Determining Elastic Properties of Particle Reinforced Polymer Composites by Numerical Modeling of their Microstructures

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Abstract. A numerical model of particle reinforced composites was created to calculate the elastic material properties. Therefore, a thermoplastic polymer filled with different types of precipitated calcium carbonate was chosen as the material. Size and shape of the particles as well as their distribution and orientation within the polymer matrix were examined with a scanning electron microscope. Representative Volume Elements (RVEs) based on different particle shapes and distributions on a micro scale were numerically modeled. Six sets of boundary conditions in displacements were applied to the RVEs to simulate three load cases of uniaxial tension (in the directions of the three global coordinate axes) and three shear load cases. These results were used to calculate the components of the stiffness tensor of the composite. This process was carried out for single particle inclusions to study the contribution of the particle to the overall elastic material properties as well as for RVEs with multiple particles, to study the contributions of the particles interactions. Lastly, a more accurate representation of real microstructures was created, taking agglomerates into consideration. Studies about the influence of the agglomerates to the elastic material properties were carried out.

Keywords: Numerical Modeling, Particles Interaction, Micromechanics, Scanning Electron Microscopy, Polymer Matrix Composites, Agglomerates.

1 Introduction

Particle reinforced polymer composites are applied in a variety of different fields satisfying the individual requirements of the intended applications in various industries. One objective of filler materials deals with changing the mechanical properties of the polymer [1]. Despite the specific filler material, the manner of modification in the mechanical properties depends on several factors like size, shape and amount of the added particles. Further, distribution and dispersion of the particles within the polymer matrix have an impact on the mechanical behavior of the composite. Thus, there is a high variation potential in the development process like changing the specific filler type or filler amount in order to reach the predefined properties. As a result, different composites can be produced and need to be analyzed. This experimental approach usually involves a high effort at producing the different composites, testing their mechanical properties and evaluating the results.

Another possible way is predicting the mechanical behavior by using numerical studies. Thereby, the mentioned effort can be reduced and the development process can be shortened. Even though every composite is created to meet specific requirements and therefore is not freely interchangeable with other particle reinforced composites, they do share the mechanics at the microscopic level. Thus, a theory has been developed that describes the mechanics at the microscopic level to predict the material behavior at a macroscopic scale. For this, studies of particle reinforced polymer composites at a micro scale are carried out to increase the insight of the mechanical behavior.

In this work a thermoplastic polymer filled with different types of precipitated calcium carbonate (PCC) serves as research subject. The objective is predicting the stiffness of the composites against tensile and shear loads. As a necessary input parameter for the numerical model both the specific size and shape of the particles as well as their distribution in the compounded composite need to be analyzed.

2 Investigation of the Filler Particles and Composites

2.1 Studied Materials and Experimental Methods

As mentioned above a thermoplastic polymer is used as the material filled with five different types of PCC. Compared to naturally gained grounded calcium carbonate PCC has several advantages. As a synthetized product it provides the possibility of creating different particle sizes and shapes [2]. As a result, the five added materials exhibit divergent sizes and shapes.

A scanning electron microscope (SEM) was used to gain the necessary information about the added particles, whereby a Hitachi SU5000 served as the device. In a first step, microscopic images were taken of the particles. The particles were placed as a thin layer onto the sample holder and attached with a conductive carbon adhesive. The images were created by detecting the secondary electrons. From the images the size and the shape of the particles were estimated. Furthermore, the aspect ratio as the ratio between the largest and the smallest dimension of the particle was calculated [3].

After investigating size and shape of the particles itself the compounded composites were studied again by using the SEM. The desired information was gained by performing a notch-impact test according to EN ISO 179-1:2010 and investigating the fractured surface. Therefore, multipurpose test specimen as defined in EN ISO 20753:2018 (type A1) were manufactured and provided with a v-notch (depth: 2 mm, angle: 45°, radius notch root: 0.25 mm). The notch was brought into the test specimen in order to ensure that every sample breaks. A Zwick-Roell PSW 5113 served as the testing device and the notch-impact tests were carried out by using a pendulum with a working capacity of 2 J. The fractured surfaces were coated by 4 nm Au layer. The images again were created by detecting the secondary electrons. On the basis of the microscopic images distribution, dispersion and the orientation of the particles within the polymer matrix were estimated.

2.2 Scanning Electron Microscopy Analysis

At first the microscopic images of the particles are examined. An image of one example taken by the microscope is shown in Fig. 1.

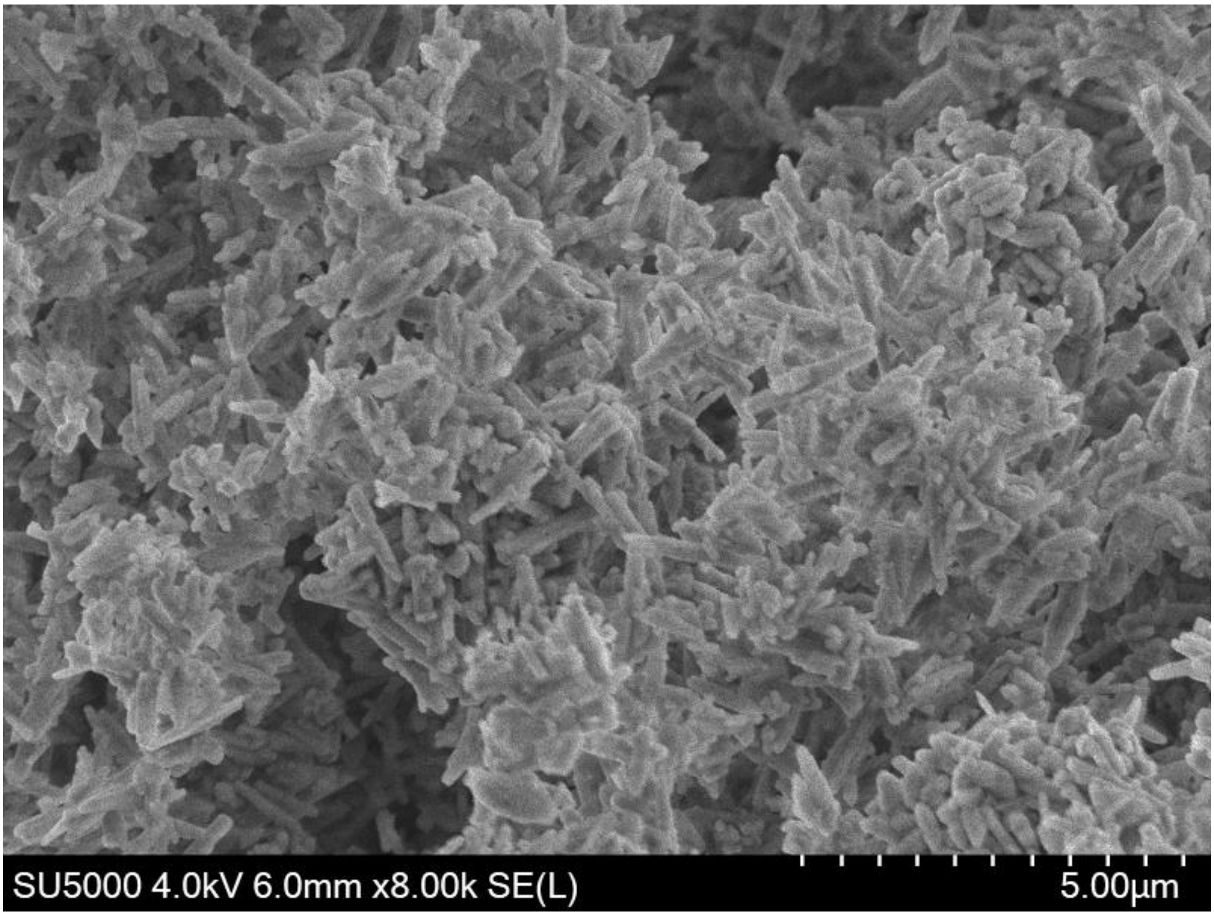

Fig. 1. SEM image of needle-shaped PCC particles

The image shows needle-shaped particles stick together in an agglomerate. The particles have an estimated length of around 1-2 µm and a width of around 0.25 µm in the center, yielding an aspect ratio from 4 to 8. All of the other four PCC-types show unique shapes as well. Besides the mentioned needle-shaped particles there are also spherulitic, skalenohedral and platelet-shaped particles. The fifth type is a mix between skalenohedrons and needles. To demonstrate the differences, the platelet-shaped PCC-type is shown in Fig. 2.

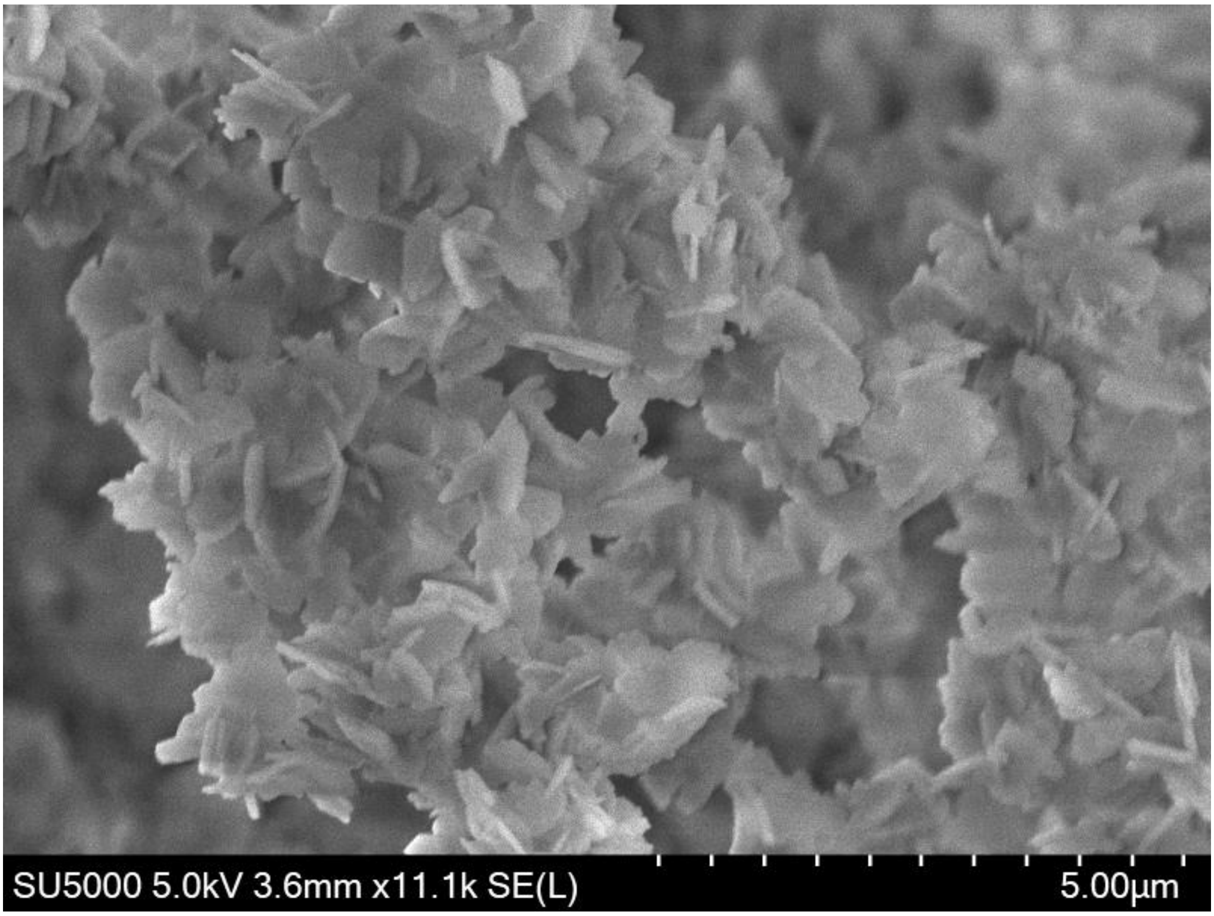

Fig. 2. SEM image of platelet-shaped PCC particles

The information gained from the investigation of the different PCC particles with the SEM is summed up in Table 1.

Table 1. Shapes, sizes and aspect ratios of the five investigated PCC particle types

PCC-type No.	Shape	Size	Aspect Ratio
1	Skalenohedrons	Length: ~ 1 µm Width: ~ 0.3-0.5 µm	~ 2-3.33
2	Needles	Length: ~ 1-2 µm Width: ~ 0.25 µm	~ 4-8
3	Mix of skalenohedrons and needles	Length: ~ 1-2 µm Width: ~ 0.5 µm	~ 2-4
4	Platelets	Length: ~ 1-2 µm Width: ~ 0.01 µm	~ 100-200
5	Spherulites	Ø: ~ 0.05-0.1 µm	1

Next, the fractured surfaces of the composites are examined aiming to get information about distribution, dispersion and orientation of the particles in the polymer matrix. As a justifiable assumption one would expect the platelet-shaped particles to have a higher orientation in flow direction of the melt during the injection molding process compared to the other four PCC-types due to their higher aspect ratio.

A microscopic image of a composite with the needle-shaped filler material is shown in Fig. 3.

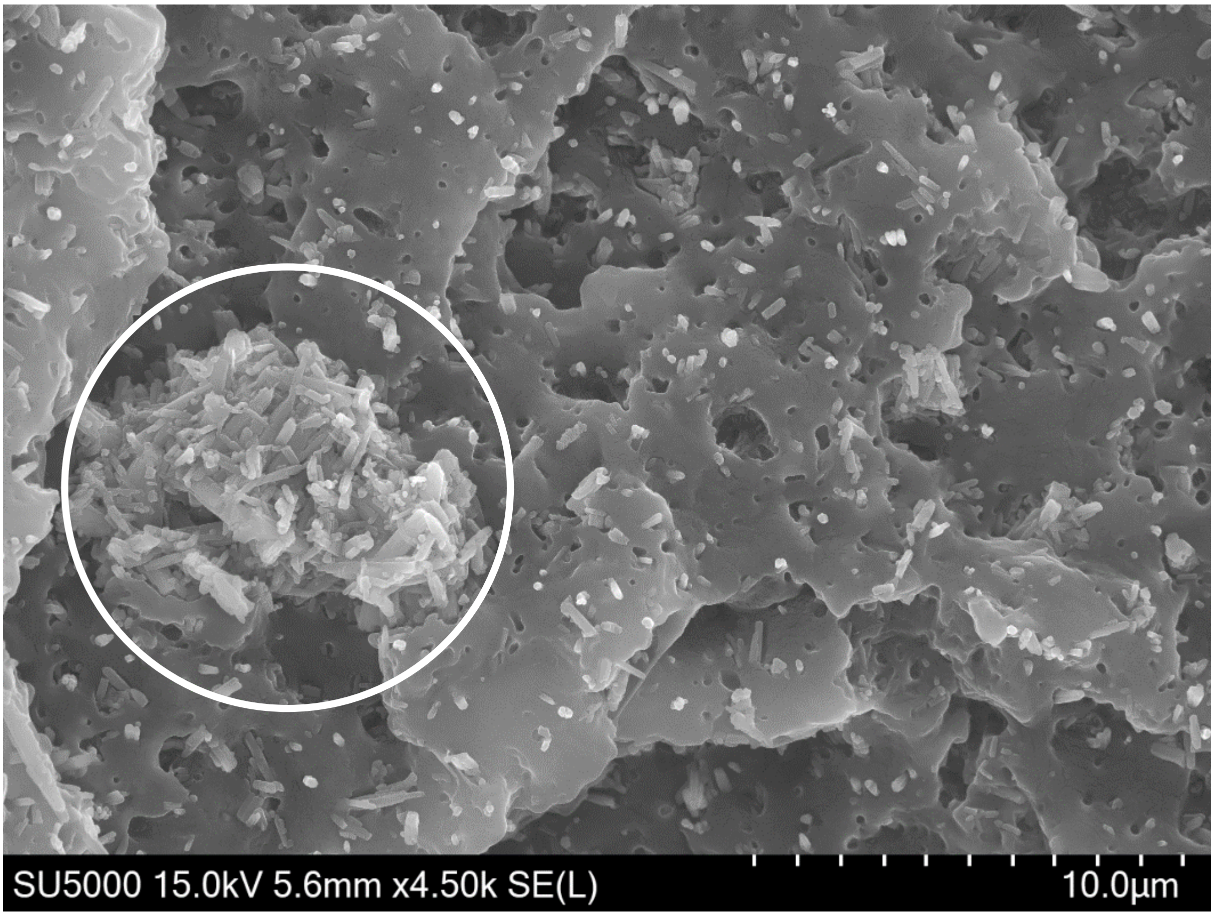

Fig. 3. SEM image of the fractured surface of the thermoplastic polymer filled with needle-shaped PCC-particles; the highlighted area marks an agglomerate

In the image one can see a mostly homogenous distribution of the particles within the polymer matrix. However, scattered residual agglomerates can still be located such as highlighted on the middle left side of the image. The compounding process could not break up the agglomerates totally. In conclusion, they must be taken into account in the numerical analysis. Furthermore, the particles show no preferential orientation within the matrix at all, which is traced back to their low aspect ratio.

This description can be transmitted analogous both to the skalenohedral-shaped particles as well as to the mixture of the two types. They also seem to have no preferential orientation in the viewed images and have a low aspect ratio. An exception are the platelet-shaped particles as presented in Fig. 4.

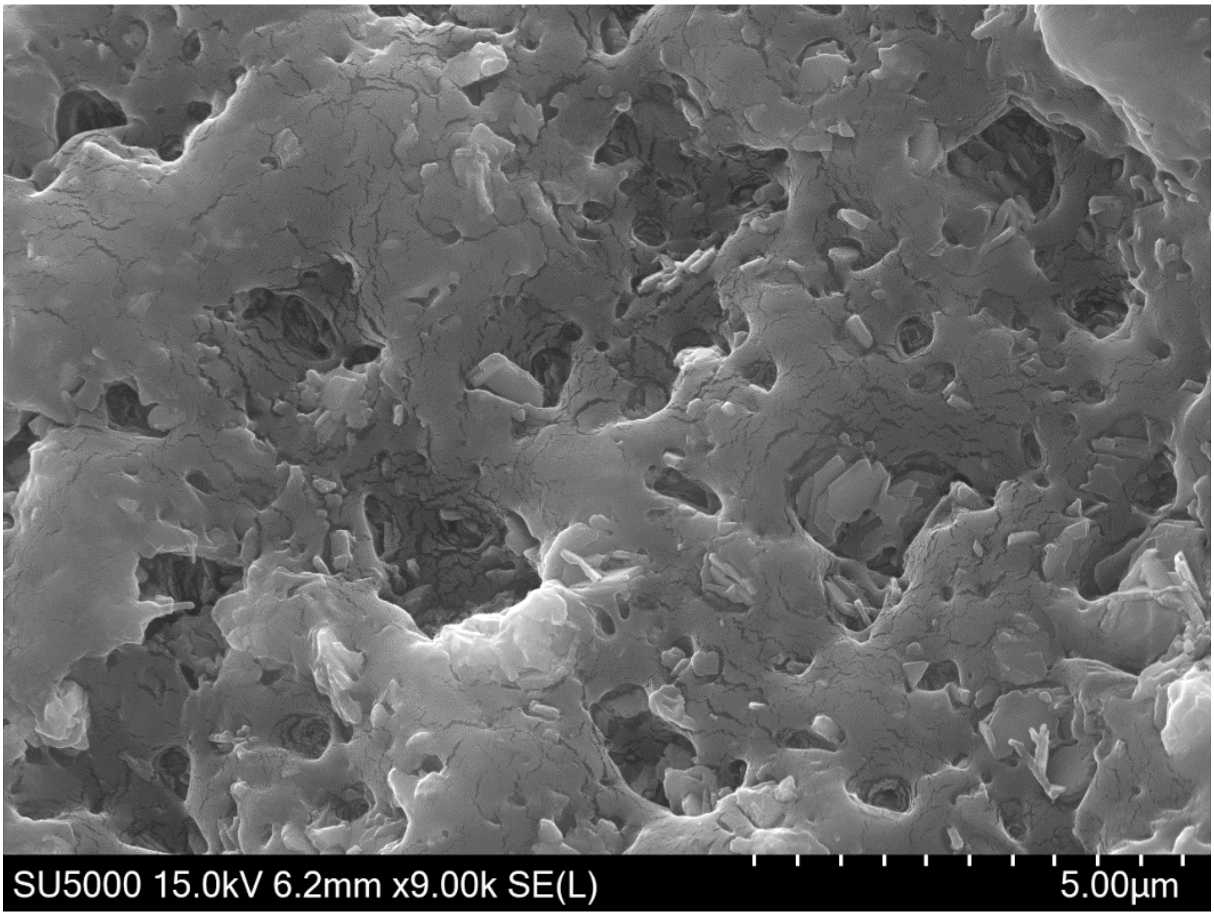

Fig. 4. SEM image of the fractured surface of the thermoplastic polymer filled with platelet-shaped PCC-particles

As expected, the particles appear to have a higher orientation whereby the base area tends to align perpendicular to the flow direction (the direction of flow is perpendicular to the image surface). Mainly the tips of the particles protrude from the fractured surface. This confirms the expectations due to the higher aspect ratio of the particles.

Finally, the spherulitic-shaped PCC-type does not have an orientation due to its particular shape.

2.3 Limitations of the Investigation

Unfortunately, the information gained from the investigation with the SEM is limited in several aspects. First, the sizes are just estimated by using the scale integrated in the micrograph and not quantitatively measured. In a similar way the conclusions made about the distribution, dispersion as well as the orientation of the particles within the matrix are limited, because they are qualitatively evaluated. Second, the examined fractured surfaces of the composites are a small section and therefore cannot be generalized for the entire specimen. On top of that, the surface was created by deploying a notch-impact test and thus was affected by a large dynamic force. This factor could also have caused an impact onto the particles, e.g. by breaking their linkage to the polymer matrix.

3 Numerical Modeling

3.1 Methodology and Assumptions for the Numerical Evaluations of Elastic Properties

An approximation of the particles by use of ellipsoids allows the analytical evaluation of the elastic properties of the composite, opening up two branches of composite evaluation methods, making it possible to compare results. On the one hand, using the Eshelby solution for ellipsoidal inclusions [4], semi-analytic methods of Mori-Tanaka [5] and Lielens [6], as well as the Dilute inclusions method [7-9] can be used as homogenization methods, to evaluate the elastic properties of the composite. On the other hand, numerical methods such as the FEM analysis can be used to study the effects of various particles onto the composite [10] properties.

In this research we utilized the numerical evaluation. For the numerical calculations Representative Volume Elements were created (RVEs) as discussed by Khisaeva et al. [11] and Gitman et al. [12]. The algorithm to create RVEs consisting of multiple periodic distributed particles is based on the Random Sequential Adsorption (RSA) algorithm proposed by Rintoul et al. [13]. Boundary conditions were placed onto the surfaces and six load cases were evaluated, as described by Drach [14], three of them being of uniaxial tension and three of them being of shear deformation.

An ideal smooth surface of the particles, as well as an ideal bonding between matrix and particles was assumed. Considering the multiple particle evaluations, no overlapping of the particles was allowed. For these calculations only the elastic behavior was considered.

3.2 Numerical Modeling of the Composite with Periodic Distributed Single Particles

In the following studies four particle shapes were taken into consideration: ellipsoidal, spherical, cubic and cubic with smooth edges, as depicted in Fig. 5. For creation of the ellipsoidal, spherical and cube particle shapes for the FE calculations analytic functions were used.

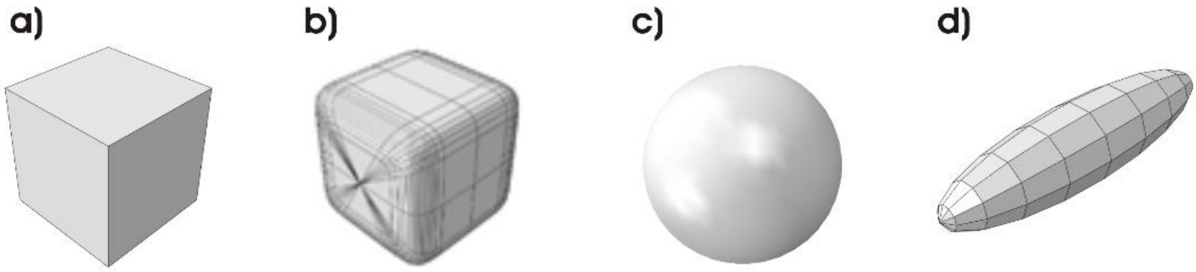

Fig. 5. Studied particles: a) Cubic, b) Cubic with smooth edges, c) Spherical, d) Ellipsoidal

Furthermore, the equations for super ellipsoid (Eq. (1)), as described by Jaklič et al. [15], were applied to create cubes with smooth edges:

$$\left(\frac{|x|}{a}\right)^n + \left(\frac{|y|}{b}\right)^m + \left(\frac{|z|}{c}\right)^k = 1, m, n, k \in \mathbb{R}_+ \tag{1}$$

The parameters influencing the radius of the corners of the cubes resulting in particle forms which are depicted in Fig. 6.

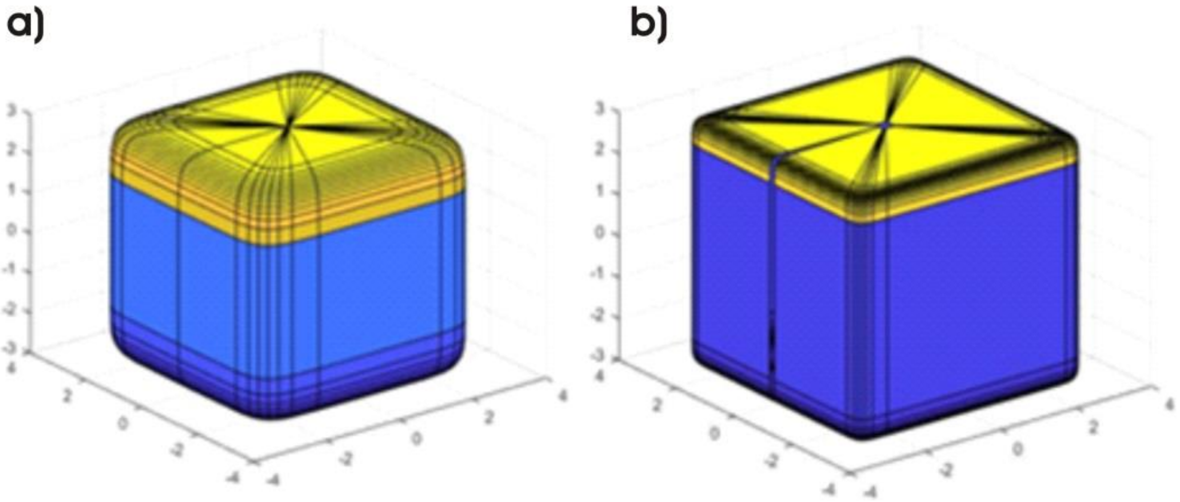

Fig. 6. Cubes with different smooth edges created by the use of super ellipsoid a) for n=m=k=8, a=b=c=3 and b) for n=m=k=20 and a=b=c=3

The particles were then embedded into a matrix, creating the RVE. Six load cases were deployed to the surface of the RVE and the stresses were calculated using numerical methods. Next, the stress volume averages were calculated. Lastly, the Young's moduli were evaluated as proposed by Drach [14]. The specific numeric calculations were done in the ABAQUS software [16].

The Young's modulus of the composite has been normalized by the Young's modulus of the particle and displayed over ψ, the surface to volume particle ratio, as proposed by Wadell [17] with slight modifications. The modified equation (Eq. (2)) is written below. Here S_P and V_P are the surface and volume of the particle respectively.

$$\Psi = \frac{S_P}{\sqrt[3]{\pi(6V_P)^2}} \tag{2}$$

The results are depicted in Fig. 7.

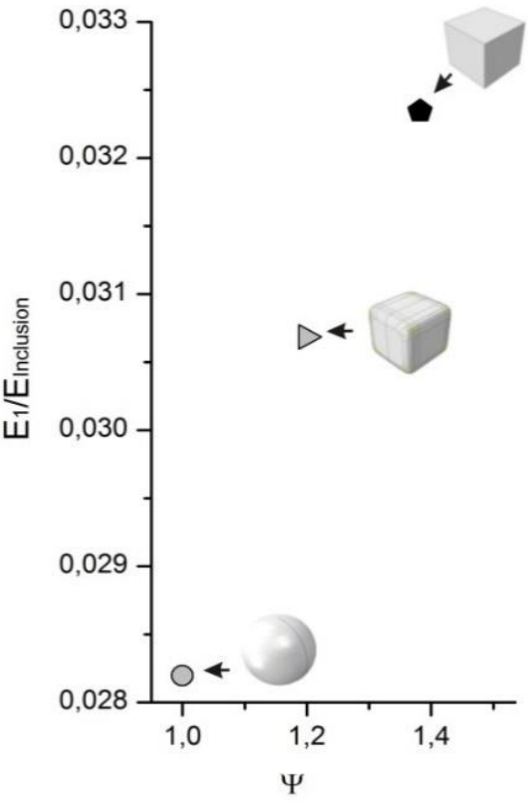

Fig. 7. Normalized young's modulus for specific particle form over surface to volume ratio

The surfaces of the particles play a measurable role for the overall elastic Young's modulus of the particle reinforced composite. The real form of the approximation cannot simply be approximated by a sphere, only taking the enclosed volume (of the particle) into consideration.

3.3 Numerical Modeling for Multiple Particles

As it was shown in the last chapter the form of the particle as well as its surface play a major role in the resulting overall elastic properties.

Up to this point only single inclusion set ups were considered under the premise that the particles are far apart from each other. So that there are no interactions, or the interactions are small to the point of being negligible. This is acceptable if the volume fracture of the particles in the composite is small. Most of the time this is not the case, as can be seen in Fig. 3. Here particles are usually close together, so that the interactions should be taking into account. Furthermore, simulations must include the formation of agglomerates, which are represented by use of particle clusters.

The positioning of the particles in a multiple inclusion set up and as clusters is realized by the use of algorithms. For this process the particles created for the single particle set-up were used. The particles are placed by the algorithm inside a cube, while allowing a certain protruding of the particles. The algorithm places particles inside the cube until the preset volume fraction is reached, as proposed by Seguardo et al. [18]. Studies were provided to estimate the appropriate amount of particles sufficient for obtaining the RVE. For a random homogenous distribution of a cube like particle the obtained RVE is depicted in Fig. 8.

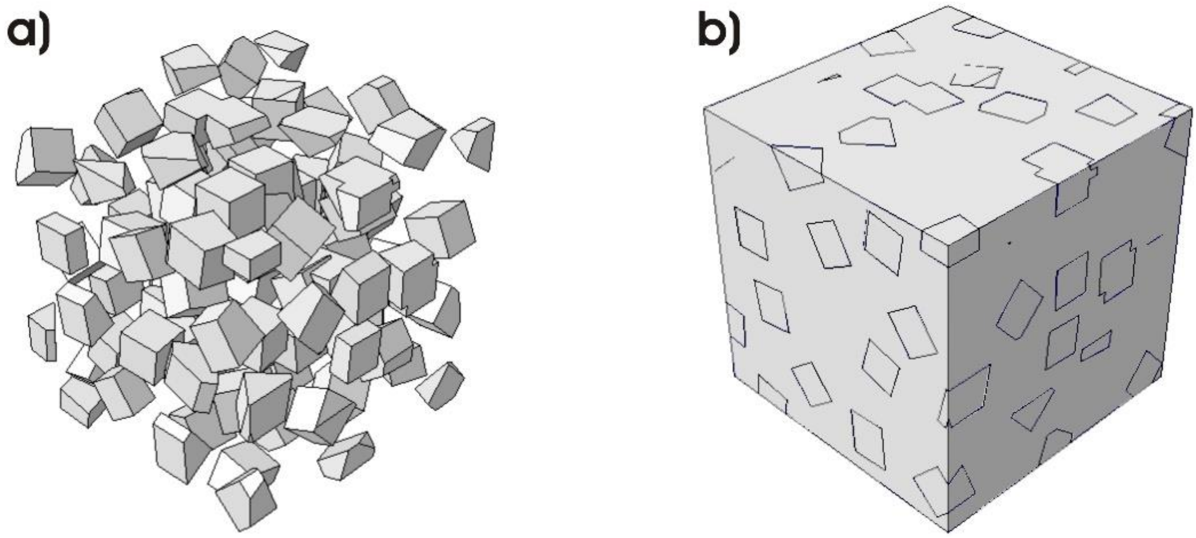

Fig. 8. RVE for random homogenous distribution of a) cubic particles, b) The same RVE with particles embedded in the matrix

Calculations were carried out for different particle forms and volume fractions considering the case of the random homogenous distribution. A closer look was taken onto the influence of the orientation of the particle on resulting elastic properties. Using self-written placement algorithms (in MATLAB [19]) the particles were generated, placed randomly and oriented within an axis direction, if needed. The following particles were studied: cubic, cubic with smooth edges, spherical and ellipsoidal (Fig. 5).

The elastic properties of the composite for each particle shape were evaluated using the ABAQUS software. The values of the normalized Young's modulus of the composite considering different particle shapes can be seen in Fig. 9, with E_C being the Young's modulus of the composite and E_P being the Young's modulus of the particle. The multiple inclusion set ups were also compared against their single inclusion counterpart. It can be seen, that the multiple particles set up achieves higher Young's moduli than the periodic distributed single particles in general. This could be attributed to the interactions of the particles having a beneficial contribution.

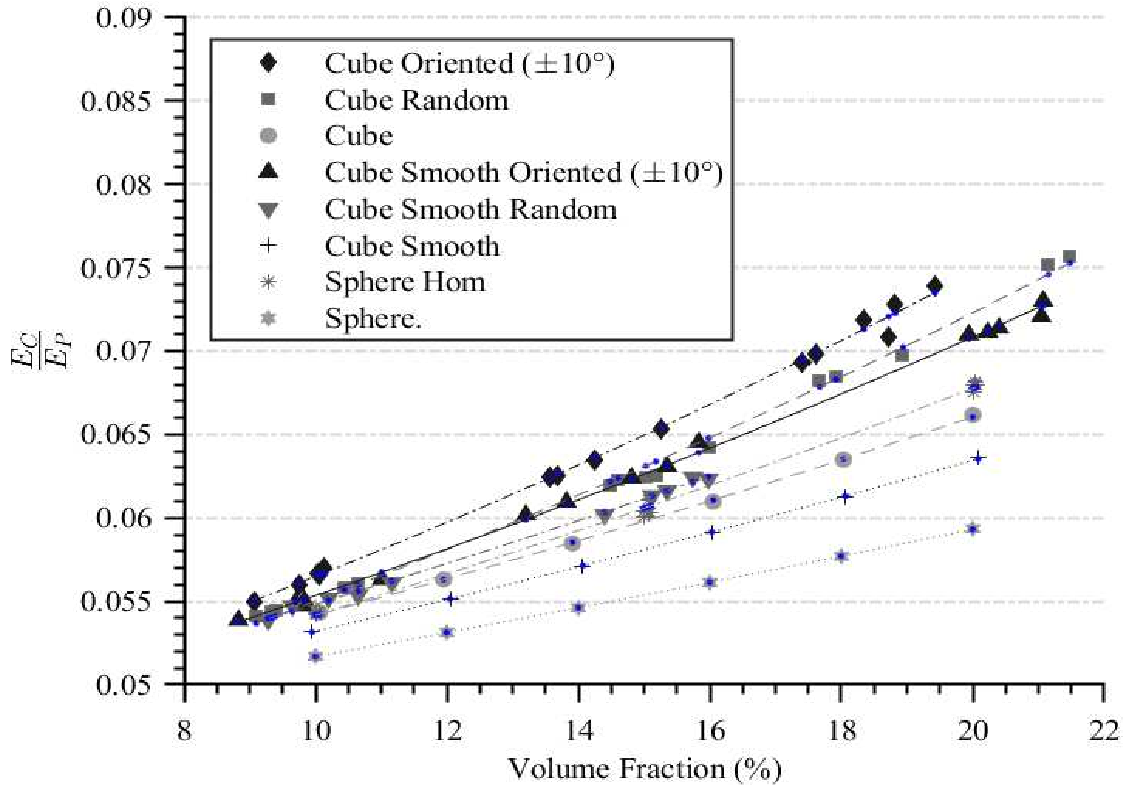

Fig. 9. Normalized effective Young's modulus of the composite for different particle shapes and distributions for X1 direction.

In general, particle shape and particle orientation play a major role on the overall elastic material properties of the composite. The approximation of the real particle in a multi-particle set-up has an influence on the quality of the predicted elastic properties as well as it has for the single particle set-up. Furthermore, the slight deviation between particles of cube like shape with smooth and sharp edges can be observed.

Finally, a study was carried out on the effects of agglomerates onto the overall elastic material properties. For this the algorithm was edited to place the particle to form a specific cluster. Here two clusters were studied. On the one hand a chain cluster of the particles and on the other hand cloud like cluster. For the chain cluster each particle is placed next to the previously placed one. The specific location for the subsequent particle is randomly selected. The general chain cluster is depicted in Fig. 10 a) b).

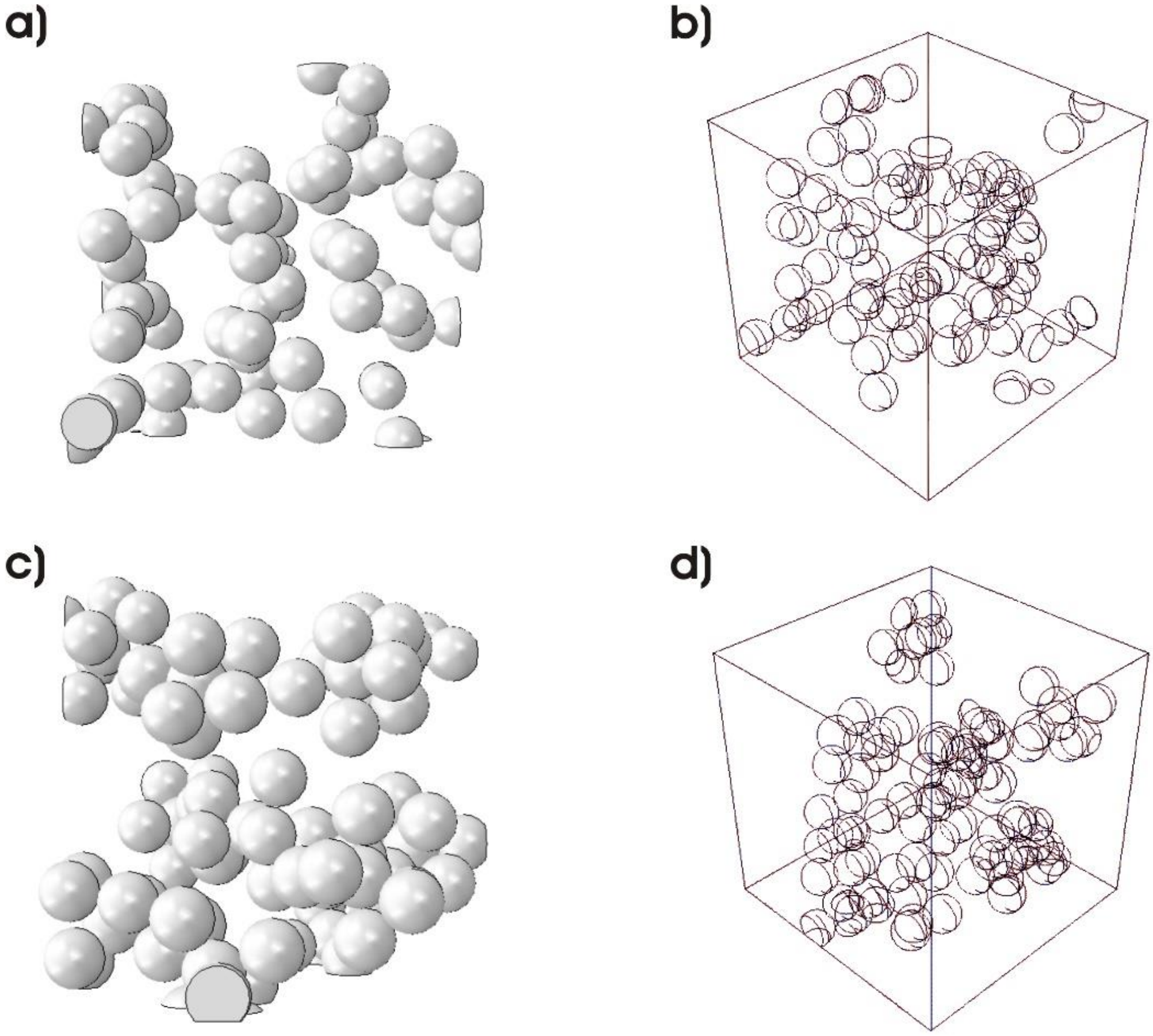

Fig. 10. a) & b) Chain cluster, c) & d) Cloud cluster for spherical particles.

For the cloud cluster all particles are placed next to the initial particle. The specific location of every subsequent particle is randomly selected. This configuration is depicted in Fig. 10 c) d).

Of further interest is the amount of particles and their effects on the overall elastic material properties. For this a study was carried out, which compares the effective Young's moduli of the composite for different chain lengths (Fig. 11) and different sizes (number of added particles) of the cloud cluster (Fig. 12).

The lengths of the chains do not seem to have an effect on the overall elastic material properties. Considering the cloud cluster a slight deviation can be observed.

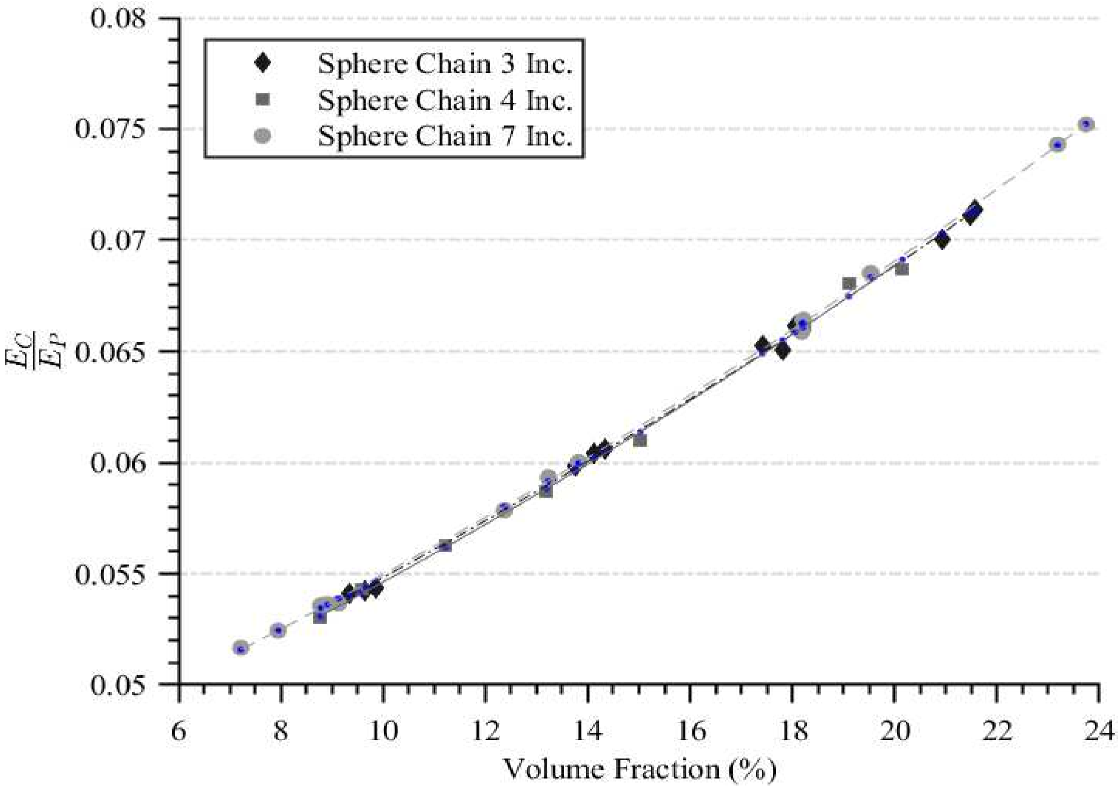

Fig. 11. Normalized effective Young's modulus of the composite for different chain lengths for X1 direction.

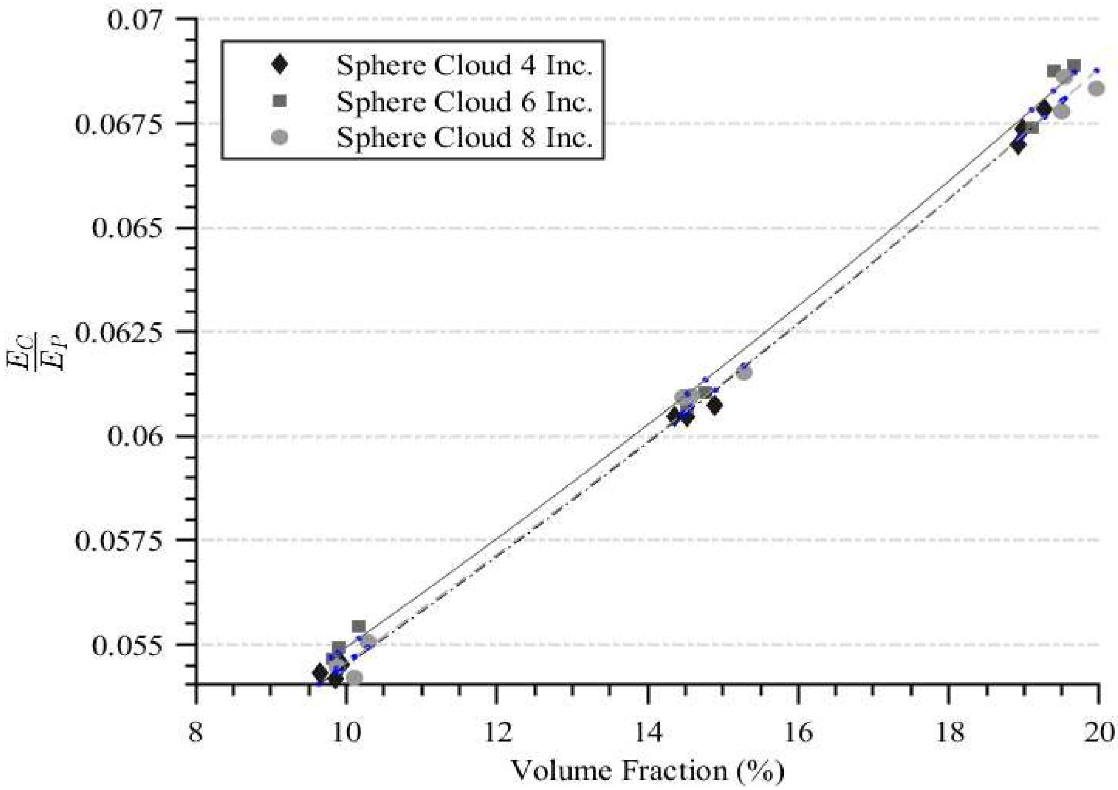

Fig. 12. Normalized effective Young's modulus for different cloud cluster sizes for X1 direction

Finally, the different placement methods, that are periodic distributed single particles, chain and cloud clusters were compared in Fig. 13.

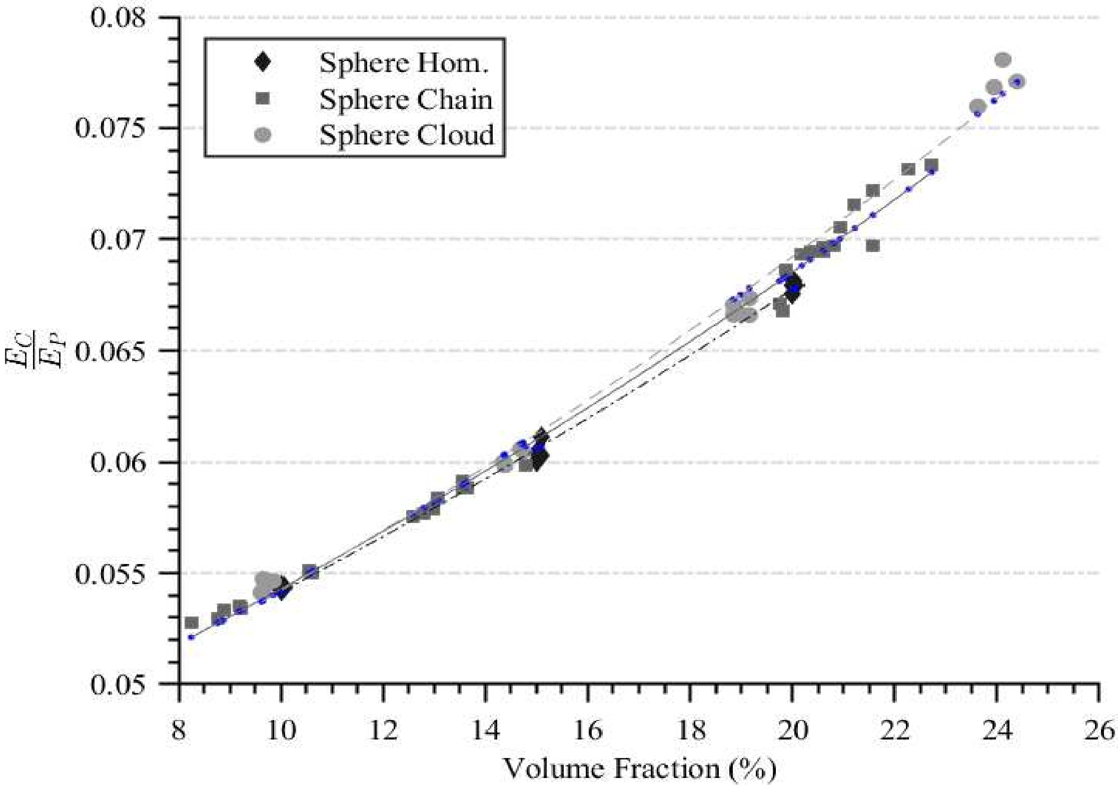

Fig. 13. Normalized effective Young's modulus of the composite for different distributions of the spherical particles in X1 direction.

It can be seen here that the cluster configurations achieve greater Young's moduli in general compared to periodically distributed single particles. The difference in Young's modulus even grows with an increase in volume fraction of the particles.

A further interesting result of the evaluation is the difference between the clusters themselves. Different cluster formations do lead to measurably different Young's moduli. Here (Fig. 13) we can see that the cloud clusters do outperform the chain clusters considering the effective Young's modulus of the composite.

In the following steps the influence of the ellipsoidal particles on the effective composite properties was studied. The algorithm used for the placement of the sphere particles beforehand was then altered to calculate the center points of the ellipsoids, which are in contact with each other. The general direction the clusters can grow is random. The difference in the cluster creation methods are which surfaces of the ellipsoids are in contact. Chain like clusters only allow contact between the surfaces of the previously and subsequently placed particles. This way enabling the different forms of particle clusters (chain and cloud). This algorithm was used to create the RVEs, as can be seen in Fig. 14. The ellipsoids are strictly oriented along the X3 axis.

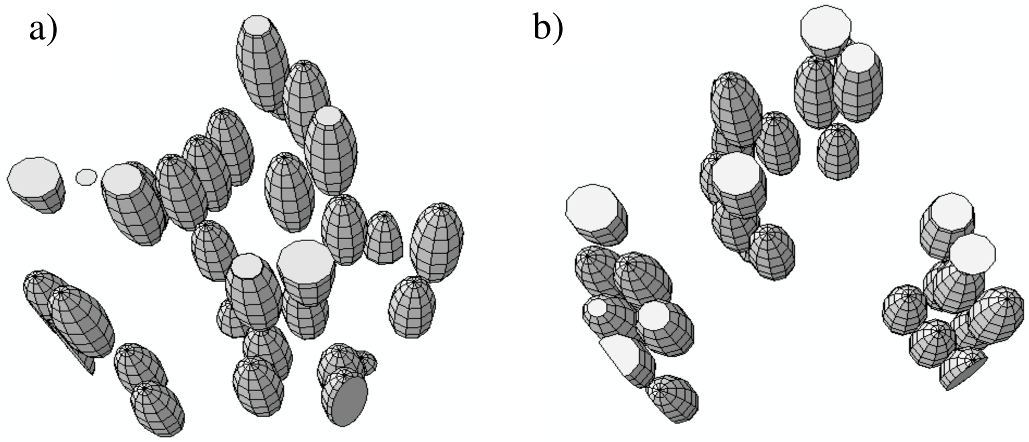

Fig. 14. Multiple particle set up for ellipsoidal particles in a) chain cluster and b) cloud cluster

The Young's moduli for the three different placement methods (periodic single (homogenous), chain and cloud cluster) were evaluated. The results for the X1 direction are depicted in Fig. 15, and those for the X3 direction are shown in Fig. 16.

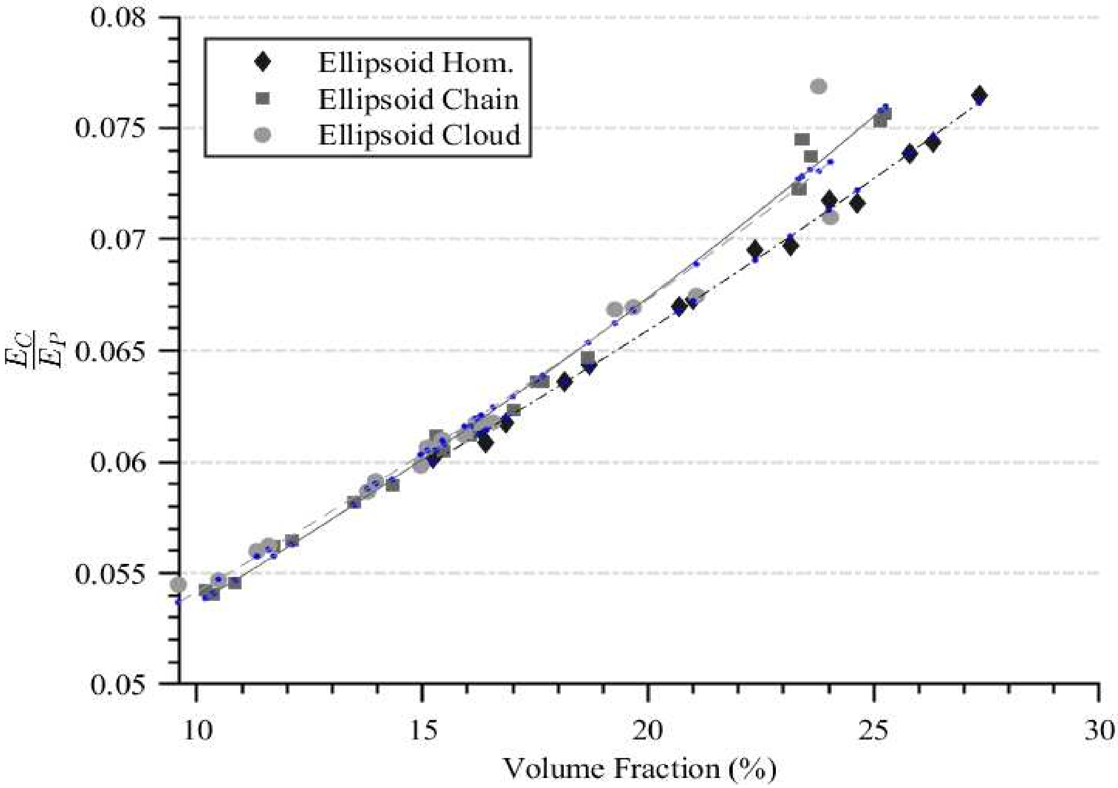

Fig. 15. Normalized effective Young's modulus of the composite for different distributions of the needle-shaped particles in X1 direction

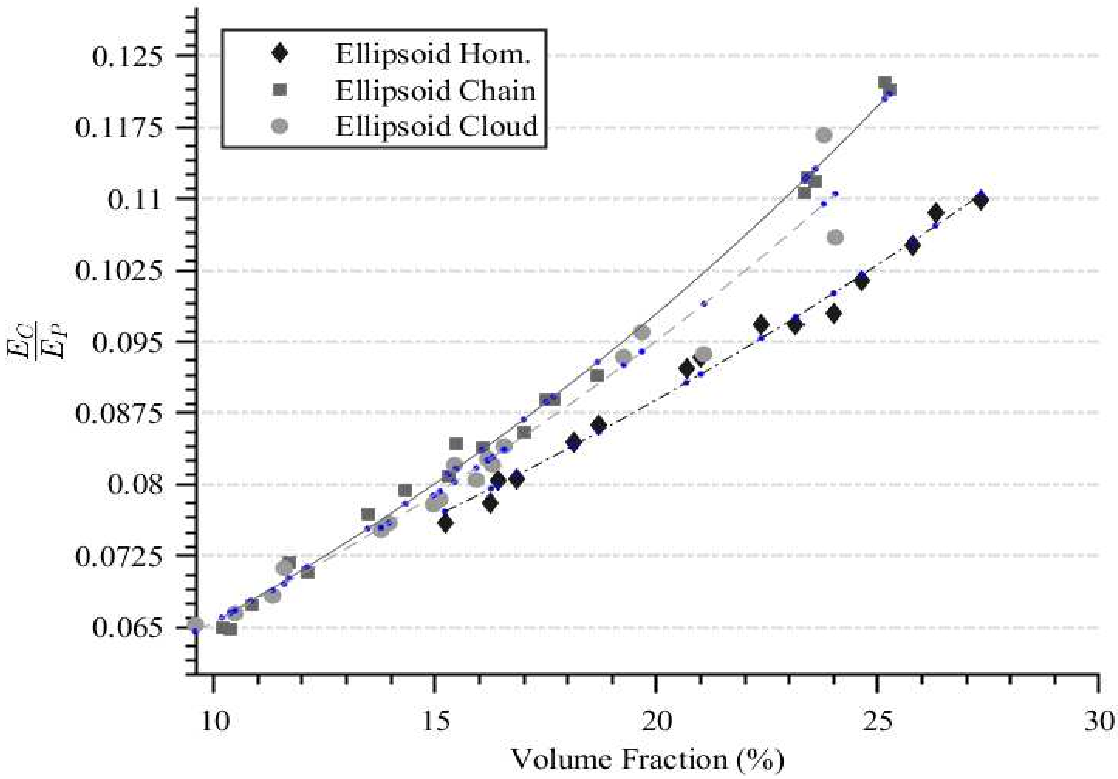

Fig. 16. Normalized effective Young's modulus of the composite for different distributions of the needle-shaped particles in X3 direction

The differences between the cluster and homogenous (periodic singular inclusion) positioning methods of the particles reappear, as was seen in Fig. 13 for sphere particles. Clusters generally outperform the homogenous distribution considering again the effective Young's modulus of the composite.

In stark contrast to the results for the spheres (Fig. 13), this time the chain clusters achieve greater Young's moduli compared to the cloud clusters, which is highlighted for the X3 direction.

The conclusion must be drawn that type of cluster and the particle cannot be studied independently from each other. The root cause of this shift in the clusters influence on the effective elastic properties requires further research.

4 Outlook

Both the SEM as well as the numerical analysis are part of a joint project and were carried out in parallel. Thereby, size and shape of the particles and their distribution within the polymer matrix were studied. A numerical model for predicting the elastic properties of the composite was built and successfully validated in numerical calculations.

In the next step, size and shape of the modeled particles as well as their orientation within the matrix will be adjusted to the above-mentioned new findings. Volume elements consisting of homogenous distributions of the particles with scattered clusters will be studied. In consequence, based on the adjusted design of the microstructure more realistic results are expected.

Furthermore, the investigation of the filler particles will be continued by examining the surface roughness of the particles. In parallel, the mechanical parameters will be also determined by carrying out experimental tests like the standardized tensile test. Thereby, the calculated parameters of the numerical investigation can be verified by comparing them to those of the experiments.

Acknowledgements

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