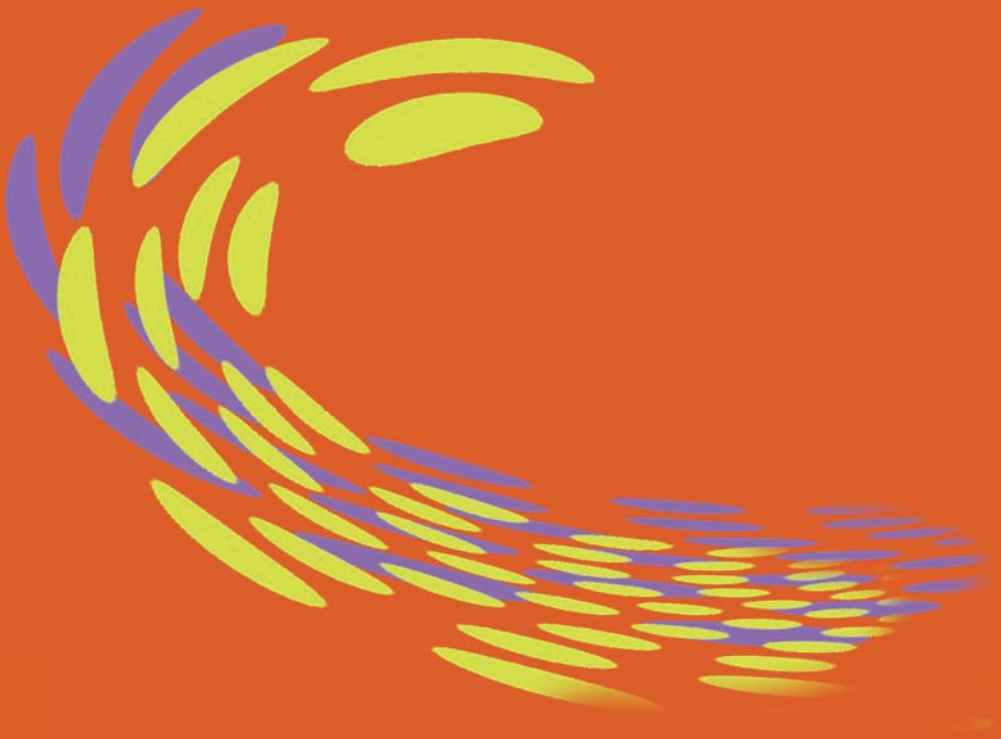
Multicomponent Polymeric Materials

From Introduction to Application



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List of Abbreviations

ACA	ε-Amino caproic acid
ASF	Atomic sensitivity factors
ATR	Attenuated total reflection
BBR	Bromated butyl rubber
B-PES	Bromide-containing aromatic copolyethersulfones
BSR	Butadiene styrene rubber
CBR	Chlorinated butyl rubber
CEP	Chlorinated ethylene-propylene
CEPDC	Chemical Engineering Process Design Centre
CEPDC	Chlorine-containing ethylene-propylene-diene cauotchoucs
CMC	Cell membrane complex
CO	Carbon oxide
CP	Chlorinated polyethylene
CSP	Chlorosulfonated polyethylene
EPDC	Ethylene-propylene-diene cauotchoucs
EVA	Ethylene vinyl acetate
EVAMA	Vinyl acetate and maleic anhydride
GB	Gradient birefringence
GBFS	Granulated blast-furnace slag
GRIN	Gradient Refractive Index
HM	Halide modification
IR	Infrared
ISIRI	Institute of Standards and Industrial Research of Iran
LMC	Low molecular compound
MFR	Melt flow rate
NR	Natural rubber
OPC	Ordinary portland cement
PC	Polymerizing composition
PCA	Polycaproamide
PHE	Poly(hydroxyl ether)
PPX	Poly(phenylxalines)
PVA	Poly(vinyl alcohol)
PVDF	Poly(vinylidene fluoride)
SC-CO_2	Supercritical carbon dioxide
Selfoc	Self focusing
SEM	Scanning electron micrographs
SGS	Sol-gel system
SIR-3	Synthetic isoprene rubber
SPIP	Scanning probe image processor
TC	Technical carbon
TEM	Transmissionelectron microscopy

TMDA	Tetramethylene acrylate
UHMWPE	Ultra-high-molecular-weight polyethylene
WPLA	Waste PET bottles lightweight aggregate
WPLAC	Waste PET bottles lightweight aggregate concrete

Preface

The book aimed at giving a detailed overview of the main and most up-to-date advances in the area of polymeric materials, through a balanced combination of theory and experiments. Since the subject is essentially an interdisciplinary area and as such it brings together scientists and engineers with different educational backgrounds, it was important to offer a research-oriented exposition of the fundamentals as well.

This book is based on the editors' extensive experience in research, development, and education in the field of materials science and especially polymer testing, polymer diagnostics, and failure analysis. The results of their work were published in several reference books about deformation and fracture behavior of polymers, in numerous single publications in peer-reviewed scientific journals, and in proceedings. Given the fact that the field of science undergoes a rapid and dynamic development, it seemed prudent to present these results here.

The book presents a comprehensive representation of knowledge provided by respected colleagues from universities and from the polymer industry.

This book is primarily designed for students of bachelor, diploma and master courses of materials science, materials technology, plastic technology, mechanical engineering, process engineering, and chemical engineering. It can be used by students, teachers of universities and colleges for supplementary studies in the disciplines of chemistry and industrial engineering. The methods of polymer testing are also essential to the development and application of biomedical or nanostructured materials. With the publication of this book we hope that it will not only serve the important task of training of young scientists in physical and materials oriented disciplines, but will also make a contribution to further the education of professional polymer testers, design engineers, and technologists.

— Gennady E. Zaikov, DSc

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1 Updates on Nanofiller Structure in Elastomeric Nanocomposites

G. V. Kozlov, Yu. G. Yanovskii, S. Kubica, and G. E. Zaikov

CONTENTS

1.1 INTRODUCTION

It is well known fact that, in particulate-filled elastomeric nanocomposites (rubbers) nanofiller particles form linear spatial structures ("chains") [1, 2]. At the same time in polymer composites, filled with disperse microparticles (microcomposites) and particles (aggregates of particles) of filler form a fractal network, that defines polymer matrix structure (analog of fractal lattice in computer simulation) [3], which results in different mechanisms of polymer matrix structure, forms micro and nanocomposites. If the first filler particles (aggregates of particles), fractal network availability results to "disturbance" of polymer matrix structure, expressed in the increase in its fractal dimension d_f [3], then in case of polymer nanocomposites at nanofiller contents change, the value d_f is not changed and equal to matrix polymer structure fractal dimension [4]. It has to been expected composites, indicated classes structure formation mechanism change defines their properties change, in particular, reinforcement degree.

At present, there are several methods of filler structure (distribution) determination in polymer matrix, both experimental [5, 6] and theoretical [3]. All the indicated methods describe this distribution by fractal dimension D_n of filler particles network. However, correct determination of any object fractal (Hausdorff) dimension includes three obligatory conditions. The first is the indicated above determination of fractal dimension numerical magnitude, which should not be equal to object topological

dimension. Any real (physical) fractal possesses [7] fractal properties within a certain scales range [8]. And at last, the third condition is the correct choice of measurement scales range itself. As it has been shown [9, 10], the minimum range should exceed at any rate self-similarity iteration.

The purpose of present chapter is dimension D_n estimation, both experimentally and theoretically, and to check, two indicated conditions to fulfill. That is to obtain of nanofiller particles (aggregates of particles) network ("chains") fractality strict proof in elastomeric nanocomposites on the example of particulate-filled butadiene styrene rubber (BSR).

1.2 EXPERIMENTAL

The elastomeric particulate-filled nanocomposite on the basis of BSR was an object of the study. The technical carbon of mark № 220 (TC) of industrial production, nano and microshungite (the mean filler particles size makes up 20, 40, and 200 nm, respectively) were used as a filler. All fillers content makes up 37 mass%. Nano and microdimensional disperse shungite particles were obtained from industrially extractive material by processing according to the original technology. Size and polydispersity of shungite particles received in milling process were monitored with the aid of analytical disk centrifuge (CPS Instruments, Inc., USA), allowing to determine with high precision the size and distribution by sizes within the range from 2 nm to 50 mcm.

Nanostructure was studied on atomic power microscopes Nano-DST (Pacific Nanotechnology, USA) and Easy Scan DFM (Nanosurf, Switzerland) by semi-contact method in the force modulation regime. Atomic power microscopy results were processed with the aid of specialized software package Scanning Probe Image Processor, Denmark (SPIP). The SPIP is a powerful program package for processing of images, obtained on SPM, AFM, STM, scanning electron microscopes, transmission electron microscopes, interferometers, confocal microscopes, profilometers, optical microscopes, and so on.

The given package possesses the whole functions numbers that are necessary for images precise analysis, included as follows:

1. The possibility of three-dimensional reflecting objects obtaining, distortions automatized leveling, including Z-error mistakes removal for examination separate elements, and so on;
2. Quantitative analysis of particles or grains, more than 40 parameters can be calculated for each found particle or pore-area, perimeter, average diameter, the ratio of linear sizes of grain width to its height distance between grains, coordinates of grain center of mass a.a. can be presented in a diagram form or in a histogram form.

1.3 DISCUSSION AND RESULTS

The first method of dimension D_n experimental determination uses the fractal relationship [11, 12] as follows:

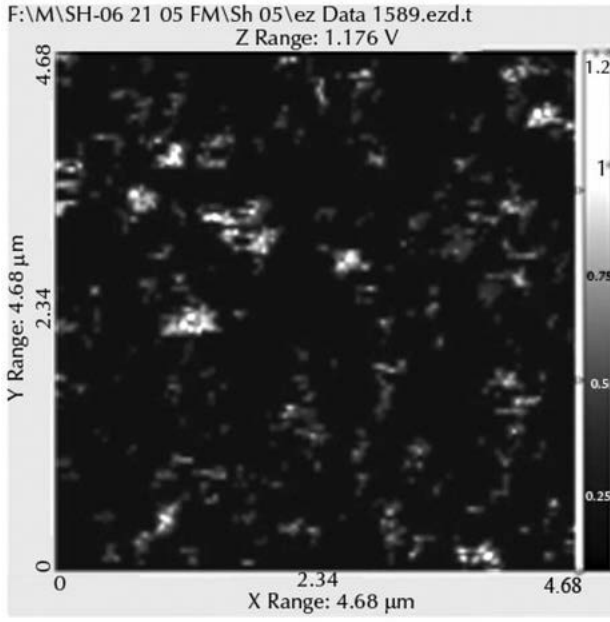
$$D_n = \frac{\ln N}{\ln \rho} \tag{1}$$

where N is a number of particles with size ρ.

Particles sizes were established on the basis of atomic power microscopy data (see Figure 1). For each from the three studied nanocomposites no less than 200 particles were measured, the sizes of which were united into 10 groups and mean values N and ρ were obtained. The dependences $N(\rho)$ in double logarithmic coordinates were plotted, which proved to be linear and the values D_n were calculated according to their slope (see Figure 2). It is obvious, that at such approach fractal dimension D_n is determined in two-dimensional Euclidean space, whereas real nanocomposite should be considered in three-dimensional Euclidean space. The following relationship can be used for D_n re-calculation for the case of three-dimensional space [13]:

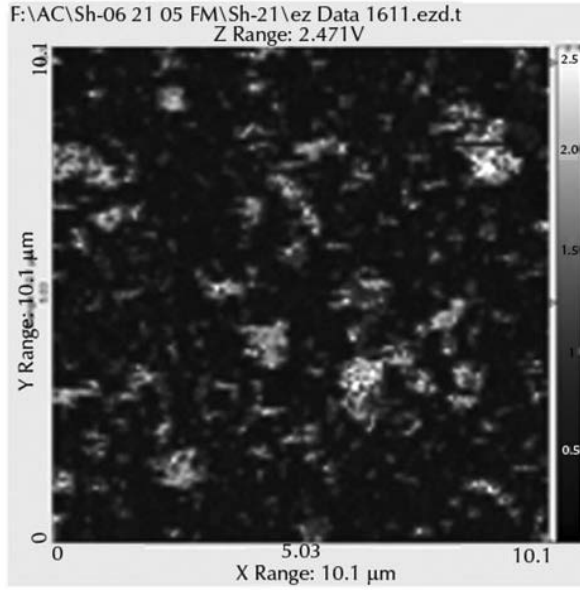
$$D3 = \frac{d + D2 \pm \left[(d - D2)^2 - 2\right]^{1/2}}{2} \tag{2}$$

where $D3$ and $D2$ are corresponding fractal dimensions in three- and two-dimensional Euclidean spaces, $d = 3$.

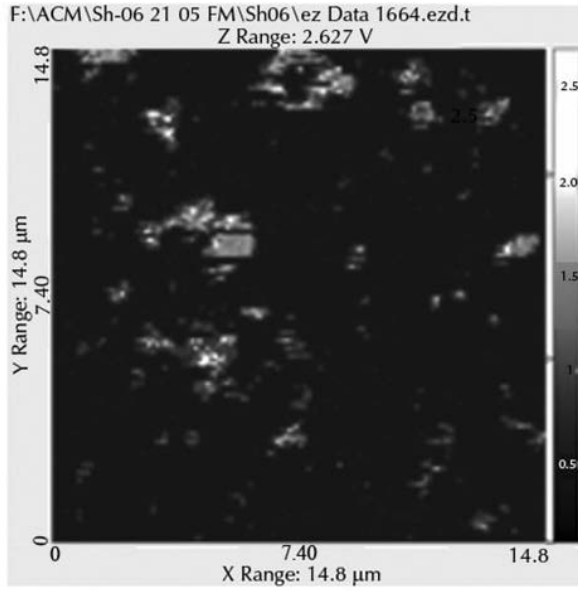


(a)

FIGURE 1 *(Continued)*



(b)



(C)

FIGURE 1 The electron micrographs of nanocomposites BSR/TC (a), BSR/nanoshungite (b), and BSR/microshungite (c), obtained by atomic power microscopy in the force modulation regime.

It calculated according to the indicated method dimensions D_n are adduced in Table 1. As it follows from the data of this table, the values D_n for the studied nanocomposites are varied within the range of 1.10-1.36, that is they characterize more or less branched linear formations ("chains") of nanofiller particles (aggregates of particles) in elastomeric nanocomposite structure. Let us remind that for particulate-filled composites poly(hydroxiether)/graphite the value D_n changes within the range of ~2.30-2.80 [5], that is for these materials filler particles network is a bulk object, but not a linear one [7].

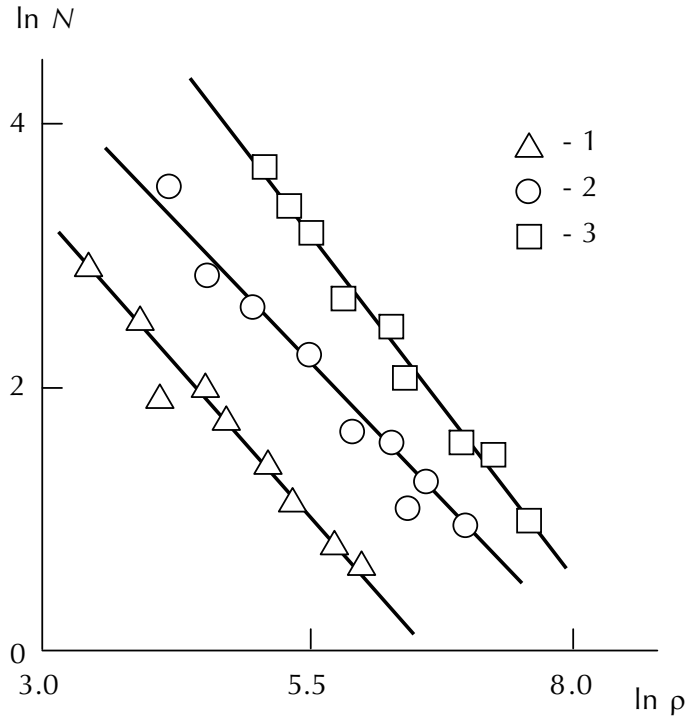


FIGURE 2 The dependence of nanofiller particles number N on their size ρ for nanocomposites BSR/TC (1), BSR/nanoshungite (2), and BSR/microshungite (3).

TABLE 1 The dimensions of nanofiller particles (aggregates of particles) structure in elastomeric nanocomposites.

The nanocomposite	D_n, the equations (1)	D_n, the equations (3)	d_0	d_{surf}	φ_n	D_n, the equations (7)
BSR/TC	1.19	1.17	2.86	2.64	0.48	1.11
BSR/nanoshungite	1.10	1.10	2.81	2.56	0.36	0.78
BSR/microshungite	1.36	1.39	2.41	2.39	0.32	1.47

Another method of D_n experimental determination uses the so called "quadrates method" [14]. Its essence consists in the following—On the enlarged nanocomposite microphotograph (see Figure 1) a net of quadrates with side size α_i, changing from 4.5 to 24 mm with constant ratio $\alpha_{i+1}/\alpha_i = 1.5$, is applied and then quadrates number N_i, in to which nanofiller particles hit (fully or partly), is calculated. Five arbitrary net positions concerning microphotograph were chosen for each measurement. If nanofiller particles network is fractal, then the following relationship should be fulfilled [14]:

$$N_i \sim S_i^{-D_n/2} \tag{3}$$

where S_i is quadrate area, which is equal to α_i^2.

In Figure 3 the dependence of N_i on S_i in double logarithmic coordinates for the three studied nanocomposites, corresponding to the relationship (3), is adduced. As one can see, these dependences are linear, that allows to determine the value D_n from

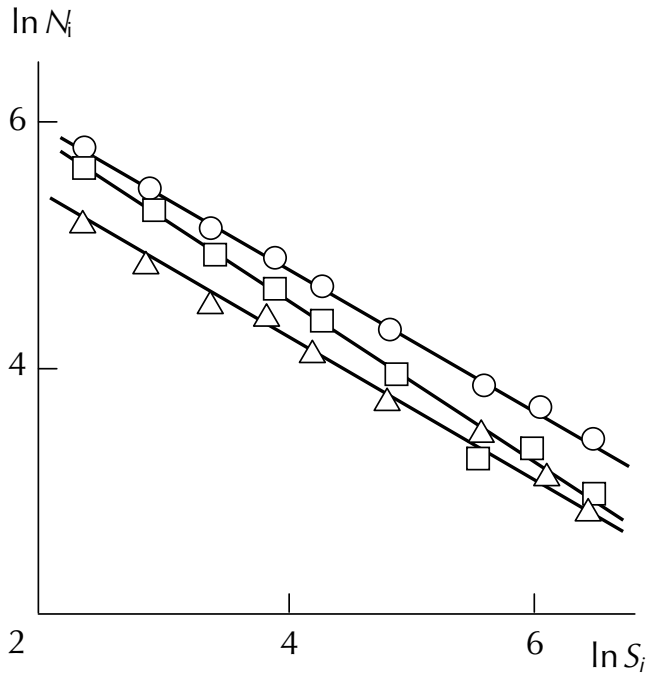


FIGURE 3 The dependence of covering quadrates number Ni on their area Si, corresponding to the relationship (3), in double logarithmic coordinates for nanocomposites on the basis of BSR. The designations are the same, that in Figure 2.