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THERMAL, ELECTRO AND ELASTO–MECHANICAL PROPERTIES OF PARTICULATE COMPOSITE MATERIALS

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The paper provides an overview of the results obtained during the realisation of the research project entitled: "Thermophysical, electrical and optical properties of disordered materials". The experimental results of measurements of mechanical (elastic shear modulus), thermophysical (thermal conductivity), electrical (electrical conductivity) properties and flammability of some chosen particulate composite materials are interpreted on the basis of the theory of effective parameters. The relations for effective parameters derived in the framework of the average field approximation are tested on the basis of experiments.

K e y w o r d s: disordered materials, elastic shear modulus, thermal conductivity, electrical conductivity

1 INTRODUCTION

The aim of this paper is to present some experimental results obtained by measuring the effective thermal, electrical conductivity and elastic shear modulus of particulate composite materials. A composite material is regarded as consisting of grains (granules of the globular form), possibly in a matrix. The arrangement of the grains is random and, therefore, the local values of parameters are dependent on space coordinates and they are also random quantities. However, on the macroscopic level the composite materials may be homogeneous and isotropic. For an experimentalist it is very important to know in which cases the composite on the macroscopic level may be characterized by effective parameters which are independent of space coordinates, because only in these cases it is justified to use the standard methods for their measurement. The problem is to determine how the effective parameters depend on the structure of the composite material on the submacroscopic level (on the length scale of linear dimension of granules) and also on the quantities which characterize individual components of the particulate composite. This information is very important especially for technologists. Knowing the relations for the effective parameters it is possible to manufacture composite materials with prescribed values of the parameters ("tailoring" of materials). It is interesting that the mathematical structure of laws describing the individual effects such as dielectric polarization, magnetization, heat flow and electric current is the same. For example in the case of heat flow and electric current the following phenomenological laws are valid:

Fourrier's law: $\boldsymbol{q} = -\lambda \operatorname{grad} T$,
Ohm's law: $\boldsymbol{i} = -\sigma \operatorname{grad} \varphi$,
Stationary heat equation: $\operatorname{div} \boldsymbol{q} = 0$,
Condition for stationary electric current: $\operatorname{div} \boldsymbol{i} = 0$,

where $\boldsymbol{q}$ and $\boldsymbol{i}$ are the heat flow and current densities, respectively, λ and σ are the thermal and electrical conductivities, respectively, T and φ are the temperature and electric potential, respectively.

According to that fact if we know the relation for effective thermal conductivity, we substitute the thermal conductivity with the electrical conductivity and in this way we obtain the relation for the effective electrical conductivity. Further interesting matter is that it can be shown that the following inequality

$$\frac{1}{< \frac{1}{\lambda} >} \leq \lambda_{eff} \leq < \lambda > \tag{1}$$

is valid, where
$< \lambda > = \sum_{n=1}^{N} c_n \lambda_n$, $< \frac{1}{\lambda} > = \sum_{n=1}^{N} c_n \frac{1}{\lambda_n}$,
c_n is the volume fraction of the n^{th} component,
λ_n is the thermal conductivity of the n^{th} component.

Inequality (1) is the specific property of the composite material. In the composite materials the percolation phase transition takes place [1]. To illustrate that effect let us consider the binary system and let the thermal conductivity of the matrix equal zero. There exists a critical volume fraction c_k of the filler which is called the percolation threshold. For $c \leq c_k$ the grains of the filler form clusters which are separated from each other and therefore the sample is thermally non-conucting ($\lambda_{eff} = 0$). At $c = c_k$ some clusters connect themselfves together and they form the percolation cluster which is spread out through the whole sample. From this moment λ_{eff} rapidly increases with the volume fraction c of filler. This effect is called percolation. If the ratio $\lambda_{matrix}/\lambda_{filler}$ is much smaller than one, percolation is more expressive. The technologist has to consider this fact at the proposal of the composition of the composite.

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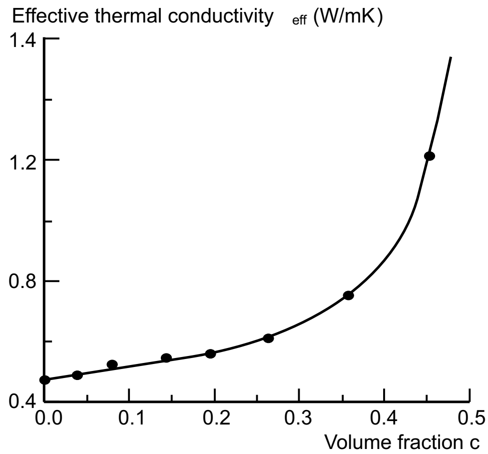

Fig. 1. λ_{eff} plotted as a function of the volume fraction c_1. (•) Experimental data; solid curve corresponds to the theory.

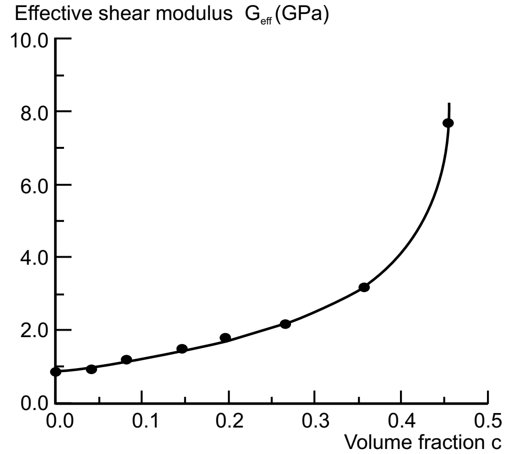

Fig. 2. G_{eff} plotted as a function of the volume fraction c_1. (•) Experimental data; solid curve corresponds to the theory.

1 EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

1.1 Thermophysical and Mechanical Properies of Particulate Composite

The purpose for manufacturing a composite material based on poleolefine (polymer) is not to vaste crude oil from which polyolefines are produced. Nowadays crude oil is a strategic material. Composite polymers are used for manufacturing plastomers. At the proposal of a suitable composite based on polymers one has to consider the following requirements: The filler must be an easily procurable and cheap raw material. The thermal conductivity of the filler has to be higher than the polymer (matrix) in order to enhance the effective thermal conductivity of the composite and so to shorten the manufactoring cycle and in this way to save energy. All these requirements have to be fulfilled at the preservation of the mechanical properties. With the enhancement of the effective thermal conductivity the mechanical properties deteriorate and, therefore, one has to find the optimal composition of the composite material. This problem was resolved satisfactorily. It was found that the composite polyethylene — $CaCO_3$ (PE-$CaCO_3$) fulfiles best the above mentioned requirements. This composite is manufactured nowadays in industry. Now we bring the experimental results.

The interpretation of the experimental results obtained by measuring the effective thermal conductivity and elastic shear modulus of the composite PE-$CaCO_3$ on the basis of the theory of effective parameters is given. The above mentioned parameters were measured in dependence on the volume fraction c_1 of $CaCO_3$ in order to reach the optimum composition. By increasing the volume fraction of $CaCO_3$ the thermal conductivity increases but the mechanical properties deteriorate, which means that the composite becomes fragile. This was the reason for searching the optimal composition of the composite material. The experimentally obtained dependence of the effective thermal conductivity or the effective elastic shear modulus on the volume fraction of the filler ($CaCO_3$) was fitted by the formula [2], [3], [4] and [5]

$$\lambda_{eff} = \lambda_1\big(B + \sqrt{B^2 + D}\,\big)^{1/t} \tag{2}$$

$$G_{eff} = G_1\Big\{\sqrt{\frac{1}{16}(d_1 + d_2 p)^2 + d_3 p} - \frac{1}{4}(d_1 + d_2 p)\Big\}^{1/t} \tag{3}$$

where

$$D = \frac{g}{1-g} r^t \qquad B = \frac{(1-r^t)c_1 + (1-g)r^t - g}{2(1-g)}$$

$$r = \frac{\lambda_{\rm PE}}{\lambda_{\rm CaCO_3}} \qquad d_1 = (1-c_1)\frac{\mu_1+1}{\mu_1-2} - 2c_1$$

$$p = \frac{G_{PE}}{G_{\rm CaCO_3}} \qquad d_2 = c_1\frac{\mu_2+1}{\mu_2-2} - 2(1-c_1)$$

$$\mu_1 = \frac{1}{\nu_1} \quad \mu_2 = \frac{1}{\nu_2} \qquad d_3 = \frac{1}{2}c_1\frac{\mu_2+1}{\mu_2-2} + \frac{1}{2}(1-c_1)\frac{\mu_1+1}{\mu_1-2}$$

ν_1 is the Poisson ratio of $CaCO_3$,
ν_2 is the Poisson ratio of PE,
t is the free parameter which will be determined from experiment,
$c_k = g$ is the percolation threshold.

The dependence of the effective thermal conductivity of PE-$CaCO_3$ on the volume fraction of $CaCO_3$ is shown in Fig. 1. The best fitting with the theoretical relation (2) was achieved at $g = c_k = 0.473 \pm 0.017$, $t = 3.03 \pm 0.7$. The relatively large dispersion of parameter t is probably due to the small number of experimental data. The dependence of the effective elastic shear modulus of PE-$CaCO_3$ on the volume fraction of $CaCO_3$ is shown in Fig. 2. From the best fitting of the experimental data with formula (3) we obtained $p = 10^{-3}$, $\mu_1 = 5.57 \pm 0.7$, $\mu_2 = 2.2 \pm 0.2$ and $t = 2.04 \pm 0.7$. Again the relatively large dispersion of the quantities μ_1, μ_2 and t is probably due to the small number of experimental data. From Figs. 1 and 2 it is seen that the theory describes the measurement quite well.

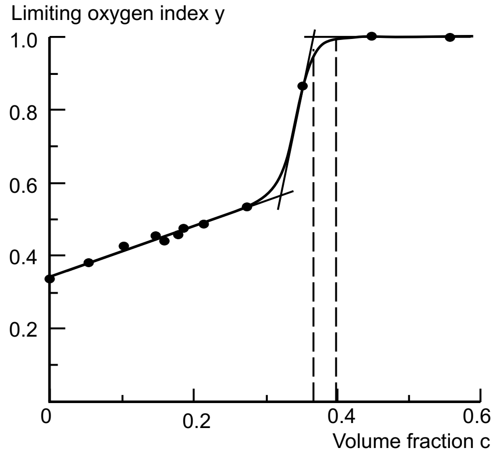

Fig. 3. Limiting oxygen index as a function of volume fraction c; (•) indicate experimental data; solid curve corresponds to the fitted formula

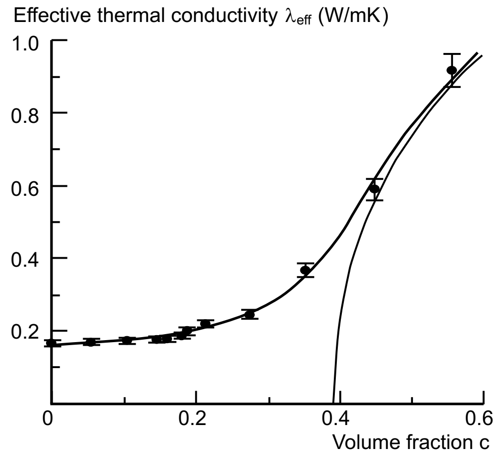

Fig. 4. Effective thermal conductivity as a function of volume fraction c; (•) indicate experimental data; solid and thin ($\lambda_2 = 0$) curve indicate theory.

1.2 Thermal Conductivity and Limiting Oxygen Index of Basic Rubber Blend-Aluminium Hydroxide Particulate Composite

The mixture of the basic rubber blend — aluminium hydroxide is used for the production of a fireproof transport bands [5]. The basic rubber blend is the matrix and hydrated alluminium hydroxide in pulverous form is the filler. The filler is characterized by a higher thermal conductivity than the matrix and, therefore, it enhances the effective thermal conductivity of the composite. Further, the filler plays the role of a fire retardant in the burning process. When the burning process begins at a certain place then it is necessary to remove the heat arising from the burning process and to stop the burning process. During the burning process the γ modification of aluminium hydroxide at 450 °C is unstable and changes according to the following chemical reaction

$$2\,\mathrm{Al(OH)_3} = (\gamma\text{-}\mathrm{Al_2O_3}) + 3\,\mathrm{H_2O}\,.$$

Due to the endothermic nature of this chemical reaction the heat is removed from the burning process and so the enhancement of temperature is prevented. Further the water vapor lowers the partial pressure of oxygen and in this way it prevents combustion. Finally, the γ-Al_2O_3 adsorbs the components of the basic rubber blend and it can inhibit the growth of a fresh surface at the combustion zone. The retardative effect of aluminium hydroxide can be explained by percolation: Every grain of the filler has a certain domain at which it prevents combustion. The domains create a cluster which is defined as follows: The domain of any grain belonging to the same cluster is in contact at least with one domain belonging to the same cluster. There exists a critical volume fraction of the filler (the percolation threshold) at which a percolation cluster arises and it is extended throught the entire sample. From this moment the burning process is stopped, as it is shown in Fig. 3. This interpretation is supported by the fact that the percolation threshold determined either from measurement of the effective thermal conductivity or from the measurement of limiting oxygen index are almost the same. The effect of fire retardation of the filler is expressed by the limiting oxygen index (LOI). The LOI is the percentage of oxygen in an oxygen-nitrogen atmosphere

$$LOI = \frac{[O_2]}{[O_2] + [N_2]} 100$$

in which a material will just burn and at which the velocity of propagation of the burning process is equal zero. The experimental data of the measurement of the LOI are shown in Fig. 3. The measurements of LOI were carried out using a modified Stanton Redcroft FTA flamibility unit in compliance with the standard [6]. The dependence of the LOI on the volume fraction of the filler c (Fig. 3) was fitted to the formula

$$LOI = y = \frac{1 + (ac + b)\exp[-d(c - c_0)]}{1 + \exp[-d(c - c_0)]}\,. \tag{4}$$

From the optimal fit the following values of parameters were obtained: $a = 0.687$, $b = 0.343$, $d = 85.$ and $c_0 = 0.344$. The empirical formula was used for a better determination of the percolation threshold. Using the graphic method, as it is indicated in Fig. 3, the interval $0.368 \div 0.4$ was determined. The percolation threshold lies in this interval. It is evident that the value of the percolation threshold obtained from the measurement of the effective thermal conductivity (see measurement of λ_{eff}) also lies in the above mentioned interval, which justifies the interpretation of the measurement of LOI on the basis of the percolation process.

The thermal conductivity λ_{eff} was measured by a stationary method [7]. The fitting of the experimental data according to theoretical relation (2) was carried out using

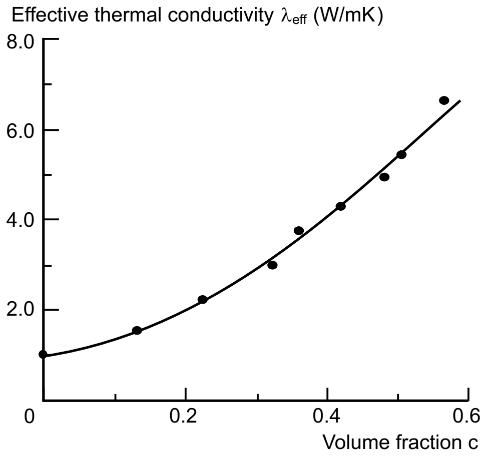

Fig. 5. (•) experimental data, solid curve corresponds to the theory.

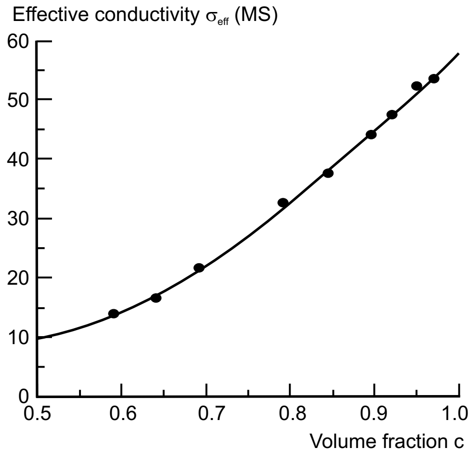

Fig. 6. (•) experimental data, solid curve corresponds to the fitted formula (2).

the standard Levenberg-Marquart method [8]. The dependence of λ_{eff} on c is shown in Fig. 4. From the best fit, the following values of parameters were obtained: $\lambda_1 = 1.506 \pm 0.132\,\mathrm{Wm^{-1}K^{-1}}$, $\lambda_2 = 0.154 \pm 0.005\,\mathrm{Wm^{-1}K^{-1}}$, $t = 2.39 \pm 0.54$ and $c_k = 0.394 \pm 0.03$, where λ_1 and λ_2 are the thermal conductivities of the filler and of the matrix, respectively; c is the volume fraction of the filler; c_k is the percolation threshold, and t is the free parameter which was determined experimentally.

1.3 The effective thermal conductivity of epoxy-resin-SiO_2

A mixture epoxy resin-SiO_2 was prepared in order to fill up electrotechnical components [9], especially a distribution transformer. The aim was to substitute the transformer oil by a suitable composite so that the composite has to fulfill the following requirements: 1) Sufficiently high dielectric strength. 2) Sufficiently high thermal conductivity for the diversion of Joule's losses which arise in the windings of the transformer. 3) Matching the thermal dilatation between the composite and the windings of the transformer.

For the enhancement of the effective thermal conductivity the filler must have a higher thermal conductivity than the matrix. As the matrix there was chosen an epoxy resin. From the several fillers it was shown that a siliceous sand SiO_2 fulfills best the above mentioned requirements. The composite epoxy resin-SiO_2 was applied in electrotechnical industry.

The dependence of the effective thermal conductivity on c is shown in Fig. 5. Experimental data were fitted by relation (2). From the best fitting we obtain the following values of parameters: $\lambda_{\mathrm{SiO_2}} = 9.88\,\mathrm{Wm^{-1}K^{-1}}$, $t = 1$ and $c_k = 0.265$.

1.4 Effective electric conductivity of copper-graphite composite material

The mixture copper-graphite is used for electrical contact-carrying current between the stationary and rotating parts of *eg* electromotors, generators, seam welding machines. Special conditions are required on the properties of this contact, particulary on their electric and thermal conductivity. It was shown that such conditions are best fulfilled by a composite composed of copper matrix showing high electric conductivity while graphite creates the secondary phase in the matrix, which ensures high sliding properties. Electrolytical copper (as matrix) with particles smaller than 70 μm and graphite (as filler) with particles smaller than 3 μm [10] were used for producing the composite. The purity of both was 99.9 %. Sometimes the graphit particles are coated by copper for improvement of the adhesion between the matrix and filler. The dependence of the effective electric conductivity is shown in Fig. 6. The experimental data were fitted according to relation (2). From the best fit we obtained the following values of parameters: $\sigma_{graph} = 0.33 \times 10^7 \Omega^{-1}\mathrm{m}^{-1}$, $\sigma_{Cu} = 0.588 \times 10^8 \Omega^{-1}\mathrm{m}^{-1}$, $c_k = 0.65$ and $t = 1$.

2 CONCLUSION

The fitting of experimental data shows the validity of the relation for effective parameters which were derived in the framework of the average field approximation. For a more accurate interpretation of experimental data it would be necessary to have these data from a wider interval of volume fraction.

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