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Prediction of mechanical properties of polymer composites with carbon fillers based on low-frequency electrical conductivity data

O.M.Lisova [2], S.M.Makhno [1,2], G.M.Gunya [2], P.P.Gorbik [2], K.O.Ivanenko[1,3], Yu.I.Sementsov[1,2]

[1] Ningbo Sino-Ukrainian New Materials Industrial Technologies Institute Co., Ltd 15th Floor, 777 West Zhongguan Road, Zhuangshi Street, Zhenhai District, Ningbo City, Zhejian Province, PRC, 315201
[2] Chuiko Institute of Surface Chemistry of National Academy of Sciences of Ukraine, 17 General Naumov Str., Kyiv, 03164, Ukraine
[3] Institute of Macromolecular Chemistry of National Academy of Sciences of Ukraine, 48 Kharkiv highway, Kyiv, 02160, Ukraine

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Polymers reinforced with carbon fillers are used in load-bearing structures, racing cars, sports equipment, aircraft and drones due to their special stiffness and strength, as well as their electromagnetic shielding or absorption properties. The search for new materials, composites and quick prediction of their properties is an urgent task of polymer materials science. The paper shows that predicting the mechanical strength of the composites is possible by measuring electrical conductivity at low frequencies and extrapolating these values using the obtained expressions. The relative mechanical bending strength has a quadratic dependence on the filler content and can be represented with satisfactory accuracy by the low-frequency electrical conductivity for the composite system.

Keywords: relative bending strength, electrical conductivity, strength limit, percolation characteristics.

Прогнозування механічних властивостей полімерних композитів з вуглецевими напвовнювачами за даними електропровідності на низьких частотах. *Лісова О.М., Махно С.М., Гуня Г.М., Горбик П.П., Іваненко К.О., Семенцов Ю.І.*

Пролімери, армовані вуглецевими наповнювачами, використовуються у несучих конструкціях, гоночних автомобілях, спортивному приладді, літаках і дронах завдяки їхній особливій жорсткості та міцності, а також властивостям електромагнітного екранування або поглинання. Пошук нових матеріалів, композитів та швидке прогнозування їх властивостей є актуальною задачею полімерного матеріалознавства. В роботі показано, що прогнозування механічної міцності можливе шляхом вимірювання їх електропровідності на низьких частотах та екстраполяції цих значень за допомогою одержаних виразів. Стаття описує шляхи оптимізації процедури встановлення діапазону вмісту наповнювача у полімерних композитах, наповнених вуглецевими матеріалами, з достатнім рівнем міцнісних та електрофізичних характеристик. Відносна механічна міцність на згин має квадратичну залежність від вмісту наповнювача, її можна зобразити із задовільною точністю по показниках електропровідності на низьких частотах для композиційної системи.

1. Introduction

Polymer composites are widely used in protective and load-bearing structures due to their low cost, low density, acceptable optical characteristics, high ductility and resistance to destruction, high specific strength and processability [1]. However, most polymer materials typically exhibit low elastic modulus (<10 GPa), which makes them ineffective when subjected to deformation. To increase the Young's modulus of polymers, reinforcing fillers such as glass fibers, metal particles [2], carbon fillers [2-4] of various forms, sizes, and origins, or natural fibers [5, 6] are usually added. It is worth noting that all reinforcement methods have a positive effect on strengthening the matrix.

At concentrations exceeding the percolation threshold, metal or carbon fillers provide additional advantages such as thermal and electrical conductivity [7]. Since the shape and aspect ratio of conductive fillers affect the charge transfer and mechanical properties of composites, it is important to understand the structure of the conductive network and percolation characteristics for optimizing the properties of polymer composite materials.

Conductive polymer nanocomposites are promising materials for flexible sensor devices that have structural flexibility, strength, and sufficient sensitivity. Sensing membranes and electrically conductive adhesives [8], as well as deformation sensors, pressure sensors, humidity, and gas sensors [9, 10], are developed and used. Polymers reinforced with carbon fibers are commonly used in high-performance racing cars, sports equipment, airplanes, and drones [11] due to their exceptional stiffness, strength, and electromagnetic shielding properties [12]. Carbon nanotubes (CNTs) are most commonly used as a reinforcing component, which can be explained by their high aspect ratio (> 10^3) and high strength (tensile strength ~ 1.8 TPa). The matrix improvement effect is further enhanced by modification of CNT by oxidation (increases for modified CNTs by ~ 32% and initial CNTs by ~ 10%) [13]. Layered structures such as polycarbonate or fabric are often inserted into bulk polymer constructions to prevent delamination.

The aim of this work is to simplify the study of mechanical properties of polymer composites with carbon fillers, in particular bending strength, to obtain maximum strength characteristics. The paper demonstrates that this can be achieved by measuring electrical conductivity of the composites at low frequencies and extrapolating these values using derived equations. The work is aimed at optimizing the methodology for determining the range of filler content in polymer composite materials filled with carbon materials to achieve sufficient levels of strength and electrophysical characteristics.

The relative bending strength has a quadratic dependence on the filler content, which can be accurately represented by the low-frequency electrical conductivity values for the composite system. From the literature, it is known that a sufficient level of strength increase for various reinforcement and modification options of the polymer matrix with fillers is approximately 60-64%. One common example is the use of carbon fiber fillers [14], which can typically increase the strength of the polymer by 2 orders of magnitude [15] and its electrical conductivity by 6 orders of magnitude near the percolation threshold [16].

Thus, it is possible to establish a range of filler content to achieve a sufficient level of mechanical reinforcement for a specific task. The bending strength test method is quite time-consuming and requires larger-sized specimens with strict geometric parameters. In contrast, measurements of electrical conductivity at low frequencies are carried out quickly, while the sample is formed up to 3 mm thick without strict geometric conditions, provided that the planes are parallel. As a result, the sample remains undamaged and suitable for use in other research methods. Electrical conductivity measurements are promising because they allow determining the maximum strength only in a narrow range of filler content, slightly above the percolation threshold. This approach reduces energy costs for sample production, decreases the costs of valuable filler and matrix materials, and saves time on the necessary work of measuring samples over a wide range of filler contents.

The aim of the study is to predict the mechanical properties and the range of sufficient strengthening of polymer composites with carbon fillers, based on electrical conductivity data.

The addition of certain types of carbon nanofillers such as graphene, carbon nanotubes, and carbon fibers into insulating polymer matrices is being considered. To demonstrate the prediction, we have cosen composite systems of pol y(chlorotrifluoroethylene) – carbon nanotubes (PCTFE-CNT), the same system with a hybrid

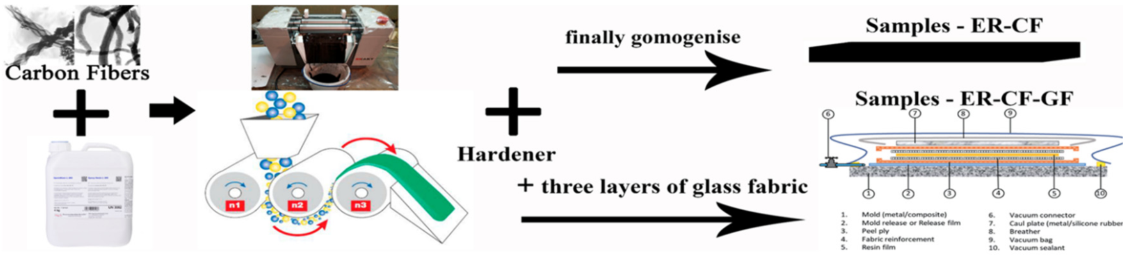

Fig. 1. Scheme of manufacturing composites ER–CF and ER–CF–GF

filler of carbon nanotubes and graphene nanoplatelets (PCTFE – CNT@GNP), as well as epoxy resin – carbon fiber (ER – CF) and (ER – CF – GF) on glass fabric.

2. Experimental

Multi-walled carbon nanotubes (CNTs) were obtained by the CVD method (TU - U 03291669-009:2009) [17]. The CNTs were dispersed by ultrasonic treatment in a suspension of graphene nanoplatelets. Ultrasonic dispersing was carried out using the UZDN-A device, at a frequency of 22 kHz, at a power of 140 W, for 2 minutes. Graphene nanoplatelets (GNPs) with a thickness of 5-10 layers and an average diameter of 0.1-2.0 μm were obtained by electrochemical exfoliation from expanded graphite (EG) foil (anodic oxidation of EG foil in weak KOH solutions) [18, 19]. The mass of GNPs was 1:10 relative to CNTs. The objects were thoroughly and extensively investigated by us [17]. The filler suspension was mixed with PTFE powder, previously moistened with ethyl alcohol. The obtained mixture was dried in a rotary evaporator at a temperature of 75 °C. After removing the water, the resulting mixture was put into a mold and samples were formed at a temperature of 232 °C and a pressure of 5 MPa. The samples PCTFE–CNT@GNP S0.5, S0.25, and S0.125 contained, respectively, 0.5, 0.25, and 0.125 g of CNTs per 100 ml of water when dispersing the carbon combined filler. For example, 0.05 g of GNPs were added to 100 ml of distilled water, dispersed for 5 minutes, and then 0.5 g of CNTs were added and dispersed for another 5 minutes. The CNT@GNP suspension was stable for a long time [20].

CNTs were obtained by grinding carbon fabric UVM-24 (TU88-USSR 259-003-89). To produce the composites, resin LR 285 (Momentive Specialty Chemicals) was mechanically mixed with CNTs in a three-roll mixer until a homogeneous color of the mixture was obtained. The hardener LH 286 (Momentive Specialty Chemicals) was added and finally homogenized in a mechanical mixer (fig. 1). The samples of the required size were poured [21].

To produce a composite with fiberglass, after thorough mixing, the prepared composition was applied to the surface of a composite package consisting of three layers of fiberglass (AEROGLASS). The sandwich-type composite glass unit was further subjected to infusion (vacuum) pressing until complete hardening. Composites with a volume content of CNTs from 0.0005 to 0.01 volume fractions were used for the study.

Electrophysical studies were carried out in the frequency range of 8-12 GHz using a non-contact method, and electrical conductivity at low frequencies of 0.1, 1, and 10 kHz was measured using a two-contact method. The relative error in determining ε′, ε″, σ did not exceed ± 5% [16].

The bending strength tests of the composites were carried out on a tensile machine 2167 P50 with automatic recording of load diagrams on a personal computer at a sliding speed of 2 mm/min, on samples measuring approximately (50×20×0.5 mm); a distance between supports was 17 mm [16].

3. Results and Discussion

The dependencies of low-frequency electrical conductivity on filler contents ranging from 0 to 0.025 volume fraction for the studied systems are presented in Fig. 2.

The obtained results were analyzed from the point of view of percolation theory according to the equation:

$$\sigma = \sigma_i(\varphi - \varphi_c)^t, \ \text{for} \ \varphi_c < \varphi \tag{1}$$

where σ_i is the electrical conductivity of the filler; φ is the volume fraction of the filler; φ_c is the filler content corresponding to the percolation threshold; t is the critical index characterizing the dimensionality of the conducting cluster.

The percolation threshold value was determined from the logarithmic dependence of the electrical conductivity on the volume fraction

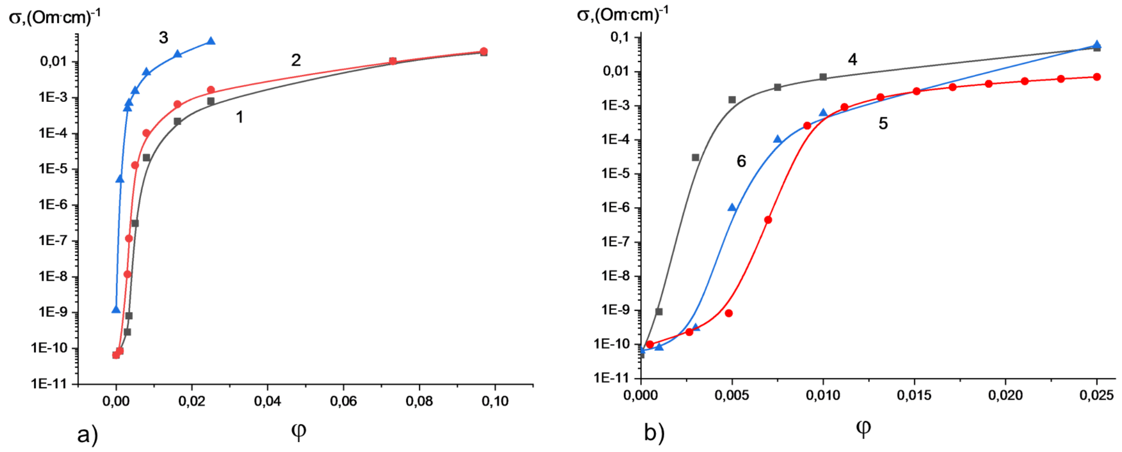

Fig. 2. Electrical conductivity of composites depending on the filler volume fraction: a – PCTFE – CNT@GNP S0.5 (1); PCTFE – CNT@GNP S0.25 (2); PCTFE – CNT@GNP S0.125 (3); b – PCTFE – CNT (4); ER–CF (5); ER–CF–GF (6).

of CNTs near the inflection point of the curve in the region of low electrical conductivity. The value of φ_c is found from the electrical conductivity graph in a semi-logarithmic scale as the abscissa value of the intersection point of the lower horizontal and inclined sections of the curve.

Taking the logarithm of equation (1):

$$lg(\sigma/\sigma_i) = t\ lg(\varphi-\varphi_c)\ , \quad (2)$$

we have a linear equation of the form $y = t\ x$. We visually draw a trend line through the experimental points and determine t from the equation of the trend line as the angular coefficient of the line. The obtained results are shown in Table 1.

Analyzing the results in Table 1, it can be concluded that there is a relationship between the content of CNTs at maximum flexural strength φmax and the percolation threshold value φ_c. The relationship can be written as:

$$\varphi_{max} = t\ \varphi_c, \quad (3)$$

where: t is the proportionality coefficient, which depends on the aspect ratio of CNTs and the uniform distribution of filler nanoparticles in the volume of the polymer. Thus, by using the dependencies of electrical conductivity on the volume fraction of carbon fillers in the polymer composites, the percolation threshold value, and the fractal indices, it is possible to predict the mechanical properties of a specific composite system, namely the filler content at which maximum improvement in mechanical properties occurs. There is a correlation between the mechanical properties and the electrical conductivity at low frequencies in the percolation threshold region of the carbon filler [22].

For the specified systems, the ultimate bending strength has been determined [16] (Fig. 2, curve 3, a-e). The filler content was calculated at which the maximum improvement in mechanical properties (φ_{max}) and the maximum relative bending strength ($K_{max}=P_{max}/P_0$) were observed (Table 1). The filler content φ_{max} is in close agreement with the inflection points

Table 1. Percolation characteristics of composite systems

№	Composities	φ_c, volume fractions	t	φ_{max}, volume fractions calculated	φ_{max} volume fractions experimental	P_{max}/P_0
1	PCTFE–CNT@GNP S0.5	0.0045	2.04	0.0092	0.0098	1.39
2	PCTFE–CNT@GNP S0.25	0.0034	1.77	0.0060	0.0059	1.42
3	PCTFE–CNT@GNP S0.125	0.00098	1.88	0.0018	0.0020	1.41
4	PCTFE–CNT	0.0015	1.81	0.0027	0.003	1.56
5	ER–CF	0.0032	1.85	0.0059	0.0056	1.41
6	ER–CF– GF	0.0027	2.10	0.0056	0.0054	1.53

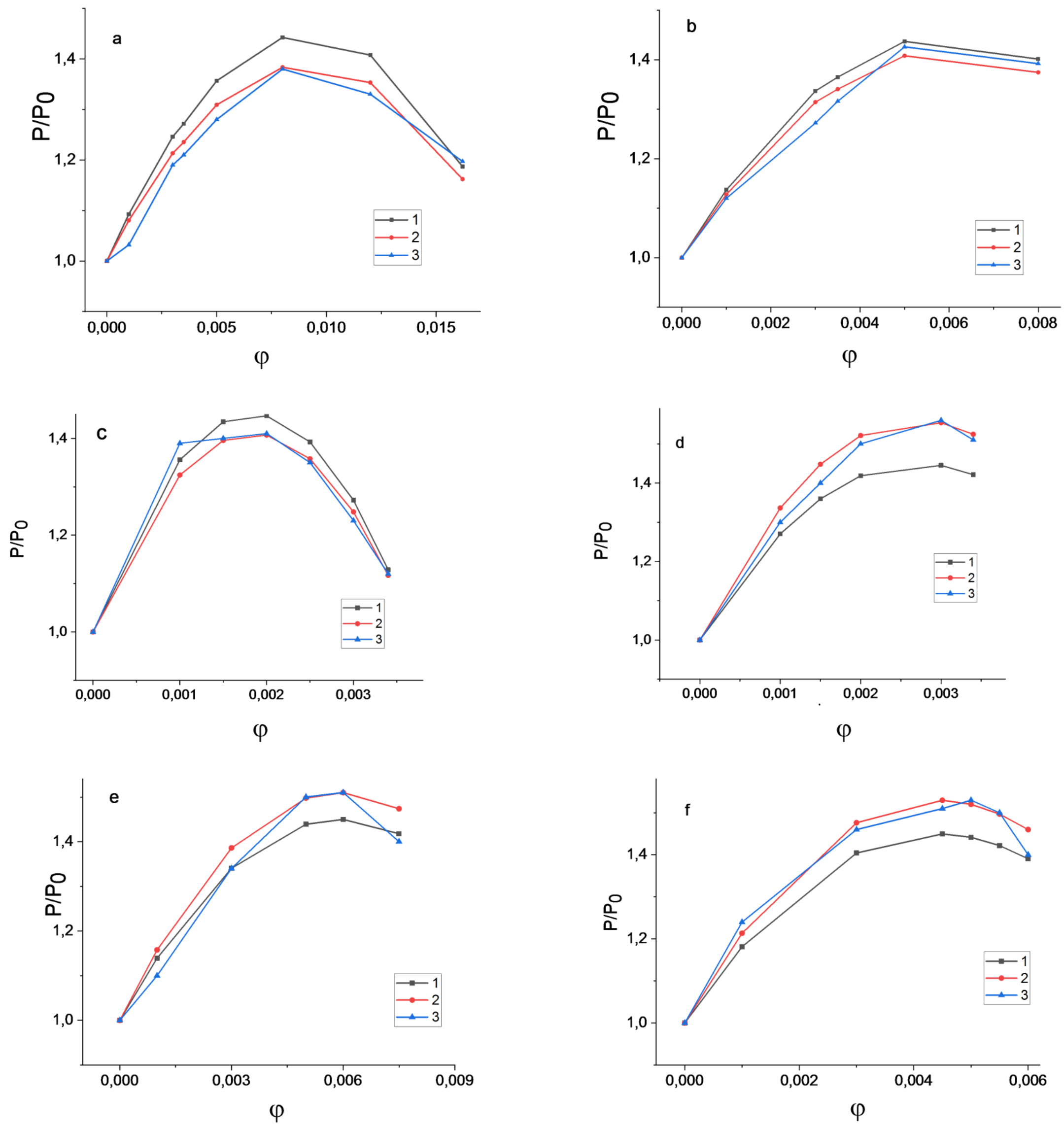

Fig. 3. Relative bending strength: 1 – calculated using equation (2) (K_{max}=1.45); 2 – calculated using equation (2) (K_{max}, experimentally determined for each system); 3 – experimental values. For systems: a – PCTFE – CNT@GNP S0.5; b – PCTFE – CNT@GNP S0.25; c – PCTFE – CNT@GNP S0.125; d – PFTFE – CNT; e – ER–CF; f – ER–CF–GF.

of the $\sigma = f(\varphi)$ dependences in the region of high values $\varphi(\sigma_{high})$. In particular, the bending strength shows optimal values in the range of filler volume fraction of 0.001–0.005 after the percolation threshold.

It has been established that the dependence of relative bending strength has a parabolic character. By superimposing Excel program trend lines on the experimental curves, it was established that the experimental dependence of the relative bending strength is described with satisfactory accuracy by a parabolic dependence of the trend line with the selected coefficients. An analytical approximation was performed based on the literature data, and as a result, a formula in the form of a quadratic equation (4) was derived, which best describes the dependence of mechanical properties on the content of the conductive filler. The coefficient K of the improvement of mechanical properties was theoretically calculated by a quadratic equation:

$$K = -\frac{K_{max} - 1}{\varphi_{max}^2}\varphi^2 + 2\cdot\frac{K_{max} - 1}{\varphi_{max}}\varphi + 1 \qquad (4)$$

where K_{max} is the coefficient of maximum improvement of mechanical properties for a specific compositional system; φ_{max} is the filler content at which the maximum strength values are obtained.

Initially, the coefficients in the equation describing the trend line were selected empirically. The results were compared with the percolation theory coefficients calculated from the percolation equation based on electrical conductivity data. We have found a match with accuracy to hundredths. The formula has been tested on five composite systems.

Equation (4) accurately describes the dependence of strength on the filler content in the range of 0 to $2\varphi_{max}$, where the mechanical properties of the composites increase. According to the literature data [23], K_{max} ranges from 1.4 to 1.5 for polymer composite systems with conductive fillers. Therefore, in order to establish the optimal range of the filler content, two approaches can be considered.

The first approach may have less accuracy but is faster to apply, since it does not require additional tests of mechanical properties. It uses the parameters t, φ_{max}, and the average value of K_{max}=1.45 (Curve 1, Fig. 3, a-f).

The second approach involves manufacturing a sample for mechanical testing (with a filler content of φ_{max}), experimentally determining the bending strength, calculating K_{max}, and using this value in further calculations according to equation (2) (Fig. 3, a-f, curve 2).

Statistical analysis of the obtained experimental results showed that the relative error of this theoretical approach in both methods does not exceed 6%, which is acceptable for investigations of various levels.

4. Conclusions

The interdependence between electrical and mechanical properties of polymer composite materials with carbon fillers has been established. Using the example of polychlorotrifluoroethylene systems with various hybrid fillers: graphene@multi-walled carbon nanotubes and epoxy resin + carbon fiber, a correlation is shown between the percolation threshold φ_c, calculated from the semi-logarithmic dependence of the low-frequency electrical conductivity on the filler content, and the filler content φ_{max}, at which the relative bending strength is maximum. The proportionality coefficient for this dependence is the fractal coefficient of percolation theory.

It was found that the relative bending strength obeys a parabolic dependence on the filler content. Based on literature data, an analytical approximation was carried out, which resulted in a quadratic equation that best describes the dependence of mechanical properties on the content of conductive filler in the range from 0 to $2\varphi_{max}$, where the mechanical properties of composites increase.

It is shown that for the studied composites, the maximum increase in bending strength is about 56%, which is a satisfactory performance indicator.

In conclusion, it should be noted that by reducing the percolation threshold in filled polymer systems, high levels of electrical conductivity can be achieved with lower filler contents, as well as higher strength properties, especially for fillers with high aspect ratio.

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