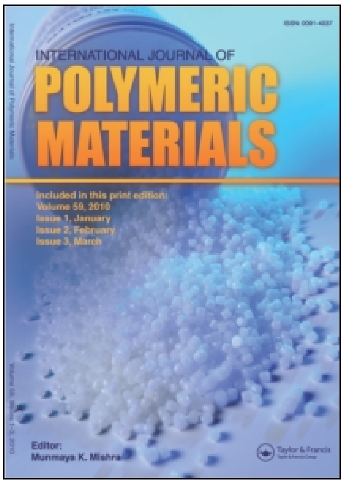

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Modelling of Mechanical Properties of Nanoparticle Filled Polyethylene

B. Lehmann[a]; A. K. Schlarb[a]; K. Friedrich[a]; M. Q. Zhang[b]; M. Z. Rong[b]
[a] Institute for Composite Materials (IVW GmbH), Technical University, Kaiserslautern, Kaiserslautern, Germany [b] Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, Zhongshan University, Guangzhou, P.R. China

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Modelling of Mechanical Properties of Nanoparticle Filled Polyethylene

B. Lehmann
A. K. Schlarb
Institute for Composite Materials (IVW GmbH), Technical University Kaiserslautern, Kaiserslautern, Germany

K. Friedrich
Institute for Composite Materials (IVW GmbH), Technical University Kaiserslautern, Kaiserslautern, Germany; Present address: AMME, University of Sydney, Sydney, NSW, Australia

M. Q. Zhang
M. Z. Rong
Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, Zhongshan University, Guangzhou, P.R. China

A continuum-mechanics approach has been applied to model the mechanical properties of high density polyethylene (HDPE) filled with differently coated SiO_2 *nanoparticles. The tensile yield stress has been predicted with a finite-element model (FE-model) taking into account the microstructural features, for example, matrix, filler content, and the interphase formed around the filler. A good agreement between the experimental and modelled data has been found. Additionally, the FE-model has been compared with a semi-empirical model and an analytical model with similar input parameters to predict the composite property. It was found that all models are congruent with respect to solution space.*

Keywords: FE-modelling, interphase, mechanical properties, nanocomposite

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Address correspondence to Dipl.-Ing. Bjoern Lehmann, Institute for Composite Materials (IVW GmbH), Technical University Kaiserslautern, 67663 Kaiserslautern, Germany. E-mail: bjoern.lehmann@ivw.uni-kl.de

INTRODUCTION

Different approaches toward modelling the mechanical properties of particulate filled polymers have been pursued in the past. In these empirical, analytical, or discrete models, a large number of parameters have been related to thermomechanical properties of the composite material: the individual properties of filler and matrix, such as the particle size and size distribution, the filler volume fraction, the interphase between filler and matrix, the adhesion between filler, interphase, and matrix, the influence of neighboring particles (e.g., overlapping stress fields), the mode of filler-packing, and so on. Nowadays, most models focus on the filler (size, content, distribution) and the interphase to derive the composite properties, as will be shown later [1–7].

The objective of this work was to predict the yield stress of particle reinforced polymers by using a finite-element model (FE-model). This model takes the mechanical properties of the particle, the interphase, and the matrix into account to derive the yield strength of the composite.

A validation of the FE-model was executed by prediction of the yield strength of high density polyethylene (HDPE) filled with nanoparticles. On the one hand, untreated nano-SiO_2 has been used as reference filler, and on the other hand, the same nano-SiO_2 with a coating of grafted polystyrene (PS), polymethylmethacrylate (PMMA), and polyethylacrylate (PEA) has been prepared. It is expected that for both coated and uncoated nanoparticles, an interphase will form around the particles. Due to the different polymers on the filler surface, it is likely that the interphase has different properties compared to the matrix material.

COMPARABLE MODELLING APPROACHES

The resulting solution space of the FE-model will be contrasted to other models with a similar input parameter set. These models are the semi-empirical model from Pukanszky et al. [1–2,5–6] and the analytical, extended van der Poel model by Maurer [7]. The approaches of these models will be reviewed to allow a better insight of the model capabilities and their differences with respect to the discrete solution by FE-modelling.

Empirical Approach

Already in the first empirical models, a distinction was made between good and no particle adhesion [8–9]. In case of no adhesion, it was assumed that the filler does not contribute to the strength of the composite, that is, no forces are transmitted.

Therefore, the yield strength of the composite σ_{yc} has been described with the reduced load-bearing cross-section (1-ψ), according to the following equation:

$$\sigma_{yc} = \sigma_{y0}(1 - \psi), \tag{1}$$

with σ_{y0} being the yield strength of the matrix.

Assuming that ψ is a power law function of the filler volume content φ, then Eq. 1 yields:

$$\sigma_{yc} = \sigma_{y0}(1 - a\varphi^{b}). \tag{2}$$

The constants a and b have to be chosen, according to particle geometry and filler distribution. For spherical fillers without adhesion and failure by random fracture, Eq. 2 can be written in the following way [9]:

$$\sigma_{yc} = \sigma_{y0}(1 - 1.21 \cdot \varphi^{2/3}). \tag{3}$$

From Eq. 3, it is obvious that the load-bearing cross-section becomes zero below a filler content of unity. Obviously, the dilemma stems from the difference in reduced cross-section (1–ψ) and the filler packing phenomena. The group around Pukanszky et. al. handled this issue by expressing the reduced cross-section (1–ψ) with a simple hyberbolic formula [1]:

$$1 - \psi = \frac{1 - \varphi}{1 + A\varphi}, \tag{4}$$

with A being a constant, describing the filler packing characteristics and the filler geometry. If $A = 2.5$, then Eq. 1 becomes with Eq. 4:

$$\sigma_{yc} = \frac{1 - \varphi}{1 + 2.5 \cdot \varphi}\sigma_{y0}. \tag{5}$$

Numerous results have shown that σ_{yc} increases with increasing filler content φ, if a reasonable adhesion between filler and matrix exists. These models with no adhesion have been elaborated for the case of good adhesion.

From the few existing models [1,10–11] that consider a good adhesion, the model from the group around Pukanszky seems to be most widely accepted [1–6]. Therefore, the following explanation focuses on just this model.

The behavior of the composite yield stress can be described by modifying Eq. 5. On the one hand, the model consists of a term describing the reduction in load-bearing section and on the other hand of an empirical, exponential term, taking into account the changes due to the filler (adhesion, interphase, etc.):

$$\sigma_{yc} = \sigma_{y0} \frac{1-\varphi}{1+2.5\cdot\varphi} \exp(B\cdot\varphi), \tag{6}$$

with σ_{y0} being the yield strength of the matrix, φ the filler content, and B a semi-empirical interaction parameter. Parameter B considers the boundary interactions at the filler surface, the specific filler surface, and the mechanical properties of the interphase:

$$B = (1 + l\cdot A_f\cdot\rho_f)\ln\frac{\sigma_{yi}}{\sigma_{y0}} \tag{7}$$

The parameter l in Eq. 7 is the interphase thickness, and ρ_f and A_f are the density and the specific surface of the filler, respectively. The yield strength of the interphase is covered by parameter σ_{yi}.

The yield stress σ_{yi} of the interphase cannot be determined in all cases unambiguously, at least from the experimental point of view. The evaluation of the interphase yield strength is quite verified if it is below the matrix yield strength. Then, the interphase yield strength corresponds to the debonding stress of the filler. In case the interphase is stronger than the matrix a distinction remains difficult.

Approaches to quantify the debonding stress σ_D have taken place quite early [12]. The adhesion between matrix and filler and the filler size have been found to be relevant parameters determining the debonding stress σ_D of the particle:

$$\sigma_{yi} \approx \sigma_D = \frac{\sigma_T}{\alpha} + \frac{C}{\alpha}\left(\frac{E_M\cdot W_{mf}}{r}\right)^{(1/2)} \tag{8}$$

In this formula the symbols are defined as follows:

σ_T	Thermal pre-stress of the filler due to differences in thermal coefficient of expansion
α	Stress concentration factor
E_M	Elastic modulus of the matrix
W_{mf}	Adhesion energy between filler and matrix
C	Constant, depends on matrix-filler system
r	Radius of the filler particle

Because the debonding stress also depends on the filler size by a factor of $r^{(-1/2)}$, a reduction in filler size is quite beneficial. Then, for nanofillers, the yield strength of the matrix is quite often lower than the debonding stress of the particle.

Analytical Approach

The composite properties can also be derived by analytical means. One established method is the solution of the extended van der Poel model [7,13]. Although this model has been developed for the composite modulus only, the results can be transferred to the yield strength as well by comparing the resulting stresses at a fixed strain. Then, the results of the standardized modulus are the same as for the standardized yield strength, valid for a linear elastic deformation only.

In contrast to other models, for example, the one from Kerner [14] and from Takano and Sakanishi [15–16], this extended van der Poel model was able to predict the properties also very well for low filler and interphase contents. This makes the application of the van der Poel model indispensible here, leaving alone the analytical solution.

The extended van der Poel model consists of a cube, representing the matrix. Inside, the cube contains a spherical filler enclosed by an interphase. Schematically, the model is shown in Figure 1.

Due to the imposed loads, the cube is in a rotationally symmetric stress state. The stress state can be expressed with the following equations:

$$\sigma_x = \sigma_y = -\sigma \tag{9}$$

$$\sigma_x = 2 \cdot \sigma \tag{10}$$

$$\sigma_{xy} = \sigma_{yz} = \sigma_{zx} = 0 \tag{11}$$

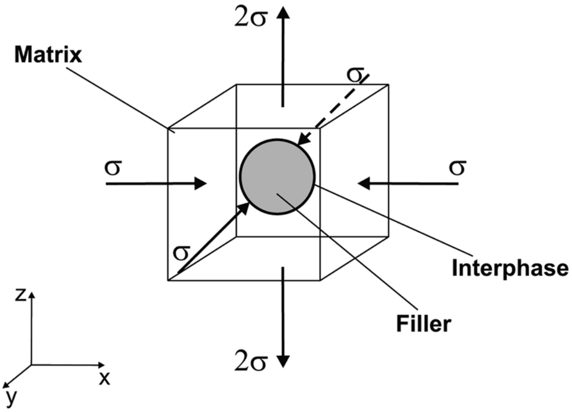

FIGURE 1 The stress state of the extended van der Poel model.

The stress state distinguishes itself due to the fact that the sum of the normal stresses equals zero, and therefore dilatational stresses are non-existent.

The premises are:

- The composite, the filler, the interphase, and the matrix all show linear elastic behavior.
- There are no *vis inertiae*.
- The composite, the filler, the interphase, and the matrix exhibit homogeneous and isotropic behavior.
- The composite contains no defects, like cavities, cracks, or crazes and displays no planar sliding, even under deformation.
- The composite is stress-free, if no outer forces are present. This means that thermal stresses are not present or can be neglected.

Under these premises, a complex system of equations can be derived. The solutions are too extensive to be quoted here, and the reader is referred to the source [7].

EXPERIMENTAL

The matrix material HDPE, Type 5000S was supplied by the Qilu Petrochemical Industrial Corp., China. The precipitated nano-SiO_2 was produced by Zhoushan Putuo Shengxing Nanomaterials Co. Ltd., China (particle size: 10 nm, specific surface area: 640 m^2/g). The surface treatment of the filler has been described in an earlier publication in detail [17].

The tensile experiments of the HDPE nanocomposites were carried out on a universal testing machine Zwick 1474 with a crosshead speed of 50 mm/min. The shape of the specimen has been in accordance with DIN 53704. For the evaluation of the Young's Modulus, tensile clips were used up to an elongation of 1%. At least three specimens were tested. The standard deviation in nearly all cases was below 2% and has not been included to improve the readability of the diagram.

The modulus of the unreinforced HDPE was 1100 MPa, and the yield strength 26 MPa.

The surface tensions were measured by a K12 surface tensiometer (Krüss GmbH, Germany) using water, acetone, alcohol, and toluene as the testing solvents.

The molecular weights of the grafting and the homopolymerized polymers were determined in a Waters 991 gel permeation chromatograph (GPC), with tetrahydrofuran as the solvent.

For solving Eqs. 6 and 7 from Pukanszky et al., the following parameters have been used: specific surface area $A_0 = 640\,\mathrm{m}^2/\mathrm{g}$, density of $SiO_2 = 2.15\,\mathrm{g/cm}^3$, yield strength of the matrix $\sigma_{y0} = 26\,\mathrm{MPa}$ and interphase thickness $l = 8\,\mathrm{nm}$, as verified by TEM measurements [18].

The extended van der Poel model has been solved with the following parameters: The modulus of the HDPE $E_{Matrix} = 1.1\,\mathrm{GPa}$. The following data have been taken from the literature: the modulus of the filler $E_{SiO2} = 72\,\mathrm{GPa}$, and the Poisson's ratio of the matrix $\nu_{Matrix} = 0.33$, and the filler $\nu_{SiO2} = 0.2$, while the Poisson's ratio of the composite and interphase has been assumed to be $\nu_{Composite} = \nu_{Interphase} = 0.33$.

FE-MODEL

Several assumptions have been made for the FE-Model: First, it is assumed that the continuum-mechanical approach is still valid, even though the unit cell size is in the range of the radius of gyration of the polymer chains and also very close to the particle size. Second, that a perfect adhesion of the phases exists until the yield point. Third, that no distinction between amorphous and crystalline phase of the matrix is necessary in order to derive the mechanical response of the composite. In other words, the bulk matrix material is not changed considerably due to the incorporation of the nanoparticles. Fourth, the interphase possesses a considerably higher yield strength than the matrix. Fifth, that shear yielding is the dominating micromechanical deformation process. This is reasonable, because this happens in composites containing small particles, especially because the debonding stress increases rapidly with decreasing particles size [12].

Figure 2 illustrates the geometry of the 2-D micro model used in this study. Due to the symmetry conditions, one fourth of the nanoparticle and the interphase in the matrix was created. The different phases have been connected by joining the nodes, thus simulating perfect adhesion. The modelling has been carried out using the FE-software ANSYS with plane 182 elements (2-D 4-Node structural solid element) in plane strain mode.

The application of the mechanical load was implemented systematically in the model. The load was constantly increased until the stress-strain curve approached the yield point.

The unit cell is subjected to the following loading and boundary conditions. Unit cell displacements in the x- and z-direction are prohibited for all nodes on the left edge to fulfil the symmetry condition with the neighboring unit cells. Further restraints of the nodes on the lower edge in y- and z-direction have been applied. External stress is applied on the unit cell on the upper edge by means of a negative pressure.

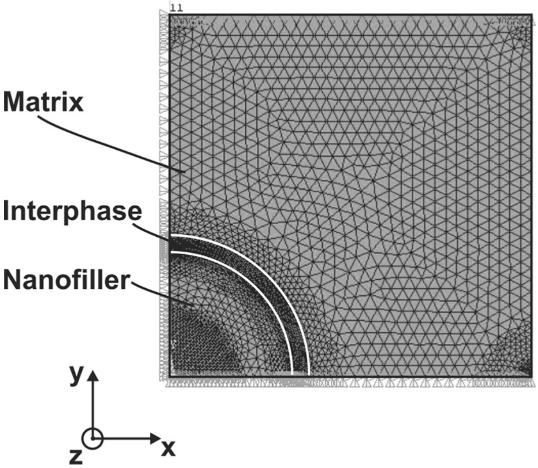

FIGURE 2 FE-micromodel of a nanoparticle and the interphase in the matrix material.

For the matrix material, a bilinear material model has been used by fitting the experimentally evaluated stress strain behavior of the matrix.

For this purpose, the engineered stress-strain data of the matrix has been converted to true stress strain data up to the yield point according to the following formulae:

$$\varepsilon_{true} = \ln(1 + \varepsilon_{eng.}), \tag{12}$$

and

$$\sigma_{true} = \sigma_{eng.}(1 + \varepsilon_{eng.}). \tag{13}$$

The interphase and the nanoparticle have been modelled with linear elastic properties. The moduli of the interphase, the interphase volume fraction, and the filler content are the independent variables and have been determined by fitting the predicted yield strength with the experimentally determined yield strength.

The volume fraction of the interphase, which forms around the filler with the radius r, has been calculated for a simple cubic packing, basically the same set-up as in Figure 2. The interphase volume fraction ν is calculated from the volume of the interphase, $V_{Interphase}$, with respect to the size of the cubic unit cell, $V_{Unit\text{-}Cell}$:

$$\nu = \frac{V_{Interphase}}{V_{Unit-Cell}} = \frac{1}{V_{Unit-Cell}}\left(\frac{4}{3}\cdot\pi\cdot(r+\Delta r)^3 - \frac{4}{3}\cdot\pi\cdot r^3\right) \tag{14}$$

where r denotes the particle radius and $(r + \Delta r)$ the radius of the interphase.

RESULTS AND DISCUSSION

In a first step, the FE-model capability has been verified by reproducing the stress-strain behavior of the unfilled material. The experimental curve for the HDPE and the modelled curve are displayed in Figure 3. The agreement between the curves is very good. The experimental curve of the HDPE displays two typical yield points, one around 2% of true strain and the second yield point at the peak of the curve. The first yield point corresponds to a fine slip within the crystallites and the second yield point to coarse slip of the lamellar crystallites [19]. Because it was not possible to detect the first yield point in the filled composites unambiguously, the second yield point was chosen as representative value of the material. It was also found that the second yield stress correlates linearly with the lamellar crystallite thickness [19].

Evidently, the agreement between the experimental and the modelled curve is very good and can be used for modelling the matrix deformation behavior within the composite. But, before taking a look at the FE-model capability by comparing the experimental with the predicted results, the following points should be analyzed:

1. changes in the bulk (matrix) material due to incorporation of the filler (e.g., crystallinity, lamellae thickness),

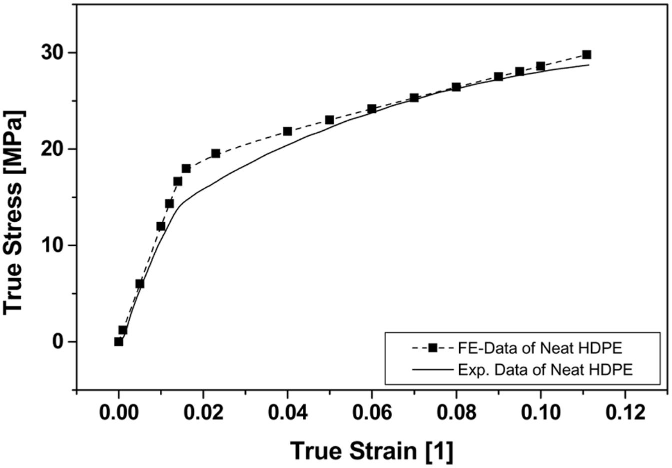

FIGURE 3 Experimental and modelled true stress–true strain curves.

2. adhesion between filler and matrix,
3. interphase properties,
4. filler size.

Remarks Concerning Point 1

Because the yield stress of HDPE is closely related to the overall crystallinity and the lamellae thickness of the crystallites [20], these two parameters have to be investigated with respect to filler content. This has already been studied for the investigated material systems in Reference [21]. It has been found that no significant changes occur in the overall crystallinity, and that no changes happen in the lamellar crystallite thickness. Eventually, it can been assumed that no changes in the bulk material occured due to the incorporation of the filler, or to be more precise, the mechanical response is unaffected with respect to filler type and content. The changes occurred only in the vicinity of the filler by formation of an interphase.

Remarks Concerning Point 2

The properties of particle filled polymers are strongly affected by the interface and/or interphase, whose properties should generally be adjusted for an improvement of the mechanical properties of the composite. For this purpose, the interaction between the phases is evaluated in a first step by studying the free surface energies of the components. From this property, a conclusion can be drawn with respect to the adhesion between the phases.

The calculation of the adhesion parameters such as the thermodynamic reversible work of adhesion W_{mf} and the interfacial free energy γ_{mf}, represented in Eqs. 15 and 16, respectively [22], enables a prediction of the strength at the filler/matrix interface and to correlate them with the mechanical properties of the composite.

$$W_{mf} = \gamma_f + \gamma_m - \gamma_{mf} \tag{15}$$

$$\gamma_{mf} = \gamma_f + \gamma_m - 2(\gamma_f^d \cdot \gamma_m^d)^{1/2} - 2(\gamma_f^p \gamma_m^p)^{1/2} \tag{16}$$

where subscripts of the surface energies γ mean $m =$ matrix and $f =$ filler. The relationship indicates the desired optimum conditions: thermodynamic work of adhesion as maximal and interfacial free energy as minimal (tends to zero) [22].

The free surface energies of the fillers have been evaluated from contact angle measurements. The results are shown in Table 1.

TABLE 1 Overview of Filler Surface Engergies Compared to the Matrix Materials

Materials	HDPE	SiO_2 as received	SiO_2-g-PS	SiO_2-g-PMMA	SiO_2-g-PEA
γ^a[mJ/m^2]	35.7^b	82.5	20.8	19.8	39.8
$\gamma_d{}^c$[mJ/m^2]	35.7	1.4	7.5	4.5	3.1
$\gamma_p{}^d$[mJ/m^2]	0	81.1	13.3	15.3	36.7

[a] Surface free energy.
[b] Data from source [23].
[c] Dispersive component of surface free energy.
[d] Polar component of surface free energy.

The free surface energy of linear HDPE is well known and has been taken from the literature [23].

The obtained surface energies can be evalulated with respect to Eqs. 15 and 16. The adhesion parameters are displayed in Table 2. It can be seen that the surface treatment increased the work of adhesion value considerably, implying that stronger interactions are likely to occur at the interface in these composites. With regard to the reversible work of adhesion, the conclusion should be that the debonding of untreated compared to treated particles should happen at lower forces.

The matching of the surface energies may not be enough to provide improved composite properties, due to the fact that no chemical bonds may form between the matrix molecule and the grafted polymer on the surface of the filler. The only way to allow a load transfer between matrix and filler is therefore to establish a highly entangled molecular network between the grafted polymer and the matrix molecules [24]. Of course, this option is missing for the untreated filler particles, but adsorbed matrix molecules should act in the same way. In the

TABLE 2 Overview of the Adhesion Parameters

	Adhesion parameters [mJ/m^2]	
Composite	Work of adhesion W_{mf}	Interfacial free energy γ_{mf}
HDPE/SiO_2-as rec.	14	104
HDPE/SiO_2-g-PS	33	24
HDPE/SiO_2-g-PMMA	25	30
HDPE/SiO_2-g-PEA	21	54

following, the discussion with respect to the molecular weight is also valid for the adsorbed matrix molecules.

The chain entanglement criterion for the maximum in load bearing capability is the critical molecular weight M_c, which needs to be exceeded [24–26]. When the M_c requirement is fulfilled, and if there is a maximum of interdiffusion of the two polymers, namely the matrix molecules and the grafted polymer, then the interphase becomes largest and strongest [24].

In case of little interdiffusion, then a weak interphase is formed. This is the case for immiscible blends, where an interphase boundary layer of 2 nm is generally found. Other, stronger types of interphase boundary layers are in the range of approx. 4–60 nm. In comparison, it has to be kept in mind that the typical radius of gyration of a polymer chain is in the range of 5–35 nm [27].

Another prerequisite for the formation of an entanglement network between the grafted polymer on the filler surface and the matrix is at least a minimum of miscibility. However, miscibility strongly depends on specific sets of conditions, namely the configuration of the polymeric molecules, molecular weight and molecular weight distribution, temperature, pressure, stress field, additives, and so on [27]. This certainly explains why no literature results have been found on the miscibility and the required M_c for the development of a good entanglement network between grafted and matrix polymer.

Typical entanglement number-average molecular weights M_c in the literature range from 1.500 to 18.000, depending on the polymer [28]. However, no values for M_c have been found for polymer chains anchored at one end, used for surface modification, namely PS,

TABLE 3 Overview of Filler Surface Treatment. Molecular Weights of Grafted Polymers. Data from Fillers Used for the Preparation of HDPE-Nanocomposites

				M_ω		M_n	
ID	Description	Percent Grafting[a]	Grafting Efficiency[b]	Grafting polymer	Homo-polymer	Grafting polymer	Homo-polymer
1	SiO_2-g-PS	8.7	56.8	2.8×10^4	5.6×10^4	1.0×10^4	4.1×10^4
2	SiO_2-g-PMMA	12	60	7.2×10^3	5.8×10^3	5.2×10^3	4.2×10^4
3	SiO_2-g-PEA	9.4	54.3	4.3×10^4	3.0×10^4	2.7×10^4	1.2×10^4
4	SiO_2-as-rec.	—	—	—	—	—	—

[a] Percent Grafting: Weight of grafting polymer/weight SiO_2.

[b] Grafting efficiency: Weight of grafting polymer/weights of grafting polymer and homopolymer.

PMMA, and PEA. In Table 3, the molecular weights of the grafted surface molecules on the surface of the fillers used for the preparation of the HDPE nanocomposites, are shown. Thus, the assumption that the molecular weights of both matrix and grafted polymer are probably higher than the required M_c can only be verified by several experimental evidences.

In a previous work, it has been found that the interphase thickness, at least of the HDPE composites, is in the range of 3–19 nm [18]. This is considerably larger than the typical interphase thickness of immiscible polymer blends (<2 nm) and thus can be regarded as evidence for a strong interphase interaction with load-bearing capability. The good adhesion of the particles to the matrix has also been confirmed by fractography of impact and tensile specimen [17,29–31]. It can therefore be concluded that the assumption of a strong interaction is confirmed and can be described in the FE-model by a rigid connection, that is, joining of the nodes of the interphase interphase with the matrix.

Remarks Concerning Point 3

As already discussed in the section on the FE-model, the interphase content and mechanical properties are input parameters.

The interphase content has been analyzed by various methods in a previous work. Results indicated, that the interphase volume content is in the range of 0.25% (by DMTA) up to 0.8% (by TEM) for all filler types and contents [18].

With respect to the mechanical properties, it has already been pointed out that it is impossible to determine the yield strength (or debonding stress) of the interphase. Especially, if the filler size is in the nanometer range and the adhesion between the matrix and the filler is good. The only alternative is the consideration of the interphase modulus. Various models exist for the evaluation of the interphase modulus, but the one from the van der Poel model seems to be the most promising, due to the analytical approach. However, the application here has proved to be unsuccessful, because the interphase modulus and interphase content values were unrealistically high.

Remarks Concerning Point 4

From the TEM investigations of the material systems, it has been found that the agglomerate size is in average around 100 nm [18]. This size has been used for modelling the properties. Exemplary representative microstructure of the composites is shown in Figure 4.

The analysis of the impact factors indicates that the chosen discrete modelling approach is reasonable. The experimental results, namely

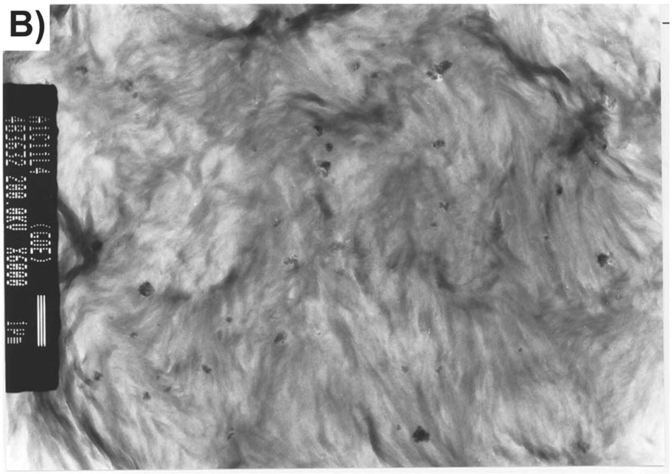

FIGURE 4 Exemplary picture of the microstructure of the material HDPE-SiO_2-g-PEA, 1 wt.% (by transmission electron microscope).

the yield strength with respect to filler content, of HDPE nanocomposites with the differently treated nanoparticles are plotted in comparison to the results from the FE-model in Figure 5. The results from the

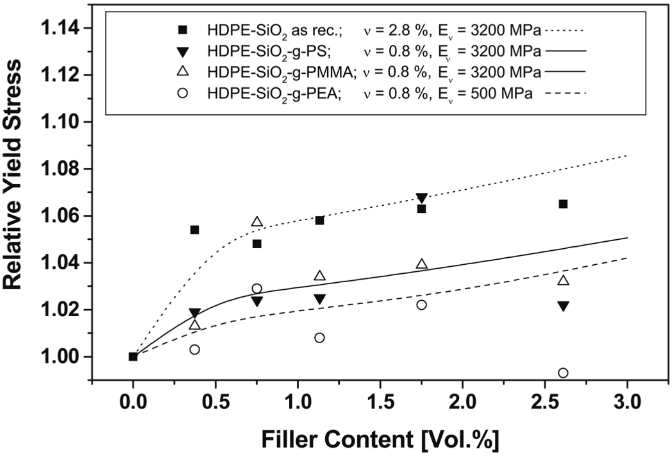

FIGURE 5 Comparison of experimental values of the HDPE nanocomposites (symbols), with calculated values for a given interphase fraction. The interphase modulus E_ν and volume fraction ν of the calculated curves, which fit the experimental data, are shown in the legend.

FE-model have been derived by modelling the system with different interphase volume fraction, interphase modulus, and filler fraction. The modelling has been concluded after reaching a good agreement between the model prediction and the experimental data.

However, at particle contents above 2 vol.%, the agreement between the predicted and the experimental values declines. The only reasonable explanation for this behavior must be the existence of agglomerates, which acted as flaws in the material and eventually led to the decline in material strength.

The HDPE-SiO_2-as-received composite material shows a good agreement for an interphase content of 2.8% and an interphase modulus of 3.200 MPa. Also, for the nanocomposites HDPE-SiO_2-g-PS and HDPE-SiO_2-g-PMMA the predicted values fit for an interphase fraction of 0.8% and an interphase modulus of 3.200 MPa. In case of the HDPE-SiO_2-g-PEA nanocomposite, the prediction matches the experimental data for an interphase volume fraction of 0.8% with an interphase modulus of 500 MPa.

All in all, the predicted interphase contents fit very well with the experimentally determined interphase volume fractions, which lies between 0.25 and 0.8 vol.% for all nanoparticle treatments [18,32]. A large difference can be observed for the system HDPE-SiO_2-as-received, which could not be explained until now.

The predicted interphase modulus of 3.200 MPa fits very well with the bulk elastic modulus of PS and PMMA. It is for both cases in the range of 3.200 MPa, varying slightly with polymer type [33]. Unfortunately, for the grafted polymer PEA no literature data on the modulus has been found, probably due to the fact that the glass transition temperature of PEA is around -7°C [34], making the comparison of the predicted modulus basically impossible. The interphase modulus of the system HDPE-SiO_2-as-received with 3.200 MPa seems to be too high because the interphase should be amorphous PE. Along with the deviation in interphase content, the different reinforcing effect of the filler SiO_2-as-received has to be investigated in more detail.

A verification of the predicted moduli may be possible in two ways. One way is the analysis of the material through nanoindentation experiments, by placing indents across nanoparticle agglomerates. However, this approach has already been pursued without success [21].

The other way is a detailed analysis of the composite modulus with models, taking the interphase into account. As already mentioned, the elaborated method of van der Poel [7] should provide the best solution. However, neither the moduli from the DMTA spectrum of the composites nor the tensile composite moduli could be matched with realistic values for the interphase modulus and content.

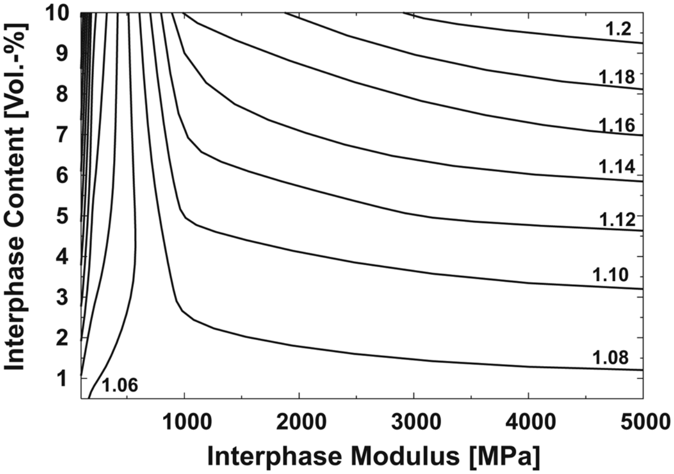

FIGURE 6 Contour plot showing the FE-solution for a filler content φ of 0.5 Vol. %. The relative yield strength of the composite σ_y is plotted as height line depending on the parameters interphase modulus E_ν and interphase content ν.

In order to derive a better understanding of the developed FE-model, the solution space has been compared to similar models, one being empirical (from Pukanszky et al.) and one being analytical (from van der Poel).

The solution space of the FE-model is shown in Figure 6 in a contour plot, for a constant filler content $\varphi = 0.5\%$. The height lines give the relative yield strength of the composite with respect to the interphase content and modulus. For interphase moduli below the matrix modulus of 1.100 MPa, changes in interphase content play a minor role. The stresses around the filler are relieved as a result of the soft interphase anyway. If the modulus of the interphase increases above the matrix modulus, then the interphase content dominates the composite yield strength. This is due to the fact that the stresses around the filler are shifted to larger radii, so that the stiff interphase eventually bears the load. This background story has been found for the linear elastic material combination long ago [35] and is not changed considerably due to the large plastic deformation of the matrix.

This is confirmed by the comparison of the FE-solution with the linear elastic solution of the extended van der Poel model. In Figure 7, the contour plot of this analytical model is shown for a filler content of $\varphi = 0.5\%$ with the variables interphase modulus and content. The height lines give the relative composite modulus or can also

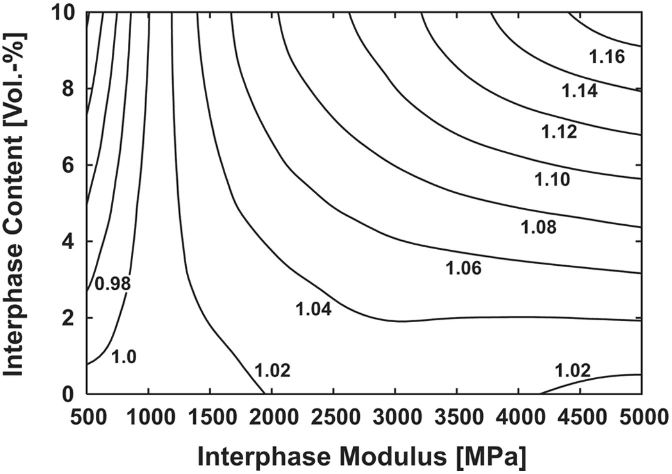

FIGURE 7 Contour plot showing the solution of the extended van der Poel model for a filler volume content $\varphi = 0.5\%$. The height lines correspond to the standardized composite modulus or can also be interpreted as the composite yield stress for the linear elastic case.

be interpreted as the relative yield strength of the composite for a fixed strain. Compared to the solution of the FE-model, the similarity is obvious. Due to the linear elastic solution of the van der Poel model,

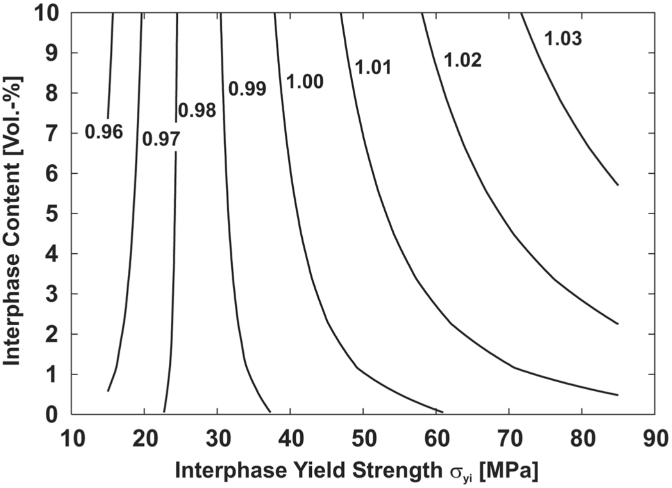

FIGURE 8 Contour plot showing the solution of the semi-empirical Pukanskzy Modell for a filler volume content $\varphi = 0.5\%$.

the influence of the interphase modulus and content is relatively equal in impact on the composite property. Thus, both models yield the same information, the solution space is congruent. The linear elastic case of the van der Poel model finds its extension in the nonlinear FE-model.

In this context, it seems fit to contrast these solutions with an empirical approach (the one from Pukanszky). In Figure 8 the contour plot, containing as height line information, the composite yield strength is shown. The independent variables are the interphase content and the interphase yield strength. In this case, the interphase yield strength can be compared to the interphase modulus. A comparison with the discrete FE-solution and the analytical solution shows again that the solution space is congruent. This outcome is unexpected because the empirical model has been derived with a completely different approach. Nonetheless, the solution explains the success of the empirical model because it has a similar solution space compared to analytical and discrete models.

CONCLUSION

HDPE nanocomposites have been manufactured with differently treated nano-SiO_2. The nanofiller has been used in unmodified and modified form. The nanofiller characteristics were changed by grafting polymers onto the surface, that is, PS, PMMA, and PEA. It was verified that the surface modification led to a good adhesion of the filler to the matrix. The results of previous material investigations on changes in the matrix and the interphase properties have been considered in the model. Additionally, for both matrix materials and the filler variations, mechanical tensile data have been gathered for low filler volume fractions, typically being smaller than 3 vol.%.

The microstructure has been modelled by an FE-model, which considered the microstructure, namely the nanoparticle, the interphase, and the matrix material. The deformation of the matrix material and the composite have been modelled up to the yield point.

The predicted material properties matched the experimental values very well. In case of the surface modified nanofillers, the predicted values of the interphase volume fraction and the interphase modulus matched the experimental data closely. Only in the unmodified case the values deviated from the experimentally determined ones.

Additionally, the solution space of the FE-model has been compared to an empirical and an analytical model with similar input and output parameters. The empirical model uses the interphase yield strength instead of the interphase modulus, but in first approximation this parameter yields a similar information. Apart from this parameter, the difference with the discrete models is negligible. The analytical model is essentially the same as the discrete model developed in this work. The exception stems from the linear elastic solution in the analytical case and the linear elastic-plastic solution in the FE-model case. All in all, it was found that the solution space in all cases was congruent.

This result confirms that the finite element approach is sound and has to be elaborated in the future.

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