

## Research Article

# PP/MMT Nanocomposite: Mathematic Modelling of Layered Nanofiller

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The comparison of calculated data from proposed mathematic model and experimentally obtained data of PP/clay nanocomposites was done with the focus on the layered shape of MMT platelets. Based on the well-known Kerner's model and the Halpin-Tsai' equation with the use of some described presumption, the mathematic model for PP/clay nanocomposite was proposed. Data from the measurement of prepared PP/clay samples were taken and compared with the calculated ones from the proposed model. The good agreement was found.

## 1. Introduction

Firstly, the mathematical description of mechanical and physical properties of composites based on a polymer matrix has been studied in 1950s [1, 2]. These and also the next studies are deduced only theoretically [3–7].

These models mainly describe the dependence of shear modulus of elasticity on the content of the filler and spherical or fibre type of filler is considered. They are named self-consistent, it means that homogenous spherical particles are placed in the homogenous continuous polymer matrix. With the increasing use of composites as construction materials in the industry models with cylindrical dispersed phase has been proposed. This was used in order to simulate short or long fibres.

The classical Kerner's model is usually presented as:

$$K = \frac{(K_f \phi / (3K_f + 4G_m)) + (K_m (1 - \phi) / (3K_m + 4G_m))}{(\phi / (3K_f + 4G_m)) + (1 - \phi) / (3K_m + 4G_m)}, \quad (1)$$

$G =$

$$\frac{\phi G_f / ((7 - 5\nu_m)G_m + (8 - 10\nu_m)G_f) + ((1 - \phi) / 15(1 - \nu_m))}{(\phi G_m / (7 - 5\nu_m)G_m + (8 - 10\nu_m)G_f) + ((1 - \phi) / 15(1 - \nu_m))}, \quad (2)$$

where  $K$  is a bulk modulus,  $G$  is shear modulus,  $\phi$  is volume fraction,  $\nu$  is Poisson ratio index  $m$  belongs to matrix, and index  $f$  belongs to filler (fibre).

The equation of Halpin-Tsai is very often cited and properly it is the conversion of Hill's equation [5, 6] for long and short fibres:

$$\frac{P}{P_m} = \frac{1 + \zeta \eta \nu_m}{1 - \eta \nu_m} \quad \text{with} \quad \eta = \frac{(P_f / P_m) - 1}{(P_f / P_m) + 1}, \quad (3)$$

where  $\nu_f = V_f / V$  (ratio of the volume of filler (fibre) to the whole volume),  $\zeta$  is a parameter that depends on the matrix Poisson ratio and on the particular elastic property,  $P$  represents the composite moduli, and, again, indexes  $m$  and  $f$  belong to matrix and fibre fraction.

In the literature one can find a lot of attempts of simplification and specification in earlier models [8–10]. The

problem of these models is the fact that they are based on the simplified assumptions that do not correspond with the real states. For example, the rigidity of prepared composites does not only depend on the volume of filler and the geometry of a stress, but also on the particle size, its shape, and the tendency to agglomerate [11–13]. Moreover, in case of aspherical particles it depends also on the particle orientation, especially in the case of layered clay nanoparticles where they are supposed to have the shape of platelets with significant aspect ratio.

Nanocomposite materials based on the polymer matrix have been studied more than twenty years. The main reason is the unusual combination of properties. They are unique in comparison with conventional composites because of their large interphase surface (connecting with aspect ratio) and very small distances between reinforcing particles [13]. In this way a very rigid net is created.

The behaviour of polymer chains in the neighbourhood of nanoparticles and the influence of the nanoparticles shape on the nanocomposite properties have been studied in the several next papers [14–16].

## 2. Theoretical

The proper model derivation (modelling).

At the majority of above-mentioned model is based on the mixing principle when the slope of the curve increases with the increasing filler content. Slope of curve represents the elasticity modulus—and it is the function of the filler content. This is valid till the composite modulus reaches for  $V_C = 1$  of the value of the filler elasticity ( $V_C$  is a volume percent of filler particles, see later). This behaviour is valid only in case of the composite filled with the long fibres oriented in the longitudinal direction. In all other cases at the condition  $V_C = 1$ , (no matrix) the composite is fully non-cohesive small pile of a filler with zero tensile modulus.

More complicated models have a disadvantage—the dependence on stress or deformational fields. In the case of our studied system PP/MMT the tensile modulus initially grows very quickly, but with the increasing filler content the slope of curve falls down. Figure 1 shows the comparison of experimental data with the Kerner's equation. Values used for this calculation form (2) were chosen only approximately based on the authors ( $V_C$  0,004, 0,008, 0,016, 0,04) in order to show how this model is far from the real data (taken from Table 3) in case of layered mineral filler in polymer matrix.

Based on these observations mentioned above we tried to deduce such an equation which at the use of the easiest mathematical apparatus would correspond with obtained experimental data and would be suitable for prognosis of future research in the use of layered nanoclays. The interval of filling was chosen between 0–10 wt. %.

The outgoing assumptions are as follows:

- (1) the filler has an unlimited modulus → it has zero deformability;
- (2) the primary deformation is observed in case of torque and strain modulus, after the created stress is measured;

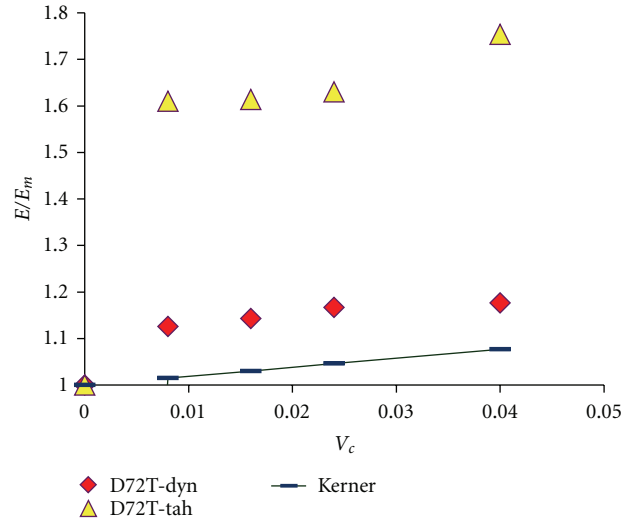


FIGURE 1: The dependence of reduced elasticity modulus on the filler content.

- (3) particles are fixed in matrix with the perfect adhesion (index  $p$ ), either free in the vacancy with the zero adhesion (index  $v$ ), nothing else, thus their volume percent  $V_C = V_{Cp} + V_{Cv}$ .

When the particles are freely inserted into the vacancies in the matrix, without any adhesion, the system behaves like an expanded material. With the growing number of ratio of  $V_{Cv}$  particles the stress at the constant deformation decreases according to the equation:

$$\sigma_K = \sigma_M * V_M, \quad \text{then } \sigma_K = \sigma_M * (1 - V_{Cv}). \quad (4)$$

On the other hand, at the deformation of the system with the rigidly fixed components the deformation  $V_M$  is higher by a part of undeformed particles and by this also the stress is higher:

$$\sigma_K = \frac{\sigma_M}{V_M}, \quad \text{then } \sigma_K = \frac{\sigma_M}{(1 - V_{Cp})}. \quad (5)$$

However, in this case of rigid fixation of both components the polymer matrix is not deformed equally. The deformation of the polymer layer at the rigid particle is almost zero. With the increasing distance from this particle the deformation increases and with the approximation to the next particle it goes to the zero again. By this the deformation gradient is created. It is similar to the speed gradient at the liquid flow along fixed plates (see Figure 2).

A complete spectrum of deformation matrix from zero at the filler particle to the maximum somewhere along particles is simplified into two values. After the layer at the thickness  $h$  in the nearest neighbourhood has the zero deformation and the more remote particles have the mentioned maximal value of deformation. However, the total average value of deformation must stay the same even after applying these assumptions.

The consequence of this thought is the increasing of the origin undeformable volume  $V_c$  by the undeformable layer

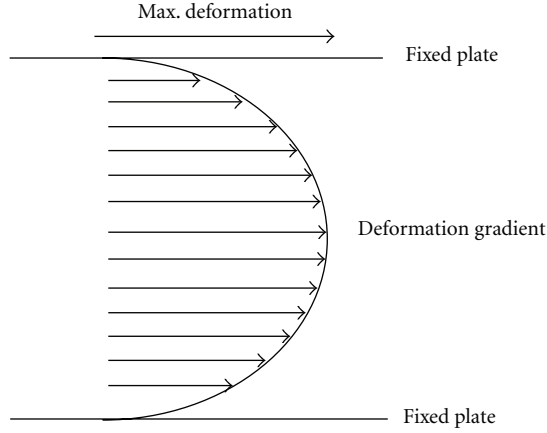


FIGURE 2: The simple scheme of the deformation gradient at the liquid flow along fixed plates.

of the matrix. This means, for example, in case of cubic filler particles with the edge  $a$  the increasing by  $6ha^2$  at one particle with the volume  $a^3$ . For the total volume of particles it is the value of  $6ha^2V_C/a^3$ , that is,  $6hV_C/a$ . By this train of thought (5) changes into:

$$\sigma_K = \frac{\sigma_M}{(1 - V_{Cp}(1 + (6h/a)))}. \quad (6)$$

The used constant “6” is valid only for the particles of cubic shape. It will be different for different shape of the filler particles. Moreover, this constant depends on the shape of the deformation field (strength, shear), when the rigid shell (standing only temporary during the composite deformation) is not spread evenly on the whole particle surface, thus, after simplifying,  $6h = h_0$ .

The next consequence based on the thought discussed above, is that the created stress and by this the rigidity of the composite depends on the size of filler particles.

At the observations it was found that the size of filler particles  $a$  depends on  $V_C$ . The content of aggregates increases with the growing of  $V_C$ . The reason is either imperfect mixing or after aggregation. Thus,

$$a = a_0(1 + kV_C), \quad (7)$$

where  $a_0$  is the size of particle for  $V_C$  convergent to zero

The constant  $k$  will be discussed later.

After the summarization of the above-mentioned thoughts (6) changes into

$$\sigma_K = \frac{\sigma_M}{(1 - V_{Cp}(1 + (h_a/(1 + kV_C))))}, \quad (8)$$

where  $h_a = h_0/a_0$ .

With the growing content of filler at the same initial deformation the stress inside composite is created and increases according to (6). This causes that proportionally to this stress the part of filler particles is breaking loose (is delaminated) from the surface of the polymer matrix. Consequently, its influence on the stress inside the composite

changes from the state (5) to the state (4). Thus, the  $V_{Cv}$  is proportional to the filler content  $V_C$  and to the existing stress in the matrix. This stress we will mark as  $\sigma_0$ . After

$$V_{Cv} = V_C * \frac{\sigma_0}{\sigma_d}, \quad (9)$$

where  $\sigma_d$  is a critical stress, at which all the filler is delaminated, thus  $V_{Cv} = V_C$ .

Now we have all mathematical apparatus needed for the calculation of the module of elasticity:

- (1) firstly, we calculate the initial stress  $\sigma_0$  caused applied deformation at zero delamination (according to (8)):

$$\sigma_0 = \frac{\sigma_M}{1 - V_C(1 + (h_a/(1 + kV_C)))}, \quad (10)$$

- (2) from the previous equation we can get the ratio of non delaminated particles is (according to (9)):

$$V_{Cv} = V_C * \frac{\sigma_0}{\sigma_d}, \quad (11)$$

- (3) next we calculate the stress equal to free particles (according to (4)):

$$\sigma_V = \sigma_M * (1 - V_{Cv}), \quad (12)$$

- (4) after we calculate the rest of fixed particles:

$$V_{Cp} = V_C - V_{Cv}, \quad (13)$$

- (5) next the stress equal to bonded particles (according to (8)):

$$\sigma_P = \frac{\sigma_M}{1 - V_{Cp}(1 + (h_a/(1 + kV_C)))}, \quad (14)$$

- (6) and the resulting stress:

$$\sigma_K = \sigma_P + \sigma_V - \sigma_M, \quad (15)$$

- (7) if the deformation at measurement is unit and it is small enough (in order to be responding to Hook's principle), after

$$\sigma_M = E_M \quad \text{and} \quad E_K = \sigma_K. \quad (16)$$

This system of equations contains only three unknown parameters of physical merit which it is necessary to estimate for the next calculation:

$\sigma_d$ —critical stress (it has connection to an adhesion degree of filler particles to the matrix);

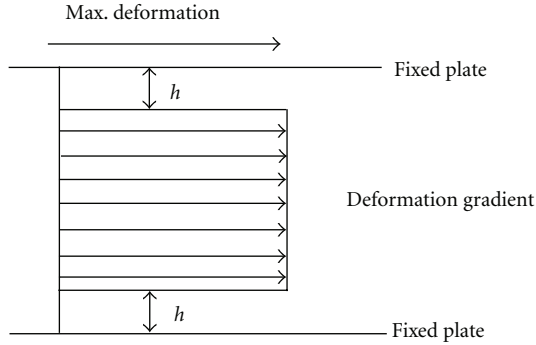


FIGURE 3: The simple scheme of the deformation gradient at the liquid flow along fixed plates—with the filler in polymer melt.

$h_a$ —proportional thickness of undeformable layer of matrix in the neighbourhood of filler particle, it is also connected with the geometry of deformational field;

$k$ —the velocity of the growing of the particle aggregation degree with regard to  $V_C$ , it decreases with the rising quality of dispersion.

In order to obtain the real result of this calculation, the particular parameters must be chosen in the values fulfilling following conditions:

$$\sigma_d > \sigma_0; \quad V_{Cv} + V_{Cp} = V_C; \quad \frac{ha}{1 + kV_C} < \frac{1}{V_C - 1}. \quad (17)$$

From the influence of the mentioned three parameters it is possible to see from the following three-dimensional graphs (Figures 3, 4, and 5) the following.

The low value of the adhesion  $\sigma_d$  between the filler and the matrix (resp. high value of  $\sigma_0$ ) causes more significant validity of (4) at the cost of (5) and the rigidity of the sample after the initial increase starts to decrease. This is visible also in the next pictures.

In case of the microscopy observations of nanocomposite samples it was found that with the growing content of nanofiller the number of agglomerates increases; thus, the average size of particles increases too. The velocity of this increase is included in the constant  $k$  (see above). The ideal requirement is to reach such a dispersion of filler nanoparticle platelets in the polymer matrix that the size of particles should not grow with the  $V_C$ , the rising of the rigidity should be maximal, thus,  $k = 0$ , respectively,  $k \gg 0$  (Figure 6).

Parameter  $h_a$  (Figure 5) represents the static part of the matrix in the neighbourhood of the undeformable particle relating to the size of the primary filler particle. After, the rest of the polymer matrix transfers higher stress and consequently the rigidity of the composite goes up. The value of this stress depends on the shape, orientation, and size of the surface of the particles dispersed during the mixing in the kneader.

Time and conditions of the kneading, the technology of the nanocomposite preparation are projected in the parameters  $k$  and  $h_a$  (dispersion of agglomerates, the breaking of lamellar particles bringing the change of the size and shape).

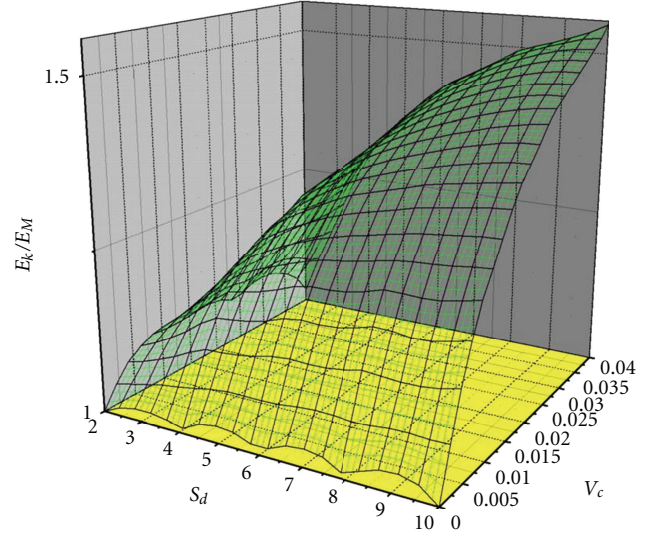


FIGURE 4: Reduced modulus of elasticity as a function of parameters  $k$  and  $V_C$ .

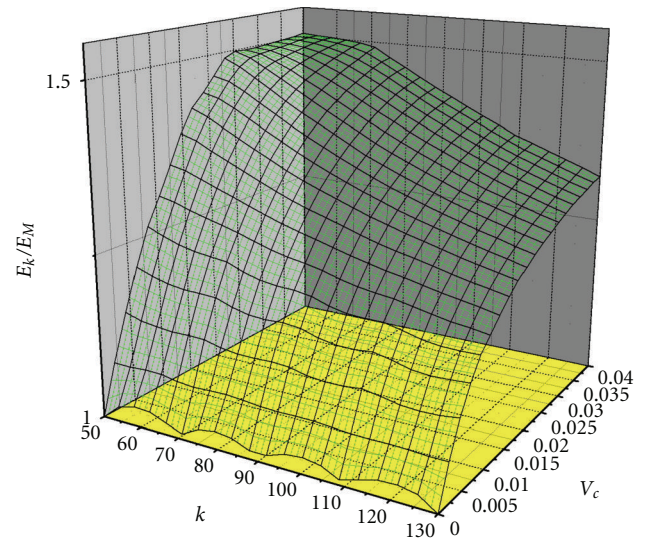


FIGURE 5: Reduced modulus of elasticity as a function of parameters  $S_d$  and  $V_C$ .

$h_a$  depends also on the method used for the measurement of the modulus of elasticity. Parameter  $\sigma_d$  is connected with material.

It is necessary to underline that the presented model (like all models) is valid for the limited interval of layered nanocomposite filling only.

### 3. Experimental

In order to verify the validity of the proposed model for the layered type of nanofiller nanocomposite samples of PP/modified MMT were prepared.

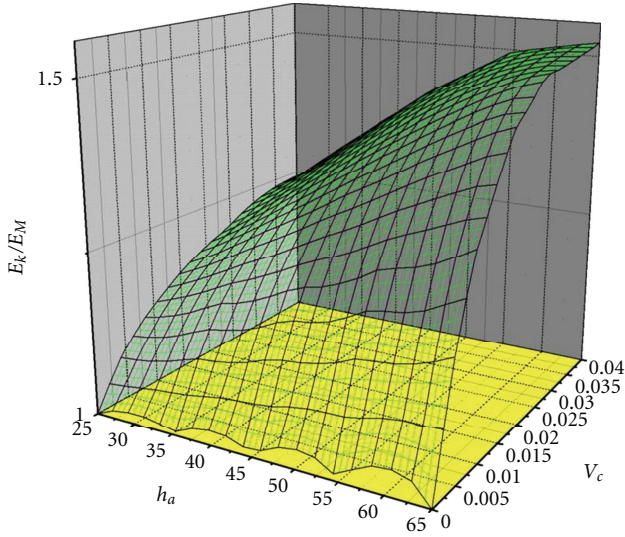


FIGURE 6: Reduced modulus of elasticity as a function of parameters  $h_a$  and  $V_c$ .

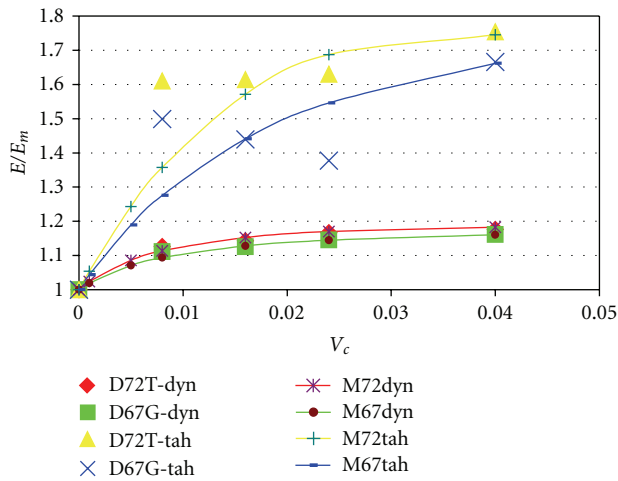


FIGURE 7: Reduced elasticity modulus as a function of nanofiller content of prepared samples.

**3.1. Materials.** Polypropylene (PP) Mosten GB 003 produced by Chemopetrol Litvínov, Czech Republic, was used as a polymer matrix. The density of chosen PP was  $907 \text{ kg/m}^3$  and melt flow index (MFI) was  $3.2 \text{ g/10 min}$  at  $230^\circ\text{C}$ .

The density of maleated polypropylene (PP-Ma) EXXELOR PO 1015 was  $900 \text{ kg/m}^3$ , MFI was 22, and contents of maleic groups were 1 wt. % (used as a compatibilizer). Maleated polypropylene was supplied by ExxonMobil Chemical Europe, Belgium. Two types of nanofiller Dellite were used (Dellite 72T and Dellite 67G); their concentration was 2, 4, 6, and 10 wt. %. The nanofiller were supplied by Laviosa Chemical Mineraria S.p.A., Italy.

**3.2. Preparation of the Polymer-Clay Nanocomposites.** All nanocomposites in this work were prepared by melt blending on a Brabender Plasticorder compounder at 40, 60, and

TABLE 1: Dynamic modulus as a function of speed of rotation of kneader and volume ratio of nanofiller D72T.

D 72T rpm. $\forall V_c$	Dyn. modulus				
	0	0,008	0,016	0,024	0,040
400	1626	1827	1796	1864	1843
600	1626	1864	1905	1911	1912
800	1626	1816	1843	1846	1905
1200	1626	1852	1827	1910	1912
1600	1626	1733	1844	1878	1950
1800	1626	1882	1854	1912	1915
2000	1626	1806	1806	1870	1874
2400	1626	1831	1884	1896	1958
2800	1626	1851	1860	1907	1901
3000	1626	1766	1824	1893	1880
3400	1626	1931	1971	2006	1991
4200	1626	1811	1885	1869	1911
Average	1626	1831	1858	1897	1913

TABLE 2: Summary of results of dynamic modulus and strength modulus for both nanofiller types (data calculated by the same way as in the case of Table 1).

rpm/V	Dynamic modulus		Shear modulus	
	D 72T	D 67G	D 72T	D 67G
0	1626	1626	733	733
0,008	1831	1807	1180	1099
0,016	1858	1830	1183	1055
0,024	1897	1862	1195	1009
0,040	1913	1888	1286	1221

80 rpm and  $220^\circ\text{C}$  for 10, 20, 30, and 40 min. The samples were prepared by pressuring at  $220^\circ\text{C}$  at 9 min and cooling was 7 min.

**3.3. DMA Analysis.** The measurement of E modulus was done by DMA analysis on the equipment DMA DX04T (company RMI) on FT TBU in Zlin. Values presented in this work are values at  $30^\circ\text{C}$ .

## 4. Results and Discussion

Resulting data of measurement of dynamic and strength modulus of elasticity for both used nanofiller types are listed in the Tables 1 and 2.

Table 3 summarizes data from Tables 1–4 averaged through the speed of rotation, estimated values of parameter, and with them corresponding calculated values of elasticity modulus. In order to give the better approach the results are listed in Figure 6.

Based on Figure 6 it is possible to say that the calculated data from the proposed model correspond very well with the experimental values. It is valid especially in case of the dynamic modulus data. This is supported by the 2D graph shown in Figure 7 where the comparison of measured (D

TABLE 3: The summary of results from Tables 1 and 2.

$V_c$	D72T-d	D67G-d	D67G-s		M67dy			Kerner	
	yn	yn	D72T-str	tr	M72dyn	$n$	M72str	M67str	$r$
0	1	1	1	1	1	1	1	1	1
0,001					1,024	1,019	1,054	1,043	0,002
0,005					1,086	1,071	1,243	1,189	0,009
0,008	1,126	1,111	1,610	1,499	1,114	1,094	1,358	1,276	1,015
0,016	1,143	1,125	1,614	1,440	1,152	1,128	1,572	1,441	1,03
0,024	1,167	1,145	1,630	1,377	1,170	1,145	1,687	1,546	1,046
0,040	1,176	1,161	1,754	1,666	1,182	1,160	1,745	1,662	1,077
$h_a$					38,1	31,1	62,3	50	
$K$					104	104	75	75	
$S_d$					3,02	3,02	8,5	8,5	

in the name) and calculated (M in the name) values for dynamic modulus is presented (data are summarised in Table 3). Modelled data were calculated with the calculated values of parameters  $h_0$ ,  $k$ , and  $\sigma_d$ . It is possible to see that real data correspond very well with the calculated ones how it was already said. In case of dynamic modulus the data meet the calculated curve almost in 100%.

The growing of the particle agglomeration with their rising content makes it possible to observe qualitatively in TEM pictures. The lowering of the parameter  $k$  is crucial for the next improvement of the reinforcing effect of nanofiller.

## 5. Conclusion

Models and mathematical descriptions of the various composite behaviours have been created for more than 50 years. Nanofillers especially due to their relatively short time of application and the specific shape and size, unique interface surface, small distance of particles, and the tendency to the agglomeration do not fit to these models.

In this work the authors tried to create a relatively simple model which with the variation of three parameters allows very nice well description of the dependency of the elasticity modulus on the filler content for the layered nanofiller type with the platelet shape of particles. This model is valid in the interval of the clay nanofiller content at least to the 10 wt. %.

Model brings the better look at the material containing particles and technological parameters influenced by the rigidity of prepared composites and the more optimal planning of the next experimental work in this field.

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## References

- [1] E. H. Kerner, "The elastic and thermo-elastic properties of composite media radiator," *Proceedings of the Physical Society B*, vol. 69, pp. 808–813, 1956.
- [2] J. D. Eshelby, "The determination of the elastic field of an ellipsoidal inclusion, and related problems," *Proceedings of the Royal Society of London A*, vol. 241, pp. 376–396, 1957.
- [3] Z. Hashin, "The elastic moduli of heterogeneous materials," *Transactions of the ASME, Journal of Applied Mechanics*, vol. 29, pp. 143–150, 1962.
- [4] Z. Hashin and S. Shtrikman, "A variational approach to the theory of the elastic behaviour of multiphase materials," *Journal of the Mechanics and Physics of Solids*, vol. 11, no. 2, pp. 127–140, 1963.
- [5] R. Hill, "Elastic properties of reinforced solids: some theoretical principles," *Journal of the Mechanics and Physics of Solids*, vol. 11, no. 5, pp. 357–372, 1963.
- [6] R. Hill, "A self-consistent mechanics of composite materials," *Journal of the Mechanics and Physics of Solids*, vol. 13, no. 4, pp. 213–222, 1965.
- [7] B. Budiansky, "On the elastic moduli of some heterogeneous materials," *Journal of the Mechanics and Physics of Solids*, vol. 13, no. 4, pp. 223–227, 1965.
- [8] L. E. Nielsen, "Generalized equation for the elastic moduli of composite materials," *Journal of Applied Physics*, vol. 41, no. 11, pp. 4626–4627, 1970.
- [9] T. B. Lewis and L. E. Nielsen, "Dynamic mechanical properties of particulate-filled composites," *Journal of Applied Polymer Science*, vol. 14, no. 6, pp. 1449–1471, 1970.
- [10] R. M. Christensen, "Solutions for effective shear properties in three phase sphere and cylinder models," *Journal of the Mechanics and Physics of Solids*, vol. 27, no. 4, pp. 315–330, 1979.
- [11] J. Jancar, J. Kucera, and P. Vesely, "Peculiarities of mechanical response of heavily filled polypropylene composites—part I

- elastic modulus," *Journal of Materials Science*, vol. 26, no. 18, pp. 4878–4882, 1991.
- [12] A. Agbossou, A. Bergeret, K. Benzarti, and N. Alberola, "Modelling of the viscoelastic behaviour of amorphous thermo-plastic/glass beads composites based on the evaluation of the complex poisson's ratio of the polymer matrix," *Journal of Materials Science*, vol. 28, no. 7, pp. 1963–1972, 1993.
- [13] Y. Bréchet, J. Y. Cavaille, E. Chabert et al., "Polymer based nanocomposites: effect of filler-filler and filler-matrix interactions," *Advanced Engineering Materials*, vol. 3, no. 8, pp. 571–577, 2001.
- [14] J. Kalfus and J. Jancar, "Relaxation processes in pvac-ha nanocomposites," *Journal of Polymer Science B*, vol. 45, no. 11, pp. 1380–1388, 2007.
- [15] J. Kalfus and J. Jancar, "Elastic response of nanocomposite poly(vinylacetate)-hydroxyapatite with varying particle shape," *Polymer Composites*, vol. 28, no. 3, pp. 365–371, 2007.
- [16] J. Kalfus and J. Jancar, "Viscoelastic response of nanocomposite poly(vinyl acetate)-hydroxyapatite with varying particle shape—dynamic strain softening and modulus recovery," *Polymer Composites*, vol. 28, no. 6, pp. 743–747, 2007.