

# Study of Thermophysical and Mechanical Properties of Particulate Composite Polyethylene–CaCO<sub>3</sub>

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**ABSTRACT:** Starting from the formulae for effective parameters of the particulate composite derived within the average field approximation, the formula for the percolation threshold is derived. The maximum value of the percolation threshold is  $\frac{1}{3}$  in the case of the isotropic granules of globular shape. Further, the experimental data obtained from the measurement of effective thermal conductivity and elastic shear modulus of the particulate composite polyethylene–CaCO<sub>3</sub> cannot be interpreted in the framework of the average field approximation. For this reason it was necessary to modify the formulae for effective parameters, and they were able to describe the experiment. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1525–1530, 1997

**Key words:** particulate composite; average field approximation; percolation threshold

## INTRODUCTION

The aim of this article is to give the experimental results obtained by measuring the effective thermal conductivity and the elastic shear modulus of the particulate composite polyethylene (PE)–CaCO<sub>3</sub>. Then the interpretation of these experimental results on the basis of the theory of effective parameters is given.

The above-mentioned parameters were measured in the dependence on the volume fraction of filling CaCO<sub>3</sub> in order to reach the optimum composition of the composite. In many applications one requires the biggest possible value of the effective thermal conductivity at the conservation of mechanical properties. To increase the value of the effective thermal conductivity it is necessary to increase the volume fraction of filling (in the case when the thermal conductivity of filling is bigger than the matrix), but increasing the volume fraction of filling caused the mechanical

properties to worsen. This meant that the composite became fragile. This is the reason for searching for the optimum composition of the composite.

The second aim of this work was to fit the experimental results to the theory and in this way to test the model for deriving the formulae of the effective parameters. The tested formulae would help a technologist to design the suitable composition of the composite to reach the desired values for the effective parameters.

Composite material is regarded as consisting of grains, possibly in a matrix. The arrangement of these grains is random, and therefore the local value of parameters is dependent on space coordinates, which are also random quantities. For an experimentalist it is very important to know in which cases composite material on the macroscopic level may be characterized by effective parameters because only in these cases it is justifiable to use the standard methods for their measurement. The necessary and sufficient conditions for using effective parameters are discussed in Beran's work.<sup>1</sup> Further, we assume that the conditions for using effective parameters are fulfilled. In such cases, there is also a problem to determine

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how effective parameters depend on the structure of the composite material on a submacroscopic level and also depend on the quantities, which characterize individual components of the particulate composite. The derivation of the formulae for effective parameters is in general a formidable task, partly due to the mathematical difficulties and partly due to the unknown  $n$ -point correlation functions. In such cases one is obliged to use approximate methods. One of those approximate methods is an average field approximation method. In the next part we discuss the formulae for effective parameters that were derived in the framework of the average field approximation.<sup>2,3</sup>

## THEORETICAL

At first we analyze the case of the effective thermal conductivity. The effective thermal conductivity,  $\lambda_{\text{eff}}$ , of a binary isotropic particulate composite is defined by solving the equation<sup>2</sup>

$$\sum_{j=1}^2 c_j \sum_{i=1}^3 \frac{(\lambda_j - \lambda_{\text{eff}})}{\lambda_{\text{eff}} + P_j^i (\lambda_j - \lambda_{\text{eff}})} = 0 \quad (1)$$

where  $c_j$  is the volume fraction of the  $j$ th component,  $\sum_{j=1}^2 c_j = 1$ ,  $P_j^i$  is the depolarization factors for an ellipsoid of the  $j$ th component along the  $i$  axis,  $\lambda_j$  is the thermal conductivity of the  $j$ th component, and  $\lambda_{\text{eff}}$  is the effective thermal conductivity of the particulate composite.

The depolarization factors fulfill on the one hand the inequalities  $0 \leq P_j^i \leq 1$  and on the other hand the following equation:

$$\sum_{i=1}^3 P_j^i = 1, \quad j = 1, 2 \quad (2)$$

Equation (1) can be arranged in the form

$$c_1(x-1)H_1A_2 + c_2(x-r)H_2A_1 = 0 \quad (3)$$

where

$$A_1 = G_{11}(x-1)^3 + G_{12}(x-1)^2 + 2(x-1) + 1 \quad (4)$$

$$A_2 = G_{21}(x-r)^3 + G_{22}(x-r)^2 + 2r^2(x-r) + r^3 \quad (5)$$

$$H_1 = G_{12}(x-1)^2 + 4(x-1) + 3 \quad (6)$$

$$H_2 = G_{22}(x-r)^2 + 4r(x-r) + 3r^2 \quad (7)$$

$$G_{j1} = P_j^1P_j^2 + P_j^1P_j^3 + P_j^2P_j^3 - P_j^1P_j^2P_j^3 \quad (8)$$

$$G_{j2} = 1 + P_j^1P_j^2 + P_j^1P_j^3 + P_j^2P_j^3 \quad (9)$$

$$r = \frac{\lambda_2}{\lambda_1} \quad (10)$$

$$x = \frac{\lambda_{\text{eff}}}{\lambda_1} \quad (11)$$

Equation (3) leads to an algebraic equation of the sixth degree. The solution of this equation can be done in general only numerically. Without solving eq. (3) we can show in a relatively simple way some of its interesting properties. At first eq. (3) describes the percolation phase transition. The percolation phase transition can be observed either for  $\lambda_1 = 0$  or  $\lambda_2 = 0$ . We consider the case when  $\lambda_2 = 0$  and therefore  $r = 0$ . For  $r = 0$ ,  $A_2 = G_{21}x^3$  and  $H_2 = G_{22}x^2$ . Introducing these quantities into eq. (3), we obtain

$$x^3(ax^3 + bx^2 + cx + d) = 0 \quad (12)$$

where

$$a = G_{12}G_{21}c_1 + G_{22}G_{11}$$

$$b = (4 - 3G_{12})G_{21}c_1 + (G_{12} - 3G_{11})G_{22}c_2$$

$$c = (3G_{12} - 5)G_{21}c_1 + (3G_{11} - 2G_{12} + 2)G_{22}c_2$$

$$d = (1 - G_{12})G_{21}c_1 + (G_{12} - G_{11} - 1)G_{22}c_2 \quad (13)$$

With regard to  $x \geq 0$ , the solution of eq. (12) is as follows:

$$x = 0, \quad c_1 \leq c_{1c}$$

and for  $c_1 > c_{1c}$  we obtain  $x$  as the root of the equation

$$ax^3 + bx^2 + cx + d = 0 \quad (14)$$

$x$  changes continuously with respect to  $c_1$ , and therefore if we put  $c_1 = c_{1c}$  into eq. (14) then eq. (14) must have the solution  $x = 0$  from which follows that  $d = 0$ . According to formula (13) we have

$$c_{1c} = \frac{G_{22}(1 + G_{11} - G_{12})}{G_{22}(1 + G_{11} - G_{12}) + (1 - G_{12})G_{21}} \quad (15)$$

where  $c_{1c}$  is the percolation threshold for the first component. It is interesting to note that the percolation threshold depends only on the depolariza-

tion factors of the grains of the particulate composite.

Now it can be shown that for  $P_j^i = \frac{1}{3}$  for every  $j$  and  $i$ , the percolation threshold gains the maximum value equal to  $\frac{1}{3}$ . This maximum value can be obtained from the conditions

$$\frac{\partial c_{1c}}{\partial P_j^1} = \frac{\partial c_{1c}}{\partial P_j^2} = 0, \quad j = 1, 2$$

The depolarization factor  $P_j^3$  is not an independent parameter with regard to (2). In reality, as will be shown, the percolation threshold has the value bigger than  $\frac{1}{3}$ .

In our case the particles of individual components are isotropic granules of globular shape. In this case eq. (1) has the following form:

$$c_1 \frac{\lambda_1 - \lambda_{\text{eff}}}{\lambda_1 + 2\lambda_{\text{eff}}} + c_2 \frac{\lambda_2 - \lambda_{\text{eff}}}{\lambda_2 + 2\lambda_{\text{eff}}} = 0 \quad (16)$$

But our experimental results obtained from measuring the effective thermal conductivity in dependence on  $c_1$  cannot be fitted according to the solution of eq. (16). This was the reason that we modified eq. (16). The modification of eq. (16) was done to obtain for  $c_1 = 1$ ,  $\lambda_{\text{eff}} = \lambda_1$ , for  $c_1 = 0$ ,  $\lambda_{\text{eff}} = \lambda_2$ , and for  $\lambda_1 = \lambda_2 = \lambda$ ,  $\lambda_{\text{eff}} = \lambda$ . These conditions can be fulfilled if the  $\lambda_{\text{eff}}$  is determined by the following equation:

$$c_1 \frac{1 - x^t}{x^t + g(1 - x^t)} + c_2 \frac{r^t - x^t}{x^t + g(r^t - x^t)} = 0 \quad (17)$$

where the parameters  $t$  and  $g$  are the free parameters determined by fitting the experimental data to the solution of eq. (17). Equation (17) was also considered by McLachlan et al.<sup>4</sup> Equation (17) can be considered as the semiempirical equation. The solution of eq. (17) is as follows:

$$\lambda_{\text{eff}} = \lambda_1 (B + \sqrt{B^2 + D})^{1/t} \quad (18)$$

where

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

$$D = \frac{g}{1 - g} r^t$$

In the case of the percolation ( $r = 0$ ), the solution of eq. (17) is

$$x = 0, \quad \text{for } c_1 \leq g = c_{1c} \quad (19)$$

and

$$x = \frac{1}{(1 - g)^{1/t}} (c_1 - c_{1c})^{1/t}, \quad \text{for } c_1 > c_{1c} \quad (20)$$

From formulas (19) and (20) one sees that  $x$  plays a role of an order parameter; therefore, we can consider that for  $c_1 = c_{1c}$  the percolation phase transition takes place. In the critical region near  $c_{1c}$  the parameter  $1/t$  can be considered as the critical index. To this assertion we have to perform some notations. The parameter  $t$  probably depends on  $c_1$ ; therefore, the value of the parameter  $t$  obtained from the experiment is not the critical index because our experimental data are outside of the critical region. In formula (18) we consider parameter  $t$  as independent of  $c_1$ . Having known the dependence of the parameter  $t$  on  $c_1$ , the number of free parameters would increase, but we do not have many experimental data for their precise determination. Within the theory of percolation<sup>5</sup> the behavior of the order parameter is the same as given by formula (20). But the value of the percolation threshold  $c_{1c} = g$  obtained from fitting the experimental results to formula (18) is bigger than  $\frac{1}{3}$ , which is the maximum value according to the average field approximation as shown earlier. We suppose that the modified eq. (17) is more close to reality than eq. (1). The fitting of formula (18) to the experiment follows.

As we mentioned in the Introduction, the effective elastic shear modulus was also measured on the PE-CaCO<sub>3</sub>. The equation for the effective elastic shear modulus was derived by Barta.<sup>3</sup> This equation has the following form:

$$G_{\text{eff}}^2 + \frac{1}{2}G_{\text{eff}}(d_1G_1 + d_2G_2) - d_3G_1G_2 = 0 \quad (21)$$

where  $G_1$  and  $G_2$  are the elastic shear modulus of the first and second component, respectively, and

$$d_1 = (1 - c_1) \frac{\mu_1 + 1}{\mu_1 - 2} - 2c_1$$

$$d_2 = c_1 \frac{\mu_2 + 1}{\mu_2 - 2} - 2(1 - c_1)$$

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

$$\mu_i = 1/\nu_i$$

and  $\nu_i$  is the Poisson ratio of the  $i$ th component.

For the fitting the experimental data to the theory it was again necessary to modify eq. (21) into the following form:

$$y^2 + \frac{1}{2}y(d_1 + d_2r) - d_3r = 0 \quad (22)$$

where  $y = (G_{\text{eff}}/G_1)^t$  and  $r = (G_2/G_1)^t$ .

Equation (21) was modified with similar conditions to eq. (16). The solution of eq. (22) is expressed by

$$G_{\text{eff}} = G_1 \left[ \sqrt{\frac{1}{16}(d_1 + d_2r)^2 + d_3r} - \frac{1}{4}(d_1 + d_2r) \right]^{1/t} \quad (23)$$

In the case of percolation ( $r = 0$ ) we obtain

$$G_{\text{eff}} = 0, \quad \text{for } c_1 \leq c_{1c}$$

and

$$G_{\text{eff}} = \frac{1}{2}G_1 \left[ \frac{3(\mu_1 + 1)}{\mu_1 - 2} \right]^{1/t} (c_1 - c_{1c})^{1/t}, \quad \text{for } c_1 > c_{1c}$$

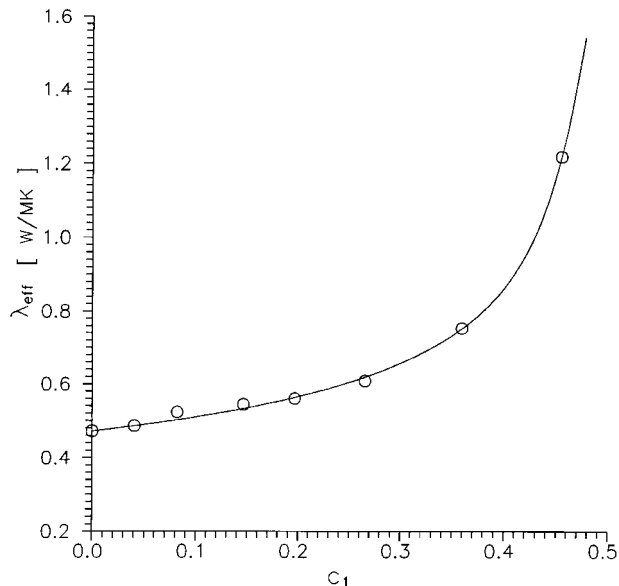
where

$$c_{1c} = \frac{1}{3} \frac{\mu_1 + 1}{\mu_1 - 1} \quad (24)$$

is the percolation threshold. We see that  $G_{\text{eff}}$  plays the role of the order parameter. In the following part the fitting of the experimental data to formula (23) will be shown.

## EXPERIMENTAL

For testing of formulas (18) and (23) we used the experimental data obtained from the measurement of effective thermal conductivity and elastic shear modulus of PE–CaCO<sub>3</sub> that were dependent on the volume fraction of CaCO<sub>3</sub>. The fitting of the experimental data to formulas (18) and (23) was made with the help of the Levenberg–Marquardt method.<sup>6</sup> In formula (18) there are three parameters  $r$ ,  $g$ , and  $t$ . Parameter  $r$  was determined from the measured data published in Eucken<sup>7</sup> and Eiermann.<sup>8</sup> The CaCO<sub>3</sub> was characterized by tensorial thermal conductivity. The diagonal form of the tensorial thermal conductivity has the following components  $\lambda_1 = \lambda_2 = 4.9298 \text{ W m}^{-1} \text{ K}^{-1}$ ,  $\lambda_3 = 4.2379 \text{ W m}^{-1} \text{ K}^{-1}$ . The grains of CaCO<sub>3</sub> are oriented randomly in the matrix;

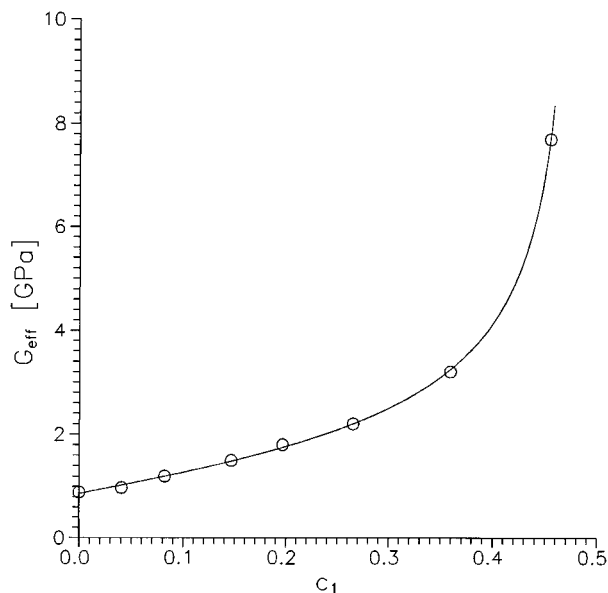


**Figure 1**  $\lambda_{\text{eff}}$  plotted as a function of the volume fraction  $c_1$ . (○) Experimental data; solid curve corresponds to the theory.

therefore, we considered the isotropic part, which is given by the relation  $\lambda_{\text{CaCO}_3} = \frac{1}{3} \sum_{i=1}^3 \lambda_i = 4.7 \text{ W m}^{-1} \text{ K}^{-1}$ . According to Eiermann,<sup>8</sup>  $\lambda_{\text{polyeth}} = 0.472 \pm 0.024 \text{ W m}^{-1} \text{ K}^{-1}$  at  $T_0 = 298.15 \text{ K}$ . The same value was also obtained from our measurement. Considering the values of thermal conductivities introduced above, we obtain  $r = \lambda_{\text{polyeth}}/\lambda_{\text{CaCO}_3} = 0.10$ .

Parameters  $g$  and  $t$  were determined from optimal fitting of the experimental data to formula (18). The fitting dependence of effective thermal conductivity of PE–CaCO<sub>3</sub> on the volume fraction of CaCO<sub>3</sub> is shown in Figure 1. The best fitting was achieved at  $c_{1c} = g = 0.473 \pm 0.017$  and  $t = 3.03 \pm 0.7$ . The relatively big dispersion of the parameter  $t$  is probably due to the small number of experimental data.

The comparison and fitting of the experimental data of the effective elastic shear modulus of particulate composite PE–CaCO<sub>3</sub> was done in the following way: we measured  $G_{\text{polyeth}} = (0.864 \pm 0.08) \text{ GPa}$ , but we did not have the value of the elastic shear modulus of CaCO<sub>3</sub> at our disposal. Therefore, we fixed the parameter  $r$  and considered the parameters  $\mu_1$ ,  $\mu_2$ , and  $t$  as the free parameters. From the best fitting of the experimental data with formula (23) we obtain  $r = G_{\text{CaCO}_3}/G_{\text{polyeth}} = 10^{-3}$ ,  $\mu_1 = 5.57 \pm 0.7$ ,  $\mu_2 = 2.2 \pm 0.2$ , and  $t = 2.04 \pm 0.7$ . Again the relatively big dispersion of quantities  $\mu_1$ ,  $\mu_2$ , and  $t$  is probably due to the small number of experimental data. From the ob-



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

tained value of  $\mu_1$  we can calculate according to formula (24) the percolation threshold  $c_{1c} = 0.494 \pm 0.011$ . We see that this value is in quite good agreement with the value obtained from the measurement of the effective thermal conductivity. The fitting dependence of the effective elastic shear modulus of the PE-CaCO<sub>3</sub> is shown in Figure 2.

In conclusion, some general discussion about the obtained results is given. Two models of derivation of the formulae for effective parameter of the particulate composite are considered. Which of these models is better can only be decided by the experiment. The experiment showed that the second modified model could better fit the experimental results in the case of the particulate composite PE-CaCO<sub>3</sub>. The models in the case of four particulate composite systems were tested. After careful analysis we decided to publish the obtained results step by step. The explanation of why the modified model is better in the case of the particulate composite PE-CaCO<sub>3</sub> is as follows. The grains of filling CaCO<sub>3</sub> were surface finished by stearic acid for improvement of the mechanical properties. The experiment showed that in the case of surface-finished grains of filling, the value of the effective parameter increased more rapidly than in the surface-unfinished grains of filling according to the volume fraction of filling. This is due to the improvement of the thermal contact between filling and matrix. If we numeri-

cally calculated the effective parameter at  $t = 1$  using the same values of parameters in the formula for an effective parameter, we obtained smaller values than those that were measured. Therefore, this is why parameter  $t$  has to be bigger than one.

With respect to the percolation threshold the following statement can be given. It is known from practice that the percolation threshold depends on the process of manufacturing. For a given process of manufacturing, the calculation of the percolation threshold on the submacroscopic level has been an unsolved problem until now. Due to the unknown dependence of the percolation threshold on the process of manufacturing, the value of the percolation threshold has to be determined by the experiment.

The known values of the percolation threshold calculated by computer simulation are known only for certain lattice models. It is interesting to note that for a bigger value of the filling factor of the lattice model, the value of the percolation threshold is smaller. The diamond lattice is relatively empty; the maximum proportion of the available volume that may be filled by hard spheres is only 0.34, which is 46% of the filling factor of the close-packed structure such as fcc or hcp. For example, the calculated value of the percolation threshold of the diamond lattice is  $0.436 \pm 0.012$ ,<sup>9,10</sup> which is closest to the measured one, but the value of the percolation threshold of the fcc lattice is only  $0.200 \pm 0.002$ .<sup>11</sup> In the case of PE-CaCO<sub>3</sub> the grains of filling, unlike the lattice models, are randomly distributed in the matrix. This was the further reason for choosing the percolation threshold as the free parameter. From the above-mentioned facts it follows that in the proposed modified model the parameters  $t$  and  $g$  have to be considered as free parameters.

## CONCLUSION

The percolation threshold was derived in the framework of the average field approximation, and it was shown that the maximum value of the percolation threshold is  $\frac{1}{3}$  in the case of the isotropic granules of globular shape. The modified formulae for effective thermal conductivity and elastic shear modulus were proposed. These formulae were used for fitting the experimental data at the optimum choice of values of the free parameters. The experiments showed that the modified formula fits the experimental data better than the

formula obtained from the average field approximation.

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