslink density of each component, and the interfacial tension. Terms for molecular weight are provided, if applicable. Specific forms of equation (37) for individual cases will be derived in the next section.

SPECIFIC FORMS FOR THE EQUATIONS

Characteristics

The experimental variables required for equation (37) are the volume fraction, density, crosslink density, molecular weight, interfacial tension and temperature.

All of these variables are measurable experimentally or obtainable by calculation from experiment.

Equation (37) can be applied to various IPN's cases in specific forms. A few of the most important follow. Others are developed in ref. 30.

(1) The case of $v_1\neq0$ and $v_2\neq0$ for sequential IPN's: With $M_1=M_2=\infty$ equation (37) is simplified to

$$D_2=4\gamma^0[\mathbf{R}T(Av_1+Bv_2)]^{-1} \tag{41}$$

Equation (41) predicts that the domain diameter of polymer II depends on the interfacial tension as well as on the crosslink densities of both networks I and II. However, an evaluation of the relative magnitudes of the constants A and B indicate that v_1 is about 10 times as important as v_2.

(2) The Case of $v_1\neq0$ and $v_2=0$:
This is a semi-IPN of the first kind. With $M_1=\infty$ equation (37) reduces to

$$D_2=4\gamma^0\left[\mathbf{R}T\left(Av_1-\frac{\rho_2}{M_2}\ln\phi_2\right)\right]^{-1} \tag{42}$$

(3) The case of $v_1=0$ and $v_2=0$:
This is the case of semi-IPN of the second kind. With $M_2=\infty$, equation (37) reduces to

$$D_2=4\gamma^{\circ}\left\{\mathbf{R}T\left(Bv_2-\frac{\phi_1}{\phi_2}\frac{\rho_1}{M_1}\ln\phi_1\right)\right\}^{-1} \tag{43}$$

POLY(n-BUTYL ACRYLATE)/POLYSTYRENE IPN'S AND RELATED MATERIALS

The present authors have carried out morphology studies using *TEM* on poly(n-butyl acrylate)/polystyrene, PnBA/PS, IPN's and related materials[5,31].

Table 1 shows the domain sizes for this system, illustrating a wide range of crosslink levels. Column A

Table 1 Experimental and theoretical domain sizes for poly(n-butyl acrylate)/polystyrene IPNs and semi IPNs

	Variables		Domain diameter, D_2 (Å)			
				Theory, $\gamma^0 = 3.65$ dynes cm^{-1}		
System*	$\nu \times 10^5$ (mol cm^{-3}) $M \times 10^{-5}$ (g mol^{-1})	Volume ratio	Experiment	*A*	*B*	*C*
	$\nu_1 = 3.7$	25/75	800	845	1170	447
	$\nu_2 = 21.8$	40/60	650	644	883	362
		50/50	550	572	725	321
IPN	$\nu_1 = 21.8$	25/75	200	207	200	141
	$\nu_2 = 21.8$	40/60	170	169	148	115
		60/40	150	143	98	93
	$\nu_2 = 21.8$:const					
	$\nu_1 = 3.7$		550	572	725	321
	$\nu_1 = 14.0$	50/50	260	224	192	137
	$\nu_1 = 21.8$		195	154	124	103
	$\nu_1 = 25.0$		120	136	108	94
	$\nu_1 = 3.7$	25/75	1250	1314	1037	441
	$M_2 = 3.0$	40/60	1000	1084	804	359
Semi-1						
	$\nu_1 = 21.8$	25/75	250	227	193	140
	$M_2 = 3.0$	60/40	180	161	97	92
Semi-2	$M_1 = 2.0$ $\nu_2 = 10.0$	33/67	3330	3260	–	–

* TEGDM for crosslinker I and DVB for crosslinker II
A Present theory
B The linear form of Donatelli equation, equation (44)
C The cubic form of Donatelli equation, equation (45)

illustrates the present theory. Columns B and C of *Table 1* contain the calculated values of the domain diameter according to linear and cubic forms of the Donatelli equation, i.e., the linear form[24]:

$$D_2 = 2\gamma^0 \phi_2 / \mathbf{R} T v_1 \phi_1 \left[\left(\frac{1}{\phi_1} \right)^{2/3} + \left(\frac{\phi_2}{\phi_1} \right) \frac{1}{v_1 M_2} \frac{1}{2} \right] \quad (44)$$

and the cubic form:

$$\frac{v_1^2 D_2^3}{c^2 K^2} \phi_1 + \left(\frac{\phi_2}{M_2} - \frac{\phi_1 v_1}{2} \right) D_2 = \frac{2\gamma^0 \phi_2}{\mathbf{R} T} \quad (45)$$

where c, $K(=r_0/M^{1/2})$ are constants, and φ represents the volume fraction. In the calculation of the domain sizes in column C (equation (45)), $c = \sqrt{2}$ and $K = 8 \times 10^{-9}$, respectively. The quantity v_1 is defined for the dry network I state[25].

Both the present theory and the Donatelli, *et al.*, theory show that the domain sizes are sensitive to the value of interfacial tension.

It should be noted that equations (44) and (45) do not provide any values for the semi-2 IPN case.

DISCUSSION

Several points developed in the theory require amplification. First, to what extent is true thermodynamic equilibrium attained in the development of the phase domains? Certainly, there are some mechanically entrapped chains. It might also be that spinodal decomposition processes rather than binodal phase separation actually takes place. If so, the extent of phase separation might be controlled by kinetic rather than thermodynamic considerations.

However, in the real case, phase separation begins before the gelation stage, mitigating (but not eliminating) the problem.

Secondly, the model in *Figure 2* needs amplification. The free energy of polymerization is ignored, as not pertinent to this problem, especially under the assumption of an isothermal process. More importantly, the going from state 3 to state 4 seems to require the passage of one chain through another. State three is only hypothetical, it must be emphasized, and used as a convenient mathematical model. As per above comment, phase separation begins before polymerization of network II is complete. The real limitation is the development of the mechanically entrapped chains.

Lastly, equation (37) and the model assumes the development of discontinuous, spherical domains. In a recent paper(32), Widmaier and Sperling showed that for midrange compositions of the poly(n-butyl acrylate)/polystyrene IPN's, significant amounts of dual phase continuity exist. The development of discontinuous spheres occurs only for very low amounts of polymer II, below about 30%.

CONCLUSIONS

A statistical thermodynamic theory describing IPN domain formation was developed and then extended to the case of semi-IPN's; each theoretical equation provided the polymer II phase domain size, D_2. This model was tested with various IPN's and related materials from the literature, and found to predict variations in the domain size over a wide range of overall composition, crosslink density, interfacial tension, and molecular weight (see also ref. 30).

The present theory can be contrasted with that of Donatelli *et al.* in several ways: (1) In the present theory, polymer I network undergoes an isotropic swelling and then subsequent deformation induced by phase separation. However, the Donatelli equation considers only polymer I deformation of isotropic swelling; deformation due to phase separation is implicit rather than explicit. (2) A contracted polymer II network is considered in the present model, while an unperturbed polymer II network remains in the Donatelli model. (3) The present model can be extended to the case of semi-2 IPN's and SIN's. (4) The Donatelli cubic equation contains a semi-empirical constant, *c*.

Both theories, however, utilize the interfacial tension between polymers I and II in a similar manner. While experimental values are known for some systems, the best fit values otherwise are in the range predicted by theory.

Some further comments about the present domain model should be made: The core-shell spherical domain model has important intrinsic limitations in the cases of extreme composition ratios and/or high crosslink densities. These morphologies are featured by the presence of polymer II phase connectivity and irregularly shaped domain structures. Thus it would be desirable to extend the present reasoning to the morphologies based on other presumable geometric domain shapes, such as cylindrical arrays or alternating lamellae.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the support of the National Science Foundation through Grant No. DMR 77-15439 A02, Polymers Program. The authors also wish to thank Mr J. Michel for his many helpful suggestions in preparing the manuscript.

REFERENCES

1 Manson, J. A. and Sperling, L. H. 'Polymer Blends and Composites', Plenum, 1976

2 Sperling, L. H. 'Interpenetrating Polymer Networks and Related Materials', Plenum, 1981

3 Olabisi, O., Robeson, L. M. and Shaw, M. T. 'Polymer–Polymer Miscibility', Academic Press, 1979

4 Bucknall, C. B. 'Toughened Plastics', Applied Science, 1977

5 Yeo, J. K., Sperling, L. H. and Thomas, D. A. *Polym. Eng. Sci.* 1982, **22**, 190

6 Cooper, S. L. and Estes, G. M. Eds., 'Multiphase Polymers', Adv. in Chem. Series 176, ACS, 1979

7 Klempner, D. and Frisch, K. C. Eds., 'Polymer Alloys II', Plenum, 1980

8 Lipatov, Yu. S. and Sergeeva, L. M. 'Interpenetrating Polymeric Networks', Naukova Dumka, Kiev, 1979

9 Krause, S. *J. Polym. Sci., A-2* 1968, **1**, 249

10 Krause, S. *Macromolecules* 1970, **3**, 84

11 Meier, D. J. *J. Polym. Sci., C* 1969, **26**, 81

12 Meier, D. J. *J. Phys. Chem.* 1967, **11**, 1861

13 Meier, D. J. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* 1977, **18**, 340

14 Leary, D. F. and Williams, M. C. *J. Polym. Sci., Polym. Phys. Edn.* 1973, **11**, 345

15 Leary, D. F. and Williams, M. C. *J. Polym. Sci., Polym. Phys. Edn.* 1974, **12**, 265

16 Pouchly, J., Zivny, A. and Sikora, A. *J. Polym. Sci., C* 1972, **39**, 133

17 Pouchly, J., Zivny, A. and Sikora, A. *J. Polym. Sci., A-2* 1972, **10**, 151

18 Bianchi, U., Pedemonte, E. and Turturro, A. *J. Polym. Sci., B* 1969, **7**, 785

19 Bianchi, U., Pedemonte, E. and Turturro, A. *Polymer* 1970, **11**, 268

20 Marker, L. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* 1969, **10**, 524

21 Helfand, E. *J. Chem. Phys.* 1975, **62**, 999

22 Helfand, E. *Macromolecules* 1975, **8**, 552

23 Inoue, T., Seon, T., Hashimoto, T. and Kawai, H. *Macromolecules* 1970, **3**, 87

24 Donatelli, A. A., Sperling, L. H. and Thomas, D. A. *J. Appl. Polym. Sci.* 1977, **21**, 1189

25 Michel, J., Hargest, S. C. and Sperling, L. H. *J. Appl. Polym. Sci.* 1981, **26**, 743

26 Flory, P. J. 'Principles of Polymer Chemistry', Cornell, Ithaca, 1953

27 Dusek, K. and Prins, W. *Adv. Polym. Sci.* 1969, **6**, 1

28 Wall, F. T. and Flory, P. J. *J. Chem. Phys.* 1951, **19**, 1435

29 Treloar, L. R. G. 'The Physics of Rubber Elasticity', 3rd Edn., Clarenden Press, Oxford, 1975

30 Yeo, J. K. *Ph.D. Thesis*, Lehigh University, 1981

31 Yeo, J. K., Sperling, L. H. and Thomas, D. A. *Polym. Sci. Eng.* 1981, **21**, 696

32 Widmaier, J. M. and Sperling, L. H. *Macromolecules* 1982, **15**, 625