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Fractal behavior of spinodal decomposition in polymer blends

Mo Song[1,*], Yuhui Huang[1], Zhenhua Sun[2], and Bingzheng Jiang[2]

[1]Guangzhou Institute of Chemistry, Academia Sinica, Guanzhou, P.O. Box 1122, People's Republic of China
[2]Changchun Institute of Applied Chemistry, Academia Sinica, Changchun 130022, People's Republic of China

Summary

Fractal behaviour of ramified domains in the late stage of spinodal phase separation in a binary polymer blend of poly(vinyl acetate) with poly(methyl methacrylate) was investigated by optical microscopic method. In the late stage of the spinodal decomposition, the fractal dimension D is about 1.64. It implies that some anomalous properties of irregular structure probably may be explained by fractal concepts.

Introduction

The dynamics of phase separation has attracted much interest and response all over the world. A lot of work on this subject has been done, and good results have been obtained. The one of famous results is that the scaling behaviour of structure function has been found in the late stage of the spinodal phase separation(1).

In the late stage of the spinodal phase separation the unmixing structures of different times have the self-similarity. This was confirmed by the scaling test of structure function(2).

By various thermal treatments(e.i. heating or cooling) a single phase polymer mixture will become an inhomogenous two-phase. When the volume fraction of one phase is less than the other, the minor phase exists as isolated particles. For such an irregular and ramified domains, we can describe its geometry approximately by fractal theory because the unmixing structures have the self-similarity(3). In this brief report, the fractal behaviour of the spinodal decomosition of poly(mehtyl methacrylate)(PMMA) with poly(vinyl acetate)(PVAc) mixtures was presented for the first time.

*To whom offprint requests should be sent

Experimental

PMMA(M_w= 1.98x10^5,M_w/M_n=2.5) and PVAc(M_w=2.6x10^6,M_w/M_n=3.2) were commercial products.The polymers in various proportions were dissolved to a total of 3 wt % in chloroform.This solution was cast onto a cover glass for microscope.Solvent was allowed to evaporate slowly at 30°C.The blends were dired under vacuum at 50°C for 72 hours.This procedure resulted in homogenous optically clear films about 4.0 μm in thickness.

The morphology of thin PMMA/PVAc(55/45 by weight) films were studied by using a optical microscope.A thin layer of the blend casted on a slide was introduced into a transparent programmable heating stage of 177.0°C, see phase diagram shown in Figure 1 (4).

Calculation method of fractal dimension.

We define the density function

$$\rho(R) = M(R)/V(R) \qquad (1)$$

where M(R) is the amount of mass inside a sphere of radius R.

The fractal geometry of the ramified domains can be expressed in terms of the mass scaling exponent,the fractal dimension,D(3)

$$M(R) \sim R^D \qquad (2)$$

hence

$$\rho(R) \sim R^{D-d} \qquad (3)$$

In general,D is less than or equal to d(Euclidean dimension) because of the open character of the fractal structure.

The fractal dimension for two-dimension ramified domains of the spinodal phase separation in polymer blends can be obtained from microscope picture by following method:using a square network(see Figure 2, lattice size=1.0 mm) to cover the picture and counting the number of occupied lattices of a given ramified domain lying within the square of length,then the number is divided by the Enclidean area,R^2,giving density, $\rho(R)$.Because of random choice of the centre sites for the square,we take an average density over many centre sites for a given size square.

Results and Discussion

Upon introduction deep into the unstable region,the spinodal phase

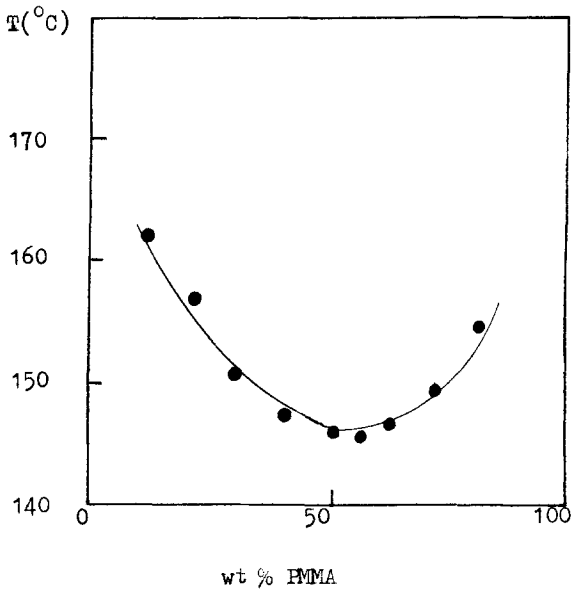

Figure 1. Phase diagram for PMMA/PVAc blends.

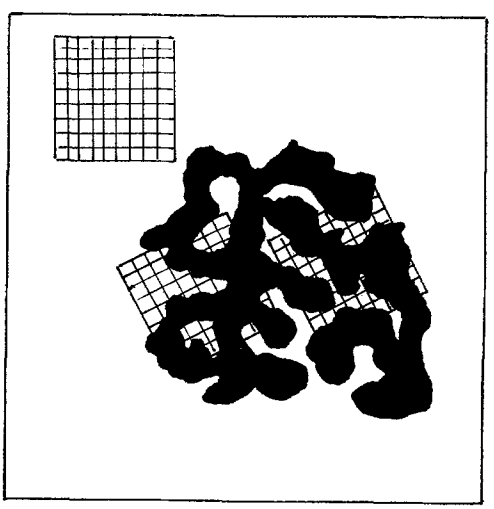

Figure 2. Schematic for density calculation.

separation process was induced and its morphology was as shown in Figure 3 at various times .The highly interconnected in micrograph was seen. With time increasing, the highly interconnected micrography breaks into droplets.

The fractal dimension for two-dimension ramified domains in the typical morphology of the spinodal phase separation was obtained from Figure 3. As

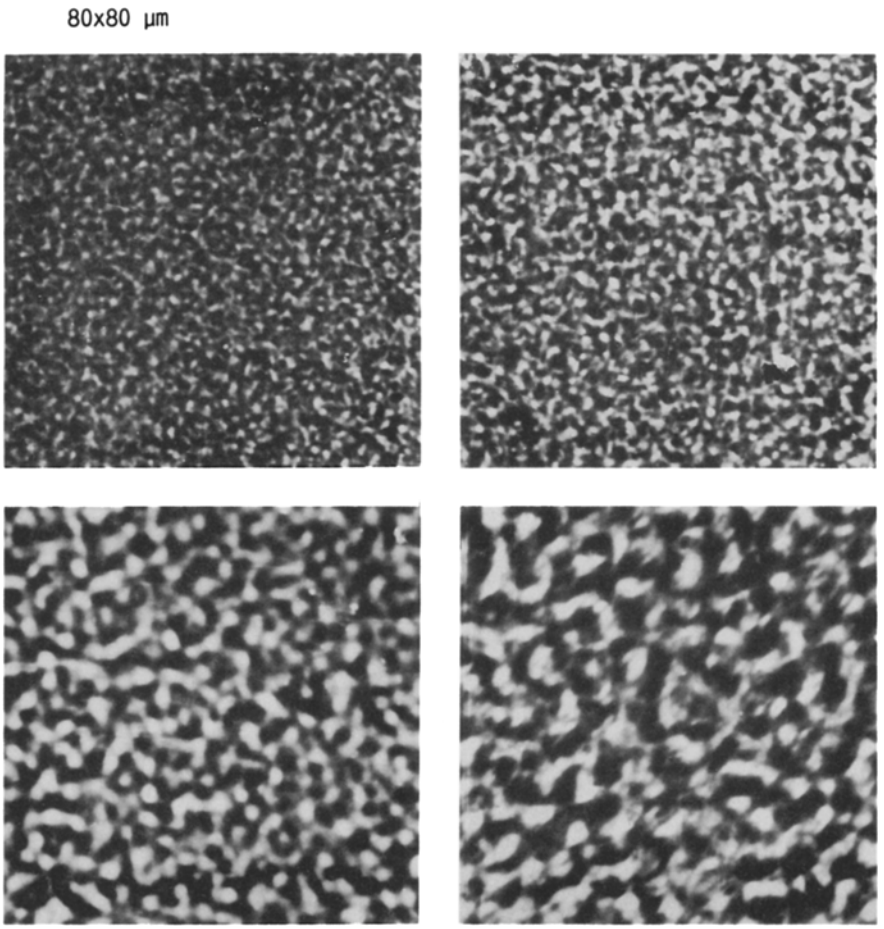

Figure 3.Four micrographs of the observed morphology during the spinodal phase separation,(a) 121 min (b) 233 min (c) 304 min and (d)376 min.

shown in Figure 4 and 5 from Figure 2(b) and (c),respectively,the density is scale-dependent.They follow a power law that corresponds to a fractal dimension about 1.64.The fractal dimensional data for different times at 177.0°C were shown in Tab.I. These results show clearly that in the late stage of the spinodal phase separation the ramified domains have the self-similar fractal character.These fractal dimensions are less than that of the two-dimension percolation cluster (D=1.9) and larger than that of the two-dimension percolation backbone (D=1.6)(3).The result predicts that the morphology of the spinodal decomposition may be described by fractal

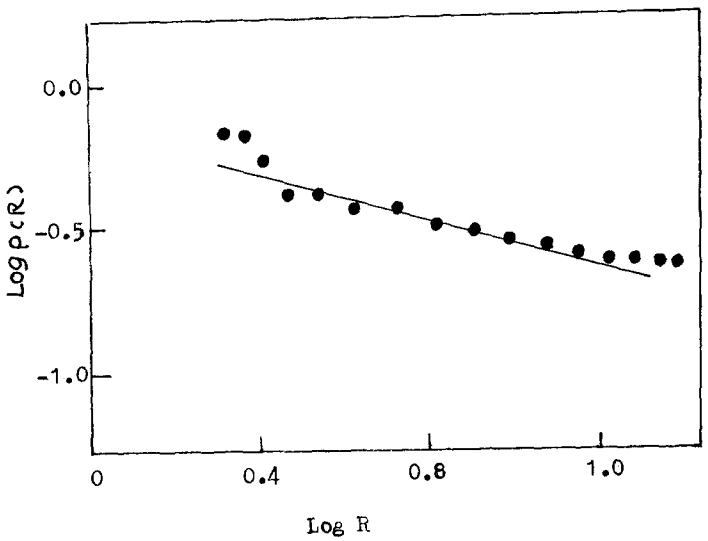

Figure 4. Polt of $\rho(R)$ vs. R from Fig.3(b).

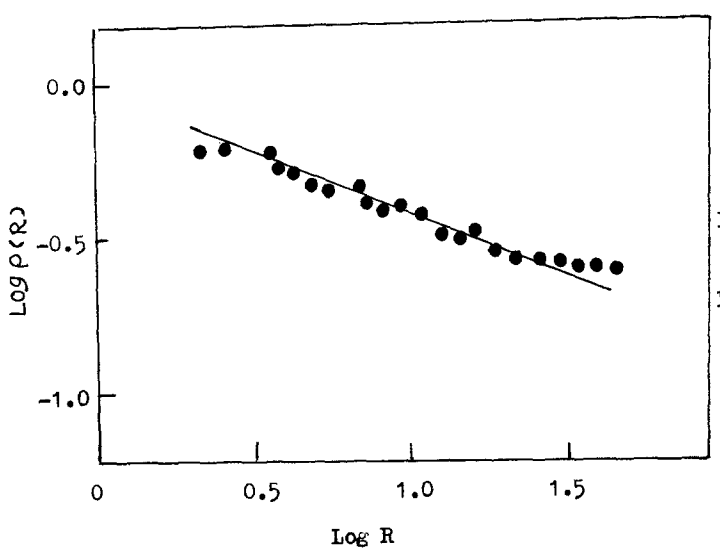

Figure 5. Polt of $\rho(R)$ vs. R from Fig.3(c).

theory(3).

Recently,Runt(5) used the same simple method to study the fractal behaviour of polystylene fracture surfaces.These imply that some anomalous properties of the irregular structure probably may be explained by fractal concepts.For example,Dozien observed experimentally that the self-diffusion constant of azobenzene molecules in porous vycor glass carrier filled by azobenzene-toluene-alcohol is much less than that in the free azobenzene-toluene-alcohol matrix(6).He explained this anomalous diffusion in terms of a self-similar fractal of the porous cluster. It is expected the property of

materials can be explained by combining the fractal character of the ramified domains with dynamics of the spinodal decomposition.But both the geometrical description of the growing objects and the dynamical growth laws of the spinodal phase separation in polymer blends are nor fully understood,more work is required on this important topic.

Table 1

Fractal dimensions for different time in the spinodal phase separation process

time(min)	fractal dimension D	error
121.0	1.65	± 0.04
233.0	1.65	± 0.03
304.0	1.64	± 0.04
376.0	1.63	± 0.04

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