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A quantitative image analysis method for the determination of cocontinuity in polymer blends*

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A new morphological parameter, 'CoContinuity', has been developed and implemented for quantitative measurement of morphology in cocontinuous blends of polymers. The basis of the CoContinuity is the extent to which the phases of a polymer blend mutually surround each other. A secondary parameter, 'CoContinuity Balance', is also presented to describe quantitatively the relative contribution of each phase to the CoContinuity. Both of these functions are dimensionless and scale-invariant, thus allowing objective comparisons of dissimilar systems. An example is given where the functions faithfully describe the evolution of a polycarbonate/poly(styrene-*co*-acrylonitrile) (PC/SAN) blend of varying phase ratio as the system progresses from discrete domains of the SAN phase in a matrix of PC, through a cocontinuous morphology of SAN and PC, and finally ends up as a mixture of discrete domains of PC in a matrix of SAN.

(Keywords: image analysis; polymer blends; cocontinuity)

INTRODUCTION

The morphology of polymer blends varies with phase ratio, composition and processing. A typical morphological evolution for increasing phase ratio of polymer A to polymer B starts with discrete domains of A in a matrix of B ($A/B<1$), moves through a cocontinuous distribution of A and B ($A/B \approx 1$), and finishes with discrete domains of B in a matrix of A ($A/B>1$). For low phase ratios, A is often seen as filled convex particles embedded in the continuous B phase. As the ratio increases, A domains begin to evolve into irregular shapes, though still recognizable as separate domains. Further increase in the phase ratio leads to A domains that extend into and surround the B phase while the B phase simultaneously extends into and surrounds the A phase. This condition is typically given the descriptor 'cocontinuous' because both phases appear to be continuous throughout the observed field. Yet-higher phase ratios yield an inversion where the A phase is now the continuous matrix and the B phase is present as separated domains surrounded by the A phase.

An example of morphological evolution is shown in the binary images of *Figures 1a–1f* taken from the work of Skochdopole *et al.*[1]. The magnification in *Figures 1a–1c* is approximately three times greater than in *Figures 1d–1f*. The dark phase is a 70/30 styrene/acrylonitrile copolymer (SAN) and the light phase is polycarbonate (PC). The phase ratios are 10%, 20%, 30%, 40%, 50% and 75% SAN in PC, respectively. The morphology in *Figures 1a–1c* shows discrete domains of SAN in a matrix of PC with domain shape becoming less regular with increasing fraction of SAN. *Figures 1d* and *1e* exhibit cocontinuity of SAN and PC, although *Figure 1e* is just beginning to show formation of discrete domains of PC in SAN. In *Figure 1f*, the morphology has 'inverted', with domains of PC clearly suspended in a matrix of SAN.

The description of this morphological evolution is normally done qualitatively, similar to that above, with imprecise adjectives and highly context-sensitive comparisons. Quantitative descriptors of the individual particles do not address the overall character of the blend. No single-valued parameter has been defined to describe quantitatively the cocontinuity of the two phases based on direct measurements of the phase domains.

This work describes a new parameter, designated 'CoContinuity', which yields a quantitative measure of the cocontinuity of a two-phase polymer blend†. The derived parameter is based on the areas and convex areas of every domain in both phases. The intention is to describe numerically, across the entire field of view, the extent to which the individual features of one phase surround the features of the other phase, as well as other features of the same phase. In addition to the mathematical formulation, a discussion of the necessary quantitative behaviour of the function and the interpretation of the measured values are presented and an example application is given.

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† Throughout this report, measured or specifically defined values will be designated with capitalized letters while generic descriptors will be treated as common words: such as the CoContinuity function, which measures the cocontinuity of two phases

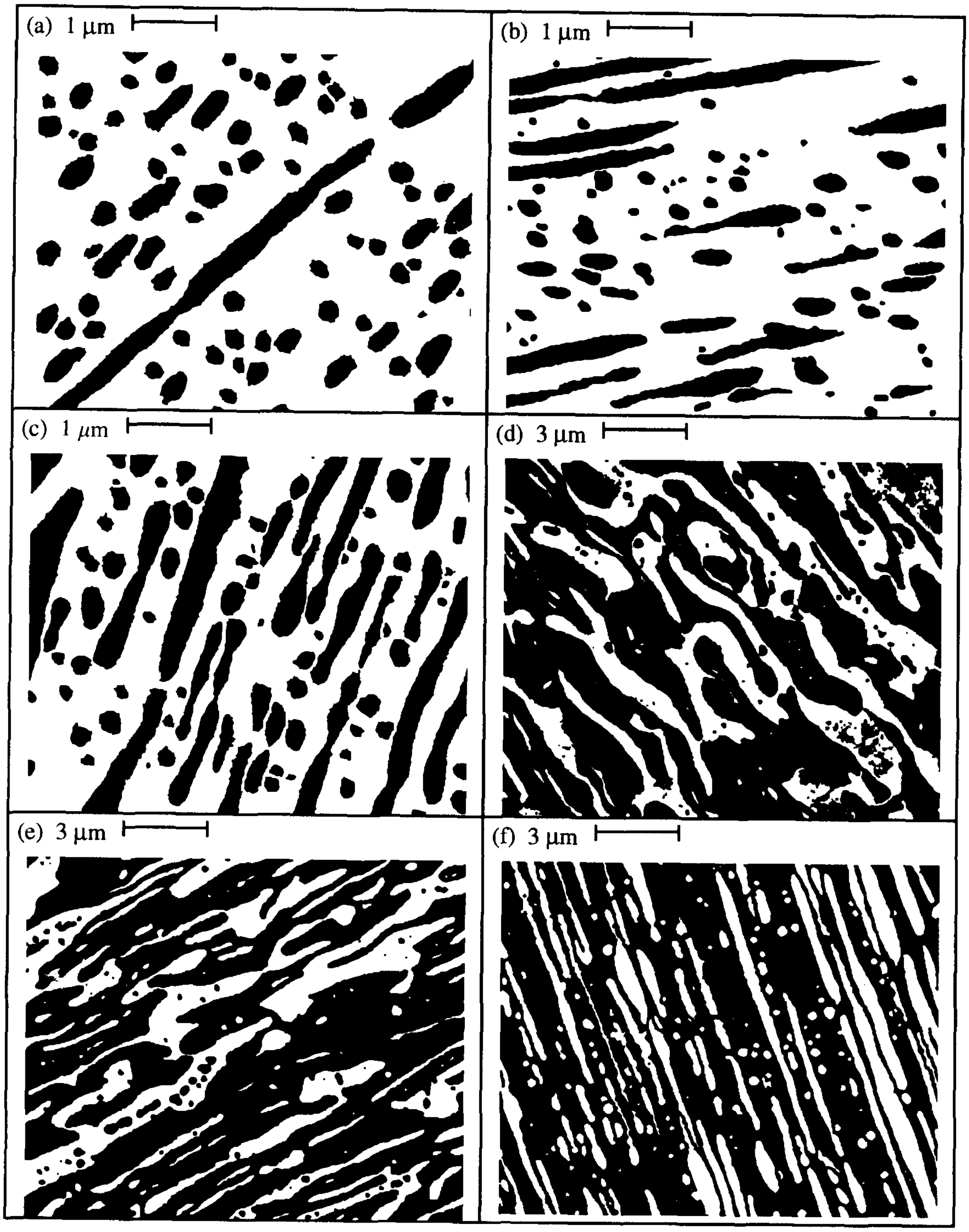

Figure 1 Binary images of PC/SAN(30%AN) blends with varying composition. The light phase is PC, dark phase is: (a) 10% SAN, (b) 20% SAN, (c) 30% SAN, (d) 40% SAN, (e) 50% SAN, (f) 75% SAN

THEORY

Micrographs of binary polymer blends typically show one phase as a different darkness than the other. The digitized form of the image is a two-dimensional array of picture elements (pixels) with values of 0 through $2^n - 1$ where n is the number of bits in the analogue-to-digital converter used to digitize the image. In order to measure the features of the two phases, designated A and B, an intensity range is selected so that pixels of one phase are within the range and pixels from the other phase are outside of the range. The image is made into a binary representation by setting all the pixels within the selected intensity range to 'black' ($=2^n - 1$) and all the pixels outside the range to 'white' ($=0$). The 'black' features are then measured.

The features of the binary image of the two phases have, among other measurable parameters, an Area and a Convex Area. The Area is simply the number of pixels within the boundary of the feature multiplied by the area per pixel. The Convex Area is the area per pixel multiplied

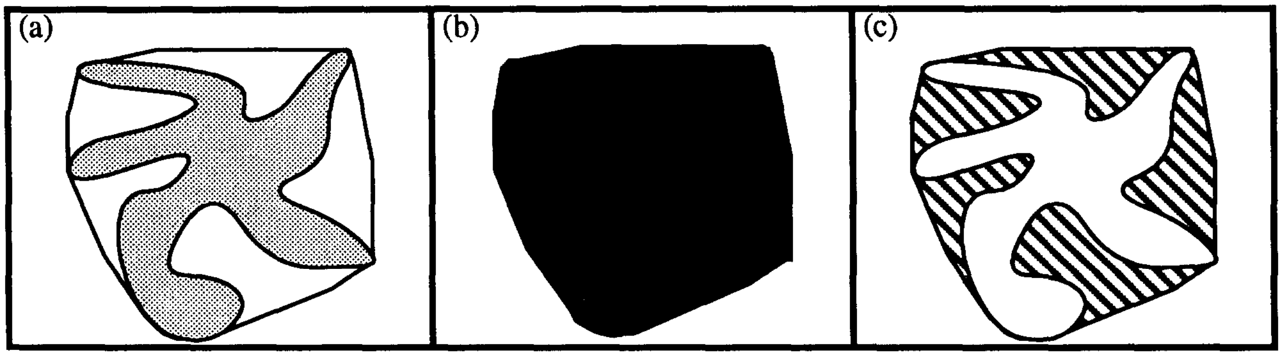

Figure 2 Examples of measurements for an arbitrary particle. (a) Amorphous particle with 32-sided equiangular polygon drawn as the Convex Perimeter. (b) Convex Area of particle from (a) = Area of Convex Perimeter. (c) Excess Coverage of the particle in (a) = Convex Area − Area

Table 1 Parameters derived from Area and Convex Area measurements of features in a binary blend. A_i and B_i are the ith features of phases A and B, respectively, and n is the number of particles in the phase being measured

Description	Code	Formula	Equation No.
Area of A	AA	$\sum_{i=1}^{n} \text{Area}(A_i)$	(1)
Area of B	AB	$\sum_{i=1}^{n} \text{Area}(B_i)$	(2)
Convex Area of A	CAA	$\sum_{i=1}^{n} \text{Convex Area}(A_i)$	(3)
Convex Area of B	CAB	$\sum_{i=1}^{n} \text{Convex Area}(B_i)$	(4)
Area Fraction of A	AFA	$\frac{AA}{AA+AB}$	(5)
Area Fraction of B	AFB	$\frac{AB}{AA+AB}$	(6)
Coverage of A	CA	$\frac{CAA}{AA+AB}$	(7)
Coverage of B	CB	$\frac{CAB}{AA+AB}$	(8)
Excess Coverage of A	ECA	$CA-AFA$	(9)
Excess Coverage of B	ECB	$CB-AFB$	(10)
CoContinuity of A and B	$CCAB$	$ECA+ECB-(ECA-ECB)\left(\frac{ECA-ECB}{ECA+ECB}\right)$	(11)
		$=\frac{4\times ECA\times ECB}{ECA+ECB}$	(12)
CoContinuity Balance	CCB	$\frac{ECA}{ECB}$	(13)

by the total number of all pixels within the convex perimeter of the feature, where the convex perimeter is defined as the 32-sided equiangular polygon that circumscribes the feature. The Excess Coverage of a given particle is the difference between the Convex Area and the Area. These different areas are illustrated in *Figure 2*. The features for the 'white' phase can be quantified by inverting the intensities (black→white, white→black) and remeasuring the image. The areas and convex areas measured for each feature can be combined to yield the derived parameters shown in *Table 1*: summed Area of A (AA), summed Area of B (AB), summed Convex Area of A (CAA), summed Convex Area of B (CAB), area fraction of A (AFA), area fraction of B (AFB), coverage of A (CA), coverage of B (CB), excess coverage of A (ECA), excess coverage of B (ECB), CoContinuity of A and B ($CCAB$) and CoContinuity Balance (CCB).

All the derived values, other than AA, AB, CAA and CAB, involve dimensionless ratios of areas relative to the total area of both phases. The Area Fractions will be less than or equal to unity, by definition; however the Convex Area, Coverage and Excess Coverage may exceed unity, due to overlapping features. The CoContinuity Balance has been introduced for two reasons: to indicate if there is a dominant phase that contributes to the CoContinuity and the extent of that domination. Here, dominance is

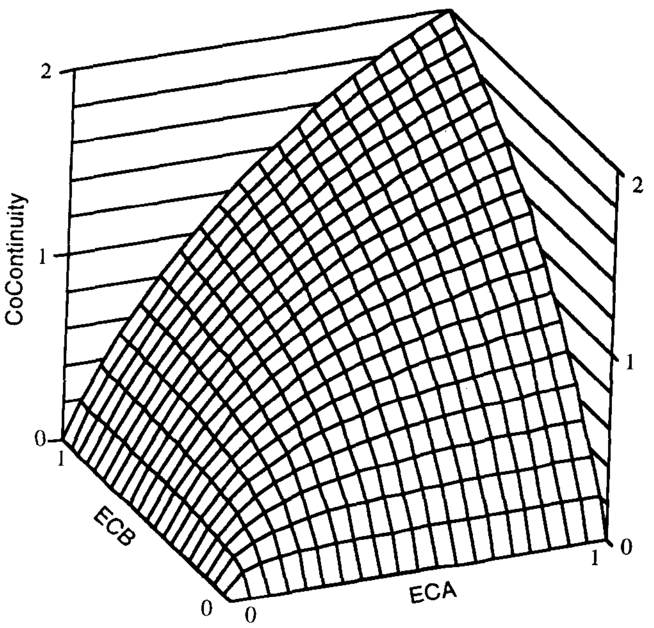

Figure 3 CoContinuity function plotted over the range $0<ECA$, $ECB \leq 1$

defined as greater excess coverage. The CoContinuity function has been calculated and plotted in *Figure 3* for values of *ECA* and *ECB* ranging between 0 and 1. The calculated values are symmetric about the line $ECA = ECB$. The value for $ECA = ECB = 0$ is undefined, owing to division by zero, so the value of 0 has been arbitrarily inserted for plotting clarity.

EXPERIMENTAL

Photomicrographs from a transmission electron microscope (TEM) used in a previous study of six examples of blends of polycarbonate (PC) and poly(styrene-*co*-(30%) acrylonitrile) (SAN) were obtained from Skochdopole *et al.*[1]. The six samples contained 10%, 20%, 30%, 40%, 50% and 75% SAN in PC and the binary images are shown in *Figures 1a–1f*, respectively. The images were scanned with a Hewlett–Packard ScanJet Plus™ eight-bit grey-scale flatbed scanner using the DeskScan™ software running on an Apple Macintosh™ computer and analysed with the Prism™ software suite from Signal Analytics on the Macintosh computer‡. Sample descriptions and image collection conditions are summarized in *Table 2*. Staining the sample with OsO_4 caused the SAN phase to appear dark and the PC phase light. Image artifacts were manually edited before analysis. The intensity selection range was set so that the SAN phase became black and the PC phase white. The SAN phase will be referred to as the A phase and the PC as the B phase. The images were analysed for CoContinuity by collecting Area and Convex Area data for features in the SAN and PC phases. The prism software will not analyse particles touching the edge of the field because of the indeterminacy of the particle beyond the field. In order to force the software to measure all the particles, a one-pixel-wide white boundary was drawn around the perimeter of the field. Since this perimeter was drawn, but not measured, in both the positive and negative images, that area will not contribute to nor detract from the measured areas of either phase.

‡ ScanJet Plus and DeskScan are trademarks of Hewlett–Packard, Macintosh is a trademark of Apple Computer, and Prism is a trademark of Analytical Vision

RESULTS

The measurements of the individual features of the two phases were combined according to the equations in *Table 1* and are summarized in *Table 3*. The total areas of the different images are not equal, owing to the magnification differences and slight variations in the scanning parameters. The CoContinuity values are plotted as a function of percentage of SAN in *Figure 4* along with qualitative observations of the morphology.

Some physical properties for the PC/SAN blends were measured in the original work. Most of the properties varied either nearly linearly with composition or changed dramatically with addition of 10% SAN to PC, then had very little change for additional SAN. The property that was most sensitive to blend morphology was the ultimate impact energy where the impact energy was high until the system passed beyond the cocontinuous regime, where it dropped to a low level. *Figure 5* shows this behaviour, along with the measured CoContinuity. It is seen that the drop in impact energy occurs beyond the maximum CoContinuity, indicating that this physical property depends on a continuous matrix of PC, which is observed in the samples up to and including 40% SAN where the PC and SAN are cocontinuous. Once the morphologically continuous matrix becomes SAN, the impact energy drops precipitously. The CoContinuity Balance verifies this change in the continuous matrix: for the samples of 10% to 40% SAN, $CCB \leq 1$, but for 50% to 75% SAN, $CCB > 1$, indicating that the dominant contributor to the CoContinuity has shifted from PC for the compositions $\leq 40\%$ to SAN for compositions $\geq 50\%$.

DISCUSSION

Requirements of a quantitative cocontinuity value

A quantitative measurement of cocontinuity must reflect what a trained observer sees when a system is described as 'cocontinuous'. In this work, it is asserted that the CoContinuity function must indicate the extent to which the features of each phase in a binary blend mutually surround each other. The Convex Area of a feature represents the area that the individual feature influences and includes the feature's actual area and the area of any other feature that is partially or fully within the convex boundary of the feature in question. The part of the Convex Area that is not part of the actual area is the area that the feature surrounds. In systems with discrete features of one material suspended in a matrix of the other, the matrix completely surrounds the discrete phase and thus has a 'surrounded' area equal to the area of the suspended phase. Convex particles, such as discs, suspended in a matrix have a convex area equal to the real area and thus have zero surrounded area. Particles that have some concave interface structure will 'surround' the material in the concave area. In systems where the

Table 2 Image collection information for polycarbonate/poly(styrene-*co*-(30%)acrylonitrile) blend images used

SAN (%)	Figure No.	Qualitative description of morphology	Image magnif.	Scan rate (dots per inch)
10	*1a*	Discrete SAN, mostly isolated discs	28 200 ×	72
20	*1b*	Discrete SAN discs and elongated ovals	28 200 ×	72
30	*1c*	Discrete SAN, mostly elongated ovals	28 200 ×	72
40	*1d*	Cocontinuous, even contribution	8 400 ×	72
50	*1e*	Cocontinuous, but weighted towards discrete PC	8 400 ×	72
75	*1f*	Discrete PC, similar to 30% SAN sample	8 400 ×	72

Table 3 Tabulated values of measured and derived parameters for digital image analysis of *Figures 1a–1f*

Cumulative measurement	Code or formula	10% SAN	20% SAN	30% SAN	40% SAN	50% SAN	75% SAN
Area of A	*AA*	9.14	12.49	18.15	305.2	397.2	439.2
Area of B	*AB*	36.19	46.26	31.46	251.7	258.7	213.3
Area of A and B	*AA*+*AB*	45.33	58.75	49.61	556.9	655.8	652.5
Convex Area of A	*CAA*	9.52	13.29	21.88	549.9	656.4	645.4
Convex Area of B	*CAB*	45.26	58.65	48.63	548.7	488.8	273.8
Area Fraction of A	*AFA*	0.2017	0.2126	0.3659	0.5480	0.6056	0.6731
Area Fraction of B	*AFB*	0.7983	0.7874	0.6341	0.4520	0.3944	0.3269
Coverage of A	*CA*	0.2099	0.2262	0.4411	0.9875	1.0009	0.9892
Coverage of B	*CB*	0.9984	0.9984	0.9801	0.9853	0.7453	0.4197
Excess Coverage of A	*ECA*	0.0083	0.0136	0.0753	0.4394	0.3953	0.3161
Excess Coverage of B	*ECB*	0.2001	0.2110	0.3460	0.5333	0.3510	0.0928
Total Excess Coverage	*ECA*+*ECB*	0.2083	0.2246	0.4213	0.9278	0.7462	0.4088
Coverage Ratio of A	*CA*/*AFA*	1.0409	1.0640	1.2057	1.8019	1.6527	1.4696
Coverage Ratio of B	*CB*/*AFB*	1.2506	1.2679	1.5457	2.1800	1.8899	1.2837
CoContinuity of A and B	*CCAB*	0.0317	0.0511	0.2472	0.9637	0.7436	0.2868
Cocontinuity Balance	*CCB*	0.041234	0.064464	0.217491	0.823942	1.126354	3.407501

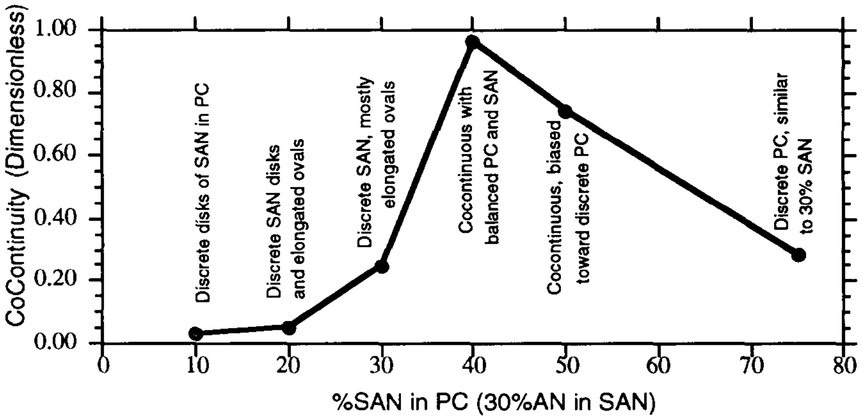

Figure 4 CoContinuity as a function of %SAN in PC/SAN blends along with qualitative observations

two phases are heavily intertwined, each phase surrounds a significant amount of the other phase. In fact, the individual features of a given phase can easily surround part or all of other features of the same phase, as well as features of the other phase. The CoContinuity function must identify the one-sided nature of a matrix that completely surrounds discrete, convex particles and identify it as having lower cocontinuity than the case where both phases are heavily intertwined with significant amounts of surrounded area from each phase as well as the intermediate case of discrete particles with some concave interfaces.

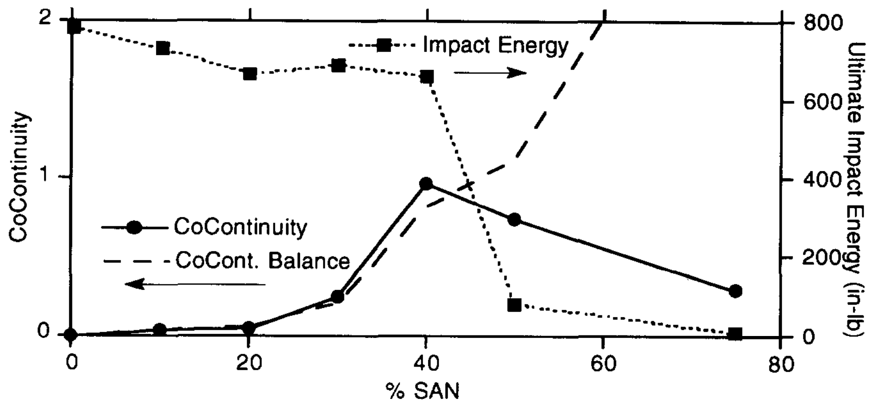

Figure 5 Comparison of ultimate impact energy with quantitative morphological evolution in PC/SAN blends of varying composition (on the vertical scale, 800 in lb ≃ 90 J)

Description of the CoContinuity function

The CoContinuity function proposed here has two basic parts. The first part is the sum of the surrounded areas, designated Excess Coverage, from both phases ($ECA + ECB$), which causes the function to increase as either phase begins to surround the other. This part of the function is sensitive to feature shapes (i.e. morphology) and phase ratios. The sum will always be greater than or equal to zero, with the lower limit occurring only in the case where there are only two features present, one of phase A and one of phase B and the interface between the areas is a single straight line. In general, ECA (or ECB) is not expected to get significantly greater than unity, as this would represent a bulk excess coverage for the A (or B) phase equal to the entire area of the field. The issue of ECA or ECB becoming greater than one is discussed below.

The second part of the CoContinuity function is dependent on the difference between the excess coverages of the two phases. If there is a significant imbalance between the contributions from each phase, this factor will correct for the difference. The coverage difference is multiplied by a factor that is the ratio of that difference to the total excess coverage, where the ratio essentially defines the significance of the difference. In this form, if the excess coverage is dominated by one phase, such as the matrix in a 'discs in matrix' morphology, the second part reduces the calculated CoContinuity appropriately. If the excess coverage is nearly equal from both phases, the second part approaches zero.

Interpretation of the CoContinuity function

Values of the CoContinuity that are near zero indicate discrete, convex particles suspended in a matrix. As the CoContinuity approaches 0.3, some combination of increased suspended phase and partially concave discrete particle morphology is present in the image. CoContinuity values from 0.3 to 0.6 are obtained when the particle–matrix interface morphology is significantly concave without much interpenetration of the particles from the same phase. Larger CoContinuity values indicate significant interpenetration, either from particles of different phases or, in special cases of highly coordinated structures, from the same phase. There is no theoretical upper limit to the CoContinuity, but, practically, values less than 2 are expected from 'typical' cocontinuous systems. The special cases where CoContinuity can exceed 2 and highly coordinated structures will be discussed below.

Experimental results

It is seen in *Figures 1* and *4* that the CoContinuity function correlates well with qualitative observations from this series of PC/SAN blends. Further, the combination of CoContinuity and CoContinuity Balance are able to explain quantitatively the ultimate impact energy behaviour shown in *Figure 5*. In particular, the CoContinuity is a maximum for the image that exhibits the highest degree of qualitatively observed cocontinuity. Additionally, the CoContinuities for 30% SAN and 75% SAN are nearly the same and the qualitative observation is that the two images are essentially identical except that one is dark particles in a light matrix and the other light particles in a dark matrix. Even though there is approximately a factor of 3 difference in magnification, the CoContinuity values are very similar, indicating that the CoContinuity function is scale-invariant. Direct interpretation of the curve in *Figure 4* shows that the morphological evolution for this blend is not symmetric with PC/SAN concentration ratio, indicating that the two components behave in fundamentally different manners when present as the continuous matrix. This conclusion is based on the sharp increase in CoContinuity going from 30% to 40% SAN, then the apparent gradual tapering down to the value at 75% SAN.

Limits on the CoContinuity measurement

As implied above, the expected range of CoContinuity for 'typical' blends is 0 to 2. This is due to the way ECA and ECB are calculated based on area fractions and the general observation that blended systems tend not to exhibit highly coordinated morphology. For example, in a 50/50 blend, the expected upper limit for ECA and ECB is more on the order of 1.0. The cases below illustrate the reason for this assumption.

Case 1: for a 50/50 blend ($AA = AB$) with $ECA = 1$, $ECB = 1$, CoContinuity = 2

$CAA = 2AA + AB = 3AA$

$CAB = 2AB + AA = 3AB$

$CAA + CAB = 3(AA + AB)$

total coverage is three times the image field area

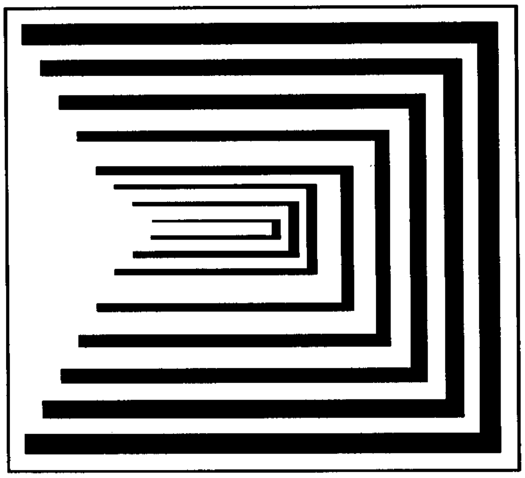

Figure 6 Example of a highly coordinated, particle-in-matrix morphology with a large CoContinuity value. Selected image analysis parameters are tabulated in *Table 4*

Table 4 Tabulated values of measured and derived parameters for digital image analysis of *Figure 6*

Measurement	*Figure 6* values
Area of A	3.21
Area of B	5.98
Convex Area of A	23.1
Convex Area of B	9.15
Area Fraction of A	0.35
Area Fraction of B	0.65
Coverage of A	2.51
Coverage of B	1
Excess Coverage of A	2.16
Excess Coverage of B	0.34
Coverage Ratio of A	7.19
Coverage Ratio of B	1.53
CoContinuity of A and B	1.19
Cocontinuity Balance	6.26

Case 2: For a 50/50 blend ($AA=AB$) with $ECA=2$, $ECB=1$, CoContinuity$=2.67$

$CAA=3AA+2AB=5AA$

$CAB=2AB+AA=3AB=3AA$

$CAA+CAB=5AA+3AB=4(AA+AB)$

total coverage is four times the image field area

In both cases, the morphology needed to obtain the conditions would be many highly intertwined particles of both phases with heavily overlapping convex areas. Case 1 shows that the convex area of each phase will be three times the actual area of the phase. Case 2 shows that the convex area of phase A is five times its actual area while the convex area of B is three times the actual area. Compare these values to the observed values in the 40% SAN example where the morphology is clearly cocontinuous: $ECA=0.44$, $ECB=0.53$, CoContinuity$=0.96$, $CAA=1.8\times AA$, $CAB=2.2\times AB$, total coverage$=2\times$(image field area).

In an artificial example, it is possible to devise a highly ordered morphology that would yield a large CoContinuity value, yet actually be discrete particles of one phase suspended in a matrix of the other. An example of such a morphology is shown in *Figure 6*. The CoContinuity for this example is 1.19, indicating a cocontinuous system, but the CoContinuity Balance is 6.3, indicating that phase A heavily dominates the CoContinuity (*Table 4*). This is clearly the case, considering the other parameters: $ECA=2.16$, $ECB=0.34$, $CAA=7.2\times AA$, $CAB=1.5\times AB$, total coverage$=3.5\times$(image field area). Although there is no reason to exclude this as a possible morphology for polymer blends, it is not likely. An important note concerning the 'morphology' shown in *Figure 6* is that, even though the phases are not apparently cocontinuous, there is a significant amount of interface between the light and dark phases, indicating that some special relationship between the materials exists.

CONCLUSIONS

The newly developed CoContinuity and CoContinuity Balance parameters provide good quantitative descriptions of cocontinuous morphology in polymer blends. The functions are well behaved over the expected range of blend morphology and can be interpreted according to physically meaningful concepts. Further, the parameters are scale-invariant, thus allowing objective comparison of systems with widely varying domain size and fundamentally different compositions.

In the example case of PC/SAN, the quantitative CoContinuity agreed very well with the qualitatively observed morphology. Further, the quantitative values of CoContinuity and CoContinuity Balance accurately describe the morphological behaviour that produces the drop in ultimate impact strength.

A synthetic example, designed to expose the limitations of the CoContinuity parameter, produced a value that would indicate that the system was cocontinuous, but the companion parameter, the CoContinuity Balance, properly indicated that one phase dominated the measurement. As with any new digital image analysis parameter, quantitation of additional examples of polymer blend morphology and correlation with subjective morphological descriptions, as well as physical properties, will be necessary to prove the applicability and value of these new parameters and to explore their limitations.

REFERENCE

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