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THE EXPERIMENTAL AND THEORETICAL ESTIMATION OF INTERFACIAL LAYER THICKNESS IN ELASTOMERIC NANOCOMPOSITES

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Abstract. The interfacial layer thickness and its elasticity modulus were determined experimentally for particulate-filled polymer nanocomposite. It has been found out that elasticity modulus of interfacial layer is 5 times greater than corresponding characteristic for bulk polymer matrix. It has been shown that the theoretical calculation of interfacial layer thickness within the frameworks of fractal model corresponds well to experimental data.

Keywords: nanocomposite, nanoparticle, interfacial layer, elasticity modulus, nanoscopic method.

1. Introduction

The determination of structural components quantitative characteristics is an important task, without which quantitative description and prediction of polymer nanocomposites properties cannot be fulfilled. In this aspect interfacial regions play a particular role, since, as it has been shown earlier, they are the same reinforcing element in elastomeric nanocomposites as actual nanofiller [1]. Therefore the knowledge of interfacial layer dimensional characteristics is necessary for quantitative determination of one of the most important parameters of polymer composites in general – their reinforcement degree. Proceeding from the above said, the purpose of the present paper is experimental determination of interfacial layer thickness with the aid of modern nanoscopic methods [2] and its theoretical calculation within the frameworks of fractal analysis [3].

2. Experimental

The elastomeric particulate-filled nanocomposite on the basis of styrene-butadiene rubber (SBR) was an object of the study. SBR of industrial production, mark SKS-30 ARK was used, which contains 7.0–12.3 % *cis*- and 71.8–72.0 % *trans*-links with the density of 920–930 kg/m³. This rubber is completely amorphous. Mineral shungite nanodimensional particles (particles average size makes up 40 nm) were used as a nanofiller. Mineral shungite of Zazhoginskogo deposit of IIIth variety makes up ~30 % globular amorphous metastable carbon and ~70 % high-disperse silicate particles. Its structure is fullerene-like one. The nanoshungite content makes up 37 mas %. Nanodimensional disperse shungite particles were prepared from industrially outputted material by original technology processing. The analysis of the shundite particles obtained in milling process was monitored with the aid of analytical disk centrifuge (CPS Instruments, Inc., USA), allowing to determine with high precision size and distribution by sizes within the range from 2 nm up to 50 microns.

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 SPIP (Scanning Probe Image Processor, Denmark). SPIP is a high-end program package for processing of images, obtained on SPM,

AFM, STM, scanning electron microscopes, transmission electron microscopes, interferometers, confocal microscopes, profilometers, optical microscopes, etc. The given package features the whole functions which are necessary for images precise analysis, including:

1) the possibility of three-dimensional objects reflecting, automated distortions leveling, including Z-error mistakes removal for examination of 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, 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 diagram form or in histogram form.

The tests concerning elastomeric nanocomposites nanomechanical properties were carried out by nanoindentation method [2] on apparatus NanoTest 600 (Micro Materials, Great Britain) in a wide range of loads from 0.01 mN up to 2.0 mN. Sample indentation was conducted in 10 points with the interval of 30 microns. The load was increased with constant rate up to the greatest given load reaching (for the load rate 0.05 millinewtons (mN) per second (s), *i.e.*, mN/s – 1 mN). The indentation rate was changed in conformity with the greatest load value, counting that loading cycle should take 20 s. The unloading was conducted with the same rate as loading. In the given experiment the “Berkovich’s indenter” was used with the angle at tip of 65.3° and rounding radius of 200 nm. Indentations were carried out in the checked load regime with preload of 0.001 mN.

For elasticity modulus calculation, the obtained in the experiment by nanoindentation course dependences of load on indentation depth (strain) in ten points for each sample at loads of 0.01, 0.02, 0.03, 0.05, 0.10, 0.50, 1.0, and 2.0 mN were processed according to Oliver-Pharr method [4].

3. Results and Discussion

In Fig. 1 the obtained according to the original methodics results of elasticity moduli calculation for nanocomposite butadiene-styrene rubber/nanoshungite components (matrix, nanofiller particle and interfacial layers), received in interpolation process of nanoindentation data, are presented. The SPIP processed polymer nanocomposite image with shungite nanoparticles allows experimental determination of interfacial layer thickness l_{if} , which is presented in Fig. 1 as steps on elastomeric matrix-nanofiller boundary. The measurements of 34 of such steps (interfacial layers) width on SPIP processed images of various sections of interfacial layer gave the average experimental value $l_{if} = 8.7$ nm. Besides, nanoindentation results (Fig. 1, figure on the right) showed that interfacial layers elasticity

modulus was only by 23–45 % lower than nanofiller elasticity modulus, but it is 6.0–8.5 times higher than the corresponding parameter of polymer matrix. These experimental data confirm that for the studied nanocomposite interfacial layer is a reinforcing element to the same extent as actual nanofiller [1, 3, 5].

Further let us conduct theoretical estimation of l_{if} value according to the two methods and compare these results with the ones obtained experimentally. The first method simulates interfacial layer in polymer composites as a result of interaction of two fractals – polymer matrix and nanofiller surface [6, 7]. In this case there is a sole linear scale l , which defines these fractals interpenetration distance [8]. Since nanofiller elasticity modulus is essentially higher than the corresponding parameter for rubber (11 times higher in the considered case, see Fig. 1), then the indicated interaction reduces to nanofiller indentation in polymer matrix and $l = l_{if}$. In this case it can be written as [8]:

$$l_{if} \approx a \left(\frac{R_p}{a} \right)^{2(d-d_{surf})/d} \quad (1)$$

where a is lower linear scale of fractal behaviour, which is accepted equal to statistical segment length l_{st} [9], R_p is nanofiller particle (more precisely, particles aggregate) radius, which for nanoshungite is equal to 167.5 nm [2], d is dimension of Euclidean space, in which fractal is considered (it is obvious, that in our case $d = 3$), d_{surf} is fractal dimension of nanofiller particles aggregate surface.

The value l_{st} is determined as follows [10]:

$$l_{st} = l_0 C_\infty \quad (2)$$

where l_0 is the main chain skeletal bond length, which is equal to 0.154 nm for both blocks of butadiene-styrene rubber [11], C_∞ is characteristic ratio, which is polymer chain statistical flexibility indicator [12] and is determined with the aid of the Equation [9]:

$$T_g = 129 \left(\frac{S}{C_\infty} \right)^{1/2} \quad (3)$$

where T_g is glass transition temperature, equal to 217 K for butadiene-styrene rubber [3], S is macromolecule cross-sectional area, determined for the mentioned rubber according to the additivity rule from the following considerations.

As it is known [13], the macromolecule diameter quadrate values are 20.7 nm² for polybutadiene and 69.8 nm² for polystyrene. Having calculated cross-sectional area of macromolecule, simulated as a cylinder, for the indicated polymers according to the known geometrical formulas, we obtain 16.2 nm² and 54.8 nm², respectively. Further, accepting the average value of the adduced above areas as S , we obtain $S = 35.5$ nm² for butadiene-styrene rubber. Then according to the Eq. (3) at the indicated values T_g and S we obtain $C_\infty = 12.5$ and according to the Eq. (2) $l_{st} = 1.932$ nm.

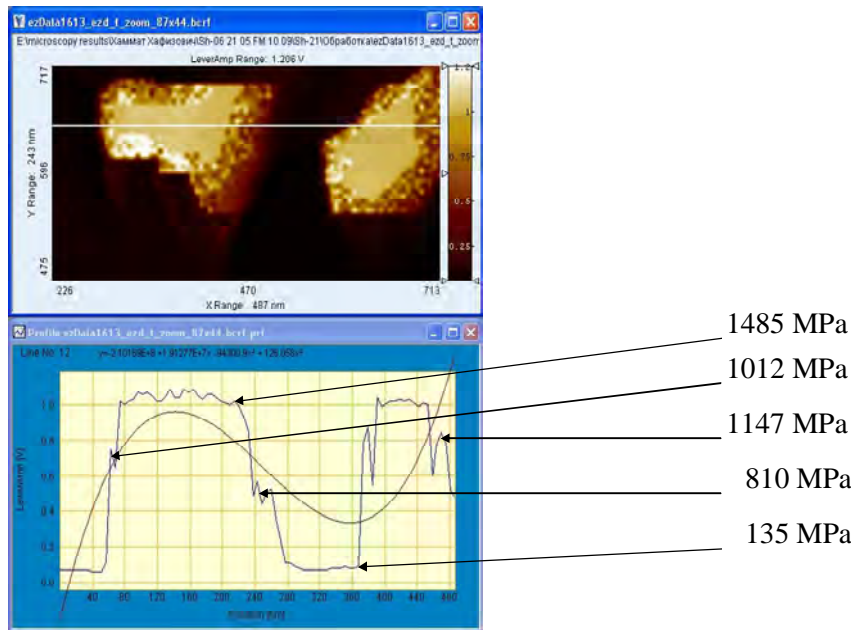


Fig. 1. The processed in SPIP image of nanocomposite butadiene-styrene rubber/nanoshungite, obtained by force modulation method, and mechanical characteristics of structural components by the data of nanoindentation (strain 150 nm)

The fractal dimension of nanofiller surface d_{surf} was determined with the aid of the equation [3]:

$$S_u = 410R_p^{d_{surf}-d} \quad (4)$$

where S_u is nanoshungite particles aggregate specific surface, calculated as follows [14]:

$$S_u = \frac{3}{r_n R_p} \quad (5)$$

where ρ_n is nanofiller particles aggregate density, determined according to the formula [3]:

$$r_n = 0.188(2R_p)^{1/3} \quad (6)$$

The calculation according to the Eqs. (4)-(6) gives $d_{surf}=2.44$. Further, using calculated by the indicated mode parameters, let us obtain from the Eq. (1) the theoretical value of interfacial layer thickness $l_{if}^T=7.8$ nm. This value is close enough to the one obtained experimentally (their discrepancy makes up $\sim 10\%$).

The second method of value l_{if}^T estimation consists in using the following two equations [1, 15]:

$$j_{if} = (d_{surf} - 2)j_n \quad (7)$$

and

$$j_{if} = j_n \left[\left(\frac{R_p + l_{if}^T}{R_p} \right)^3 - 1 \right] \quad (8)$$

where φ_{if} and φ_n are relative volume fractions of interfacial regions and nanofiller, accordingly.

The combination of the indicated equations allows to receive the following formula for l_{if}^T calculation:

$$l_{if}^T = R_p \left[\left(d_n - 1 \right)^{1/3} - 1 \right] \quad (9)$$

The calculation according to the formula (9) gives $l_{if}^T=10.8$ nm for the considered nanocomposite, which also corresponds well enough to the experimental value (in this case discrepancy between l_{if} and l_{if}^T makes up $\sim 19\%$).

Let us note in conclusion an important experimental observation, which follows from the SPIP processing results of the studied nanocomposite surface scan (Fig. 1). As one can see, at one nanoshungite particle surface from one to three (in average – two) steps can be observed, structurally identified as interfacial layers. It is significant that these steps width (or l_{if}) is approximately equal to the first (the closest to nanoparticle surface) step width. Therefore, the indicated observation supposes that in elastomeric nanocomposites at the average two interfacial layers are formed. The first one is formed in the result of interaction of nanofiller particle surface with elastomeric matrix; consequently, molecular mobility in this layer is frozen and its state is glassy-like. The second layer is formed in the result of interaction of glassy interfacial layer with elastomeric polymer matrix. The question whether only nanocomposite interfacial layer or both serve as reinforcing element is the most important from the practical point of view. Let us perform the following quantitative estimation to find an answer to this question. The reinforcement degree (E_n/E_m) of polymer nanocomposites is given by the Eq. [3]:

$$\frac{E_n}{E_m} = 1 + 11(j_n + j_{if})^{1.7} \quad (10)$$

where E_n and E_m are elasticity moduli of nanocomposite and matrix polymer, accordingly ($E_m=1.82$ MPa [3]).

According to the Eq. (7) the sum $(\varphi_n + \varphi_{if})$ is equal to:

$$j_n + j_{if} = j_n (d_{surf} - 1) \quad (11)$$

if one interfacial layer (the closest to nanoshundite surface) is a reinforcing element and

$$j_n + 2j_{if} = j_n (2d_{surf} - 3) \quad (12)$$

if both interfacial layers are a reinforcing element.

In its turn, the value φ_n is determined according to the equation [16]:

$$j_n = \frac{W_n}{r_n} \quad (13)$$

where W_n is nanofiller mass content, ρ_n is its density, determined according to the formula (6).

The calculation according to the Eqs. (11) and (12) gave the following E_n/E_m values: 4.60 and 6.65, respectively. Since the experimental value $E_n/E_m = 6.10$ is closer to the value calculated according to the Eq. (12), then this means that both interfacial layers are reinforcing element for the studied nanocomposites. Therefore the coefficient 2 should be introduced in the equations for value l_{if} determination (for example, in the Eq. (1)) in case of nanocomposites with elastomeric matrix. Let us remind that the Eq. (1) in its initial form was obtained as a relationship with proportionality sign, *i.e.* without fixed proportionality coefficient [8].

4. Conclusions

Nanoscope methodics used in the present paper allow to estimate both interfacial layer structural special features in polymer nanocomposites and its sizes and properties. For the first time it has been shown that in elastomeric particulate-filled nanocomposites two consecutive interfacial layers are formed, which are reinforcing element for the indicated nanocomposites. The proposed theoretical methods of interfacial layer thickness estimation, elaborated within the frameworks of fractal

analysis, provide sufficient correspondence to the experimentally obtained data.

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ЕКСПЕРИМЕНТАЛЬНА І ТЕОРЕТИЧНА ОЦІНКА ТОВЩИНИ МІЖФАЗНОГО ШАРУ В ЕЛАСТОМЕРНИХ КОМПОЗИТАХ

Анотація. Експериментально визначені товщина міжфазного шару та його пружність для полімерних нанокмполімерів з порошковим наповнювачем. Встановлено, що модуль пружності міжфазного шару в 5 разів перевищує відповідну величину матриці блочного полімеру. Показано, що теоретичні розрахунки товщини міжфазного шару в межах фрактальної моделі добре узгоджуються з експериментальними даними.

Ключові слова: нанокмполімер, наночастинка, міжфазний шар, модуль пружності, наноскопічний метод.