Multifractal Analysis. A New Method for the Characterization of the Morphology of Multicomponent Polymer Systems

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SYNOPSIS

It has been demonstrated that use of polymeric emulsifiers under usual processing conditions in the melt state is a powerful technique for preparing polymer alloys. Digitized representation of optical micrographs of thin sections of blends of a low-density polyethylene and polystyrene (20 wt % PE-80 wt % PS) containing 2 and 5 wt % of two hydrogenated polybutadiene-polystyrene block copolymers exhibit different degrees of homogeneity as well as different morphological structures which can be studied by a multifractal analysis. We show how these differences are reflected in the $f(\alpha)$ spectrum of singularities which can be obtained by a box counting method in the canonical approximation. We have found a correlation between the $f(\alpha)$ curves and the mechanical properties of the corresponding samples: the samples which area the less multifractals have the best mechanical properties.

Keywords: multifractal analysis of morphology of multicomponent polymer systems

INTRODUCTION

Fayt et al.[1-6] have clearly demonstrated that moderate amounts of poly(hydrogenated butadiene-*b*-styrene) diblock copolymers (HPB-b-PS) significantly increase both tensile strength and elongation at break of blends of polystyrene (PS) with various types of polyethylene (PE). Block copolymers act as emulsifiers; in other words, each sequence is selectively miscible with its own polymer phase and is supposed to be located preferentially at the interface. The resulting morphology depends on the interfacial activity of the copolymer as well as the microrheology of the emulsified blends.

On a purely economic basis, the fabrication of these polymer blends is of interest only if a minimum quantity of block copolymer can be used. Indeed, it has been observed that only small amounts (1–2%) of copolymer are sufficient to obtain a stable dispersion of the phases and that the blend morphology still changes progressively when the block copolymer percentage increases up to about 5% (i.e., a percentage for which the ultimate mechanical properties have asymptotically reached their optimum value). In their studies, Fayt et al. considered the effect of two types of low-molecular weight copolymers: "tapered" and "pure" diblock polymers. They found that the former confers the highest tensile strength, ultimate strength, elongation at break, and energy to break. It thus appears plausible that the type of morphology stabilized by these copolymers has some bearing on the improved physical properties. Obviously any such correlation between the morphology and the physical properties is of considerable practical importance.

The morphology exhibited by micrographs of the multicomponent polymer system is reminiscent of many systems resulting from nonlinear growth or complex turbulent processes which exhibit scale-dependent properties. The concept of noninteger or fractal dimensions[7] has been found to be useful for the characterization of this type of disordered structure. Recently, however, it has been realized that in

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many cases a more detailed characterization can be obtained using the formalism of multifractals introduced first in the theory of turbulence[8] and chaotic motions in general.[9] In this case, the structure is described by a continuum of generalized dimensions D_q or alternatively by a spectrum of scaling indices α.[10] This method has been recently applied to a variety of heterogeneous materials such as sedimentary rocks.[11]

In the system considered, pieces of immiscible polymers are fractionated into smaller units by a mixing process and stabilized in a co-continuous structure by a copolymer. Although the two systems considered, blends with "tapered" and "pure" copolymers, appear as well dispersed, the complexity of the interlocked structure suggests that their morphology may exhibit different self-similar properties in different parts of the sample and that the multifractal analysis is a relevant method to investigate their morphological differences from an image analysis of the micrographs.

The aim of this report is to demonstrate that the values of a small set of these generalized dimensions determined in a limited length-scale range, which will be specified later, can be considered as a signature characterizing the blend morphologies produced by various concentrations of the two copolymers.

IMAGE ANALYSIS

For this study, we used blends of a low-density polyethylene and polystyrene (20 wt % PE–80 wt % PS) containing 2 and 5 wt % of two hydrogenated polybutadiene–polystyrene block copolymers (SE-4: tapered diblock, 33% PS, $\bar{M}_n$ = 80,000; SE-5: pure diblock, 50% PS, $\bar{M}_n$ = 80,000). Details concerning the behavior of these copolymer in PE/PS blends are given in refs. 1–6.

In order to perform image analysis, thin sections (1 μm thick) were prepared by ultramicrotomy. This is the maximum thickness which does not produce an overlap of images. They were observed with a transmission optical microscope and digitized with the Noesis software on a Microvax II. In both cases, from a concentration of 2% copolymer a co-continuous two-phase morphology is observed. The images corresponding to these two-dimensional sections have been digitized in 256 levels of gray in a matrix of 512 × 512 pixels. We assume that the system is isotropic and that images obtained from different section planes have statistically the same morphological properties.

Figure 1 shows digitized images corresponding to PS/PE blends (80/20) with 2% (up) and 5% (down) of tapered (SE-4) (left) and pure diblock (SE-5) (right) copolymer added. The morphological differences of these polymer blends have been described qualitatively in ref. 6. Here we introduce a quantitative method to characterize these differences and relate them to their different mechanical properties. After image digitization, it was necessary first to perform a careful thresholding transformation. This operation allows one to extract the selected phase on the basis of its grey level. The result is that actual images are converted into binary ones. Before the thresholding transformation Laplacian filtering was performed to enhance the contrast between the two phases. To be sure that the thresholding transformation does not produce systematic errors and losses of information giving rise to a modification of the morphological structure, we varied the level of thresholding over a small interval compatible with the constituent concentrations and observed that this does not affect the results discussed in later sections.

Figure 2 shows the binary representation of Figure 1. In order to account for the statistical fluctuations between different samples and between locations within each thin section, various positions were chosen at random. A total of 10 images for each type of blend were digitized, filtered and binarized by the same method.

THE MULTIFRACTAL FORMALISM

The multifractal formalism relies on the fact that the highly nonuniform probability distribution arising from the nonuniformity of the system often possesses rich scaling and self-similarity properties which vary from point to point. The statistical properties of a measure (in our case, local density) can be expressed in terms of the interwoven sets of dimensions D_q[9] or alternatively the $f(\alpha)$ spectrum of singularities.[10]

Consider a 2-D cut of the intertwined polymers. Let the 2-D plane be digitized with black and white pixels corresponding to the two homopolymers. Here the black pixels will represent the minor phase. Further divide the 2-D plane into N boxes of linear length (δ/L) where L is the total image extent. In that way the number of the boxes is $N = L^2/\delta^2$ in the grid. Let p_i denote the proportion of the total

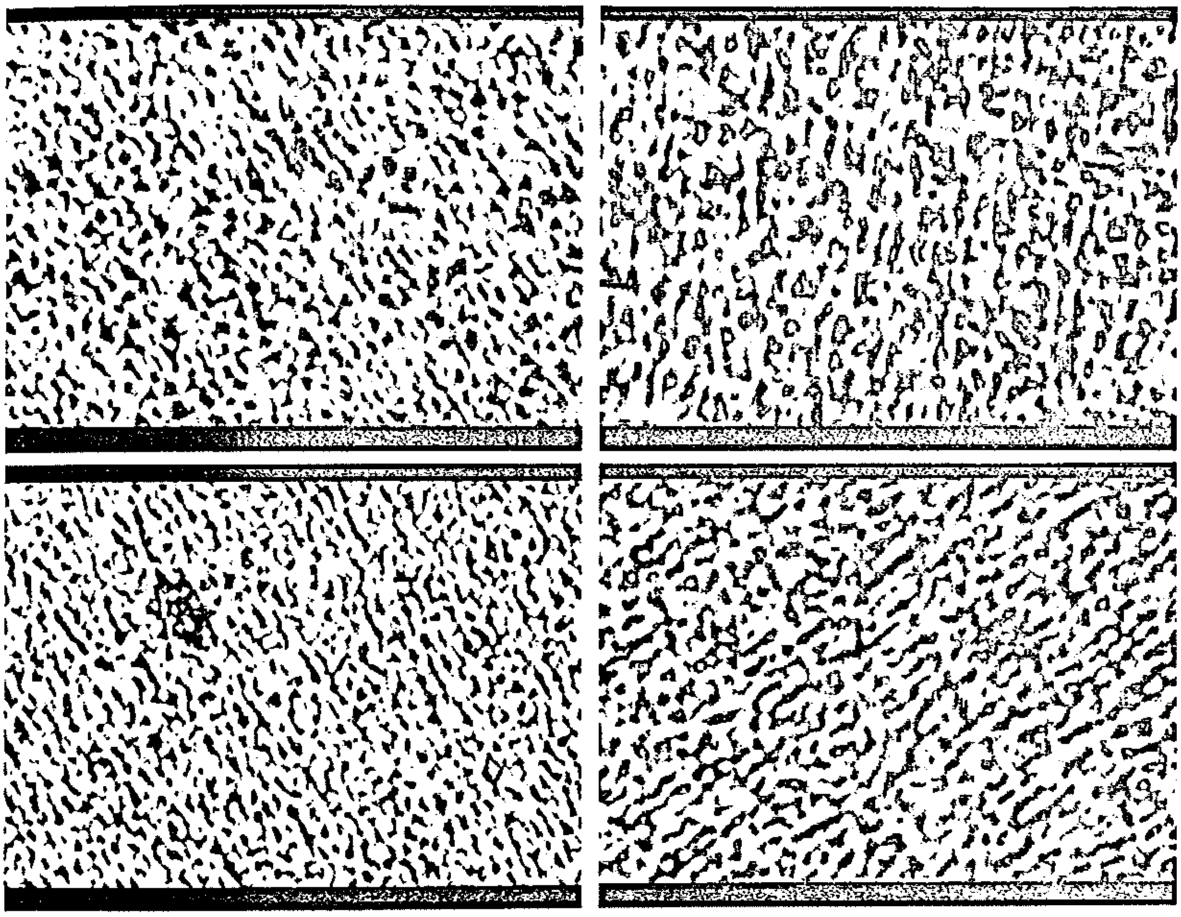

Figure 1. Digitized images corresponding to PS/PE blends (80/20) with added 2% (up) and 5% (down) of tapered (SE-4) (left) and pure (SE-5) (right) diblock copolymers. The length of the image corresponds to 50 μ.

mass of the image inside the i-th box determined by counting the number of black or white pixels in the box. Then let us introduce the partition function

$$Z(q) = \sum_{i=1}^{N} p_i^q(\delta) \qquad (1)$$

where $N \propto 1/\delta^2$ is the number of boxes in the grid. The so-called order-q generalized dimensions are obtained from an assumed power-law behavior of the partition function in the limit $\delta \to 0$ $(N \to \infty)$

$$Z_q \propto \delta^{(q-1)Dq} \qquad (2)$$

Then,

$$D_q = \lim_{\delta \to 0} \frac{1 \ln(\sum_{i=0}^{N(\delta)} p_i^q)}{q - 1 \ln \delta} \quad q = 0, 1, 2, \ldots \qquad (3)$$

For $q = 0$, we obtain the similarity dimension

$$D_0 = -\lim_{\delta \to 0} \left(\frac{\ln N(\delta)}{\ln \delta} \right) \qquad (4)$$

which is the usual box-counting fractal dimension defined by Mandelbrot,[7] which describes the scaling of the density.

For $q = 1$, we have

$$D_1 = -\lim_{\delta \to 0} \frac{S(\delta)}{\ln \delta} \qquad (5)$$

where

$$S(\delta) = -\sum_{i=0}^{N(\delta)} p_i \ln p_i \qquad (6)$$

By analogy with statistical mechanics, we can relate each p_i to a microstate and the structure of the

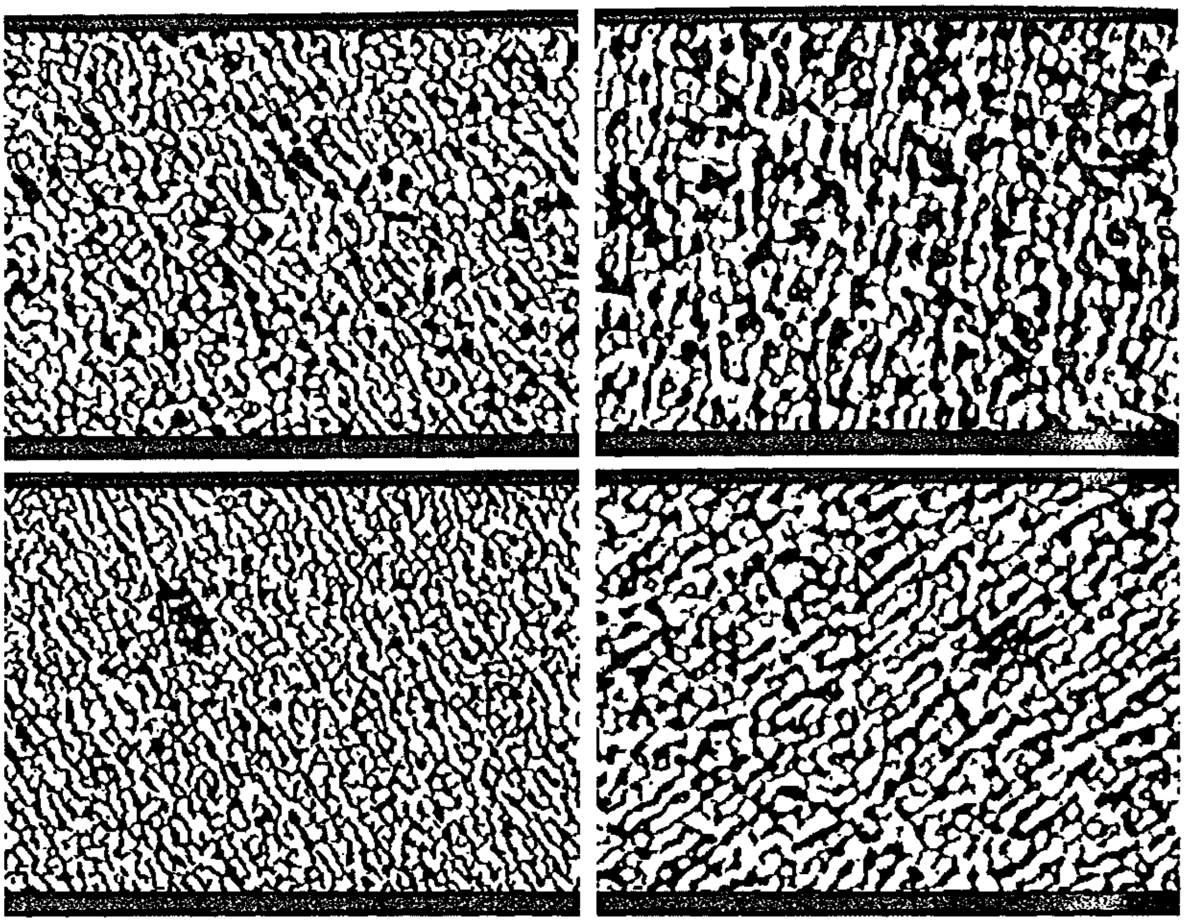

Figure 2. Binary representation of Figure 1.

alloy to a macrostate. Then, $S(\delta)$ is the information entropy of structure, i.e., the information gained by the knowledge of each p_i with accuracy δ. D_1 is called the information dimension and tell us how the information on the morphology increases as $\delta \rightarrow 0$. For $q = 2$, we have

$$D_2 = \lim_{\delta \to 0} \left(\frac{C_2(\delta)}{\ln \delta} \right) \qquad (7)$$

where

$$C_2(\delta) = \sum_{i=0}^{N(\delta)} p_i^2 \qquad (8)$$

This quantity is the probability that two image points lie within the box δ^d, i.e., the probability that two points are separated by a distance smaller than δ. D_2 is called the correlation dimension.

For $q = 3, 4 \cdots$ an infinite set of generalized dimensions $D_3, D_4, \cdots$ associated with higher order correlations between triplets, quadruplets $\cdots$ of points on each box can be defined. From eq. (2), for homogeneous fractals when all p_i are the same, all dimensions D_q have the same value; in general $D_q > D'_q$ for any $q' > q$. Then, the difference between D_0 and the other dimensions D_q, $q = 1, 2 \cdots$ is a measure of the nonuniformity of the structure.

An alternative and equivalent way to study the scaling properties of complicated fractal objects is by considering their spectrum of singularities.[10] We assume that in each box the measure p_i increases with the size δ as $p_i \propto \delta^{\alpha_i}$, and in this case we say that there is a singularity of type i. The meaning of the index α_i becomes obvious if we consider the density in a box of size δ: $p_i / \delta^d \propto \delta^{\alpha_i - d}$ for a d-dimensional space. Whenever $\alpha_i < d$, the density increases indefinitely as the box-size shrinks, and represents spikes (singular regions) in the distribution of density, smaller values of α_i represent larger spikes. On the other hand, α_i values greater than d represent smooth (or regular) distributions. The index α_i

therefore characterizes 'singularities' of different strengths. Now, corresponding to each α_i, one can identify a fractal dimension $f(\alpha)$ if one assumes that the number $N_\delta(\alpha)$ of boxes of size δ covering the iso-α set varies as $N_\delta(\alpha) \propto \delta\text{-}f(\alpha)$.

In this picture, local singularities of different strengths are distributed on interwoven sets of fractal dimensions $f(\alpha)$. A curve of f versus α is therefore an intuitive and mathematically precise method of disentangling and characterizing the multifractal measure in terms of these sets. The generalized dimensions D_q and the singularity spectrum $f(\alpha)$ are equivalent. Using an analogy with the formalism of equilibrium statistical mechanics it is possible to show, using the partition functions (1), that the canonical average $\langle \alpha(q) \rangle$ and $\langle f(q) \rangle$ are related by a Legendre transformation[5]

$$\langle \alpha(q) \rangle = d/dq((q-1)D_q); \langle f(\alpha(q)) \rangle = q\langle \alpha(q) \rangle - (q-1)D_q \tag{9}$$

In that case it is possible to determine $f(\alpha)$ directly using the following expressions

$$\langle f(q) \rangle = \lim_{\delta \to 0} \frac{\sum_i \mu_i(q,\delta) \ln \mu_i(q,\delta)}{\ln \delta} \tag{10}$$

and

$$\langle \alpha(q) \rangle = \lim_{\delta \to 0} \frac{\sum_i \mu_i(q,\delta) \ln p_i(\delta)}{\ln \delta} \tag{11}$$

where $\mu_i(q)$ are normalized probabilities for boxes of δ

$$\mu_i(q,\delta) = \frac{(p_i(\delta))^q}{\sum_j (p_j(\delta))^q} \tag{12}$$

Varying q is a trick for exploring the different regions of α. For large and positive q, we are looking for small values of α: i.e., parts of the object in which the measure is highly concentrated (high values of p_i). For large and negative q, we study parts of the object for which the measure (density) is very small (small values of p_i) and corresponds to the larger values of α. At $q = 0$, $f = 2$ is simply the usual fractal dimension. This turns out to be the maximum possible value of f. In the case of a homogeneous fractal, the $f(\alpha)$ spectrum is concentrated on a single point $\alpha = D_0 = D_q$. In contrast multifractal measures which are characterized by a monotonic decreasing dependence of D_q versus q have a distribution of values of α in a finite range ($\alpha_{\min} - \alpha_{\max}$) while $f(\alpha)$ turns out to be a single peaked function with D_0 as its maximum.

Since its introduction a few years ago, the concept of multifractals has undergone many refinements, and warnings have been formulated concerning its applicability to real systems. Contrary to mathematical objects where the limit $\delta \to 0$ can be defined rigorously, in real systems, power law scaling is limited to a range $a \ll \delta \ll L$ where a is the "particle" size and L is an upper limit which is system dependent. For mass multifractals one should be aware of the possibility of transient corrections to the asymptotic behavior which may yield transient deviations of D_1 from D_0 and thus apparently by nontrivial curve of $f(\alpha)$ which should disappear when $L \gg \delta \gg a$. The behavior of $f(\alpha)$ for large α depends critically on the size dependence of rare measures, which does not necessarily obey a power law and therefore should be interpreted with great care. As $|q|$ increases, the white noise in the images reduces the scaling region and finally washes out the manifestation of any deterministic noise.

Fortunately, in practice one needs only a very limited subset of dimensions D_q or $f(\alpha)$ in order to describe the important physical consequences of particular density distributions. Aharony[13] has derived the bounds D_q should obey to be physically meaningful. The results we have obtained lie within these bounds.

INVESTIGATION OF THE MORPHOLOGY OF POLYMER BLENDS PRODUCED BY PURE AND TAPERED COPOLYMERS

As mentioned earlier, it has been observed[1-6] that only a small amount of copolymer is required to obtain a seemingly homogeneous and stable dispersion of the phases. Furthermore, the blend morphology seems to change when the block copolymer content increases up to about 5%; i.e., a percentage for which the ultimate mechanical properties have reached their optimum value.

To perform the multifractal analysis, we first calculated the normalized probabilities $\mu_i(q, \delta)$ [Eq. (11)] on each binary image using a box-counting method. The analysis is made with boxes having linear dimensions ranging from $\delta = 10$ to 512 pixels. This corresponds in real images to size between 1 to 50 μ. According to eqs. (10) and (11) the plots of $\sum_i \mu_i(q, \delta) \ln p_i$ versus $-\ln \delta$ and $\sum_i \mu_i(q, \delta) \ln \mu_i(q, \delta)$ versus $-\ln \delta$ have slopes equal to $f(q)$ and

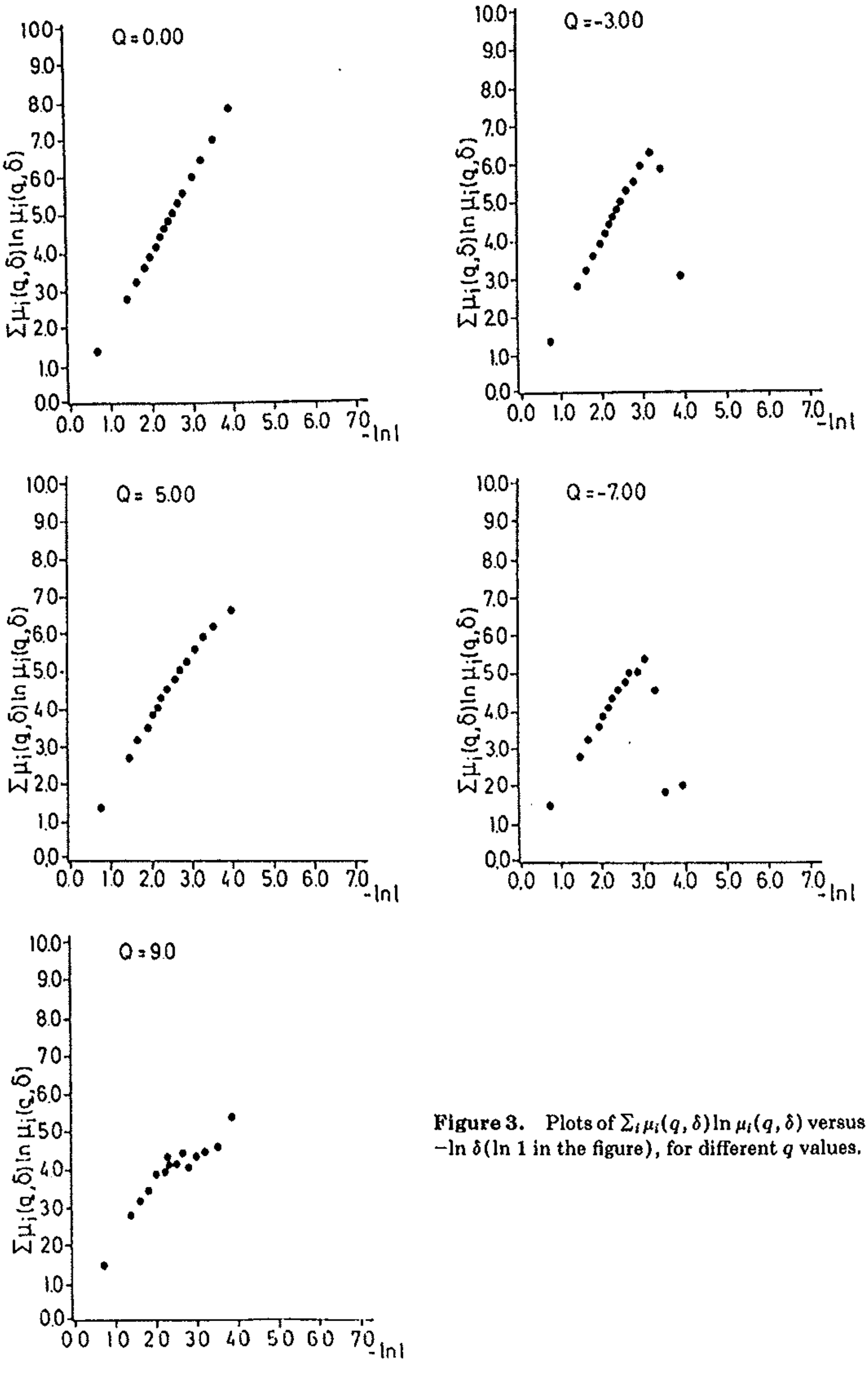

Figure 3. Plots of $\sum_i \mu_i(q,\delta) \ln \mu_i(q,\delta)$ versus $-\ln \delta$ (ln 1 in the figure), for different q values.

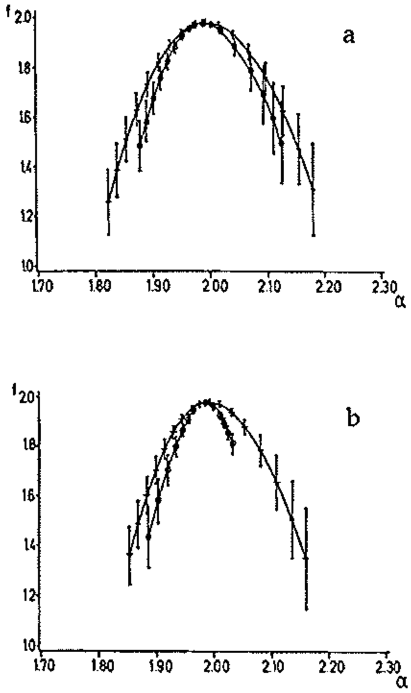

Figure 4. (a) $f(\alpha)$ spectra for samples with 2% and 5% of SE-5. (b) $f(\alpha)$ spectra for samples with 2% and 5% of SE-4.

$\alpha(q)$, respectively. Figure 3 shows some examples of these plots. Each point corresponds to the average value obtained from ten samples of each type. The q values were varied between −10 and 10.

We can see that the length of the scaling region (where the slope in the ln − ln plot is linear) strongly depends on q. For small $|q|$, this region extends over all the range considered. For large $|q|$, the self-similar range decreases as discussed in the preceding section.

Figure 4a, b shows the $f(\alpha)$ versus α relations for the four samples. To build these curves we have chosen the smallest self-similar range compatible with the curves of Figure 3 (i.e., the scaling region $20 \leq \delta \leq 512$). We can see that the increase of copolymer concentration decreases the quantity $\alpha_{max} - \alpha_{min}$ and therefore the multifractal character of the blends. The 5% SE-4 samples has the smallest distribution of α, around $\alpha = 2$ and a distribution of $f(\alpha)$ between 1.4 and 2.

The morphological differences between the four structures we analyze are clearly reflected by their spectrum of exponents α and their corresponding dimensions $f(\alpha)$. We can see that the increase of copolymer concentration decreases the quantity $\alpha_{max} - \alpha_{min}$ and therefore the multifractal character of the blends. The 5% SE-4 samples has the smallest distribution of α, around $\alpha = 2$. In the three other samples the copolymer has not reached its optimum effect and there are still large local heterogeneities around the average density: the broad distribution of α indicates that high local-density regions ($\alpha < 2$) are compensated by low-density hairy or thinly connected features ($\alpha > 2$). It is assumed that these thin regions cannot support stresses and consequently reduce the mechanical properties of the samples. In contrast 5% SE4 samples exhibit more or less uniform connected ribbonlike structures of the phase, and hence have better mechanical properties (Table I).

Similar conclusions can be reached by examining the values of the generalized dimensions. Table I shows results obtained for D_q, $0 \leq q \leq 3$, calculated in the range $10 \leq \delta \leq 512$ pixels for both tapered and pure systems together with their strength at break.

A first observation indicates that in all cases the Hausorff dimension D_0 is very close to 2. This means that the density is practically independent on δ on scales larger than a few times the smallest homogeneity. Moreover, the first-order correlation functions scale with a D_q very close to the Euclidean dimension 2. This confirms the experimental finding that only a small quantity of diblock copolymer is needed to obtain a good dispersion of the phases. However, Table I shows that the method is precise enough to quantify the small difference in the morphology responsible for their different mechanical properties.

Table I. Values of D_q and Tensile Strength for a 80 PS/20 PE Blend Modified with SE-4 or SE-5

80 PS/20 PE	D0	D1	D2	D3	Strength at Break (MPa)
2% SE-4 (tapered)	1.98	1.97	1.95	1.91	35
5% SE-4 (tapered)	1.98	1.98	1.97	1.95	40
2% SE-5 (pure)	1.97	1.95	1.94	1.89	34
5% SE-5 (pure)	1.98	1.97	1.96	1.93	35

CONCLUSIONS

We have established the applicability of multifractal analysis to heterophase polymers blends by showing that the $f(\alpha)$ curves are different for various concentrations of two different copolymers. The multifractal curve can accordingly be considered as a signature of the morphology of the network.

It is well known in the theory of composites that the mechanical properties are optimized when the reinforcement fibers form an ordered continuous network. It is therefore not surprising that the sample which is the less multifractal has the best mechanical properties since its microgeometry best fulfils these conditions as compared with the other three samples. We have found that if the scale range is correctly chosen we can find a correlation between the $f(\alpha)$ curves and the mechanical properties of the corresponding samples. These encouraging results prompt us to apply the same type of approach to a number of important heterophase situations, the results of which will be reported in future articles.

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