NON-DESTRUCTIVE DETERMINATION OF MORPHOLOGICAL PARAMETERS OF POLYMER BASED PARTICLE COMPOSITES BY MEASURING PERMITTIVITY

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Abstract
Additives give polymers specific properties (e.g., electrical, optical, mechanical properties). However, it remains a challenge to embed shear-sensitive flaky particles (ssFP) in a polymer. Conventional mixing fractures many ssFPs, which deteriorates the composite's properties. The aim of this study was to develop a non-destructive testing technique which allows to monitor the successful aspect ratio preservation of ssFPs after mixing. The testing is based on the measurement of the composite's permittivity via the cavity perturbation technique. We rely on the microstructure property correlations developed by Ondracek [*Z. f. Werkstofftechnik*, 8:280-287, 1977] to determine the aspect ratio of the embedded ssFPs. An epoxy with mica-based ssFP was used as model system where the ssFPs featured a mean area equivalent diameter of 42 µm. The morphology of the ssFPs was determined by the analysis of scanning electron microscopy images and modelled via spheroids. The analysis of the measured composite's permittivity shows that the determination of a mean particle aspect ratio is possible via measuring the composites' permittivity. This preliminary study demonstrates that the presented technique can be considered as a promissing non-destructive testing method for monitoring the integrity of embedded ssFPs.

1. Introduction

To endow polymers with specific properties (e.g., electrical, optical, mechanical properties) a variety of additives are added to the polymers, forming a polymer based particle composites. Flaky particles such as pearl luster pigments have unique luster and color effects. It is a challenge to embed shear-sensitive flaky particles (ssFP) intactly into a polymer matrix. The mixing process often fractures these particles, which deteriorates the composite's properties (e.g. electrical, optical, mechanical properties). Thus, techniques are required to embed ssFPs without applying destructive shear forces. To render an in-situ optimization of the mixing process possible a suitable, preferably non-destructive technique is necessary to monitor the integrity of the ssFPs.

Beside the intrinsic properties of the individual phases, the properties of a multiphase material depend on the microstructure of the composite. This is the geometrical arrangement and the geometry of the individual phases. To predict the properties of a composite it is possible to use bound concepts [2-6] or concept based on the stereometric microstructure data of the composite [1]. Bound concepts gather information on the property range theoretically possible for any combination of the individual phases. In contrast, concepts based on the composite's stereometric microstructure predict the composite's properties concrete – not a range of properties. In the following, we turn to the concept used by Ondracek [1]. This concept describes the embedded particles as spheroids, which are aligned in the same

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direction. Hereby, a variation of the spheroid's aspect ratio enables the description of closed-cell composites based on plate-like up to a fibrous particle shape.

1.1. Aim of the Study

The aim of this study was to develop a non-destructive characterization technique for the integrity of shear-sensitive flaky particles with high aspect ratios – particles with an area equivalent diameter of several micrometers and a thickness below one micrometer. To this end, we tested the hypothesis that the mean aspect ratio of the particles embedded into a polymer matrix can be determined via measuring the composites permittivity and applying the concept presented by Ondracek [1].

2. Materials and Methods

The following section provides information on the used raw materials such as the resin system and the particulate fillers, the sample preparation as well as the characterization of the composites and the geometrical particle model. In addition, the cavity perturbation technique as well as the applied concept to determine the composite's morphology will be detailed.

2.1. Materials

The resin system used in this study was prepared by mixing the epoxy resin Biresin CR81 (Sika Deutschland GmbH Stuttgart, Germany) with the hardener Biresin CH81-6 (Sika Deutschland GmbH Stuttgart, Germany). According to the manufacturers instructions, the resin and hardener were mixed in a ratio of 10:3 parts per weight. As filler a mica-based flaky particle system was used – Iriodin 153 (pearl flash pigment, Merck KGaA, Darmstadt, Germany). Iriodin 153 are titania coated mica pigments with a particle size between 30 and 100 μm.

2.2. Sample Preparation

All samples were prepared by adding the particles (Iriodin 153) to the previously prepared epoxy resin while stirring the suspension with a propeller at 1,000 rpm for 3 minutes. To eliminate voids the suspension was exposed to a vacuum for 10 minutes. Afterwards, the suspension was cast into a cylindrically shaped mold (diameter: 5 mm, length: 6 cm) and curred at 80 °C for 12 h. The particle volume fraction was determined by the amount of particles added into the resin under consideration of the particle's (2.8 g/cm³) and the resin's density (1.14 g/cm³). A list of the prepared samples is given in Table 1.

Table 1. Prepared composites – name, individual phases (matrix and filler) and composition.

Name	Matrix	Filler	Particle Volume Fraction [%]
R1	CR81/CH81-6	none	0
P01	CR81/CH81-6	Iriodin 153	1
P05	CR81/CH81-6	Iriodin 153	5
P10	CR81/CH81-6	Iriodin 153	10

2.3. Composite Characterization

To investigate the morphology of the filler particles, only they were dispersed in ethanol (0.01 wt%) and pipetted on a carbon substrate. After the ethanol evaporated the samples were imaged using a field

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emission scanning electron microscope (SEM; AURIGA 60, Carl-Zeiss Company, Germany) and an atomic force microscope (AFM; Dimension 3100, Digital Instruments, Santa Barbara, CA, USA). The particle's area aquivalent diameter and circularity were extracted from the SEM images. Height AFM images were taken to determine the particle's thickness.

2.4. Geometrical Particle Model

The flaky particles were geometrically approximated via spheroids. Therefore, the particle's thickness and the particle's area aquivalent diameter were used as rotation axis ($\boldsymbol{z}$) and the diameter of the spheroid's equator ($\boldsymbol{x}$), respectively. In addition, a constant particle volume was assumed.

2.5. Cavity Perturbation Technique

To determine the permittivity of the prepared samples the cavity perturbation technique was used. An illustration of the experimental setup and a detailed description of its function are provided by Jäger et al. [7]. The waveguide of the instrument works in the frequency range from 2.44 to 2.45 GHz. Before each measurement, a calibration of the setup was made by measuring the empty cavity. Afterwards, the sample was placed inside the waveguide and the changes were measured. Each sample was measured three times and subsequently averaged. For each composition three samples were measured.

2.6. Microstructure Property Correlation

The model concept used in this study describes the embedded phase/particles as spheroids with a mean orientation ($\boldsymbol{\alpha_P}$). This model allows to describe filler phase microstructures from a plate-like up to a fibrous one by adjusting the spheroid's aspect ratio. In addition, the special case of a spherical particle is included when the aspect ratio is one.

In the following, the particle volume fraction is assigned by $\boldsymbol{c_P}$. $\boldsymbol{\varphi_M}$ and $\boldsymbol{\varphi_P}$ refer to the (dielectric) property values of the matrix and the particles, respectively. The property value of the composite phase microstructure $\boldsymbol{\varphi_C}$ is predicted by considering the particle's mean aspect ratio $\boldsymbol{z/x}$ ($\boldsymbol{z}$ – mean particle thickness/spheroid's axis of rotation, $\boldsymbol{x}$ – particle's mean area equivalent diameter) and their mean orientation $\boldsymbol{\alpha_P}$. This can be determined by solving the following implicit equation (Eq. 1) for φ_C [1]:

$$1 - c_P = \frac{\varphi_P - \varphi_C}{\varphi_P - \varphi_M}\left(\frac{\varphi_M}{\varphi_C}\right)^R \left(\frac{\varphi_C - \varphi_P\left(1 - \frac{1}{2F_P + (1-3F_P)\cos^2(\alpha_P)}\right)}{\varphi_M - \varphi_P\left(1 - \frac{1}{2F_P + (1-3F_P)\cos^2(\alpha_P)}\right)}\right)^T \tag{1}$$

$$R = \frac{F_P(1-2F_P)}{1 - 2F_P - (1-3F_P)\cos^2(\alpha_P)} \tag{2}$$

$$T = \frac{F_P(1-2F_P)}{1 - 2F_P - (1-3F_P)\cos^2(\alpha_P)} + \frac{2F_P(1-F_P)}{2F_P + (1-3F_P)\cos^2(\alpha_P)} - 1 \tag{3}$$

$$F_P = \frac{z^2\left(\frac{\pi x}{z} - 2\sqrt{1 - \frac{z^2}{x^2}} - \frac{2x\sin^{-1}\left(\frac{z}{x}\right)}{z}\right)}{4(x^2 - z^2)\sqrt{1 - \frac{z^2}{x^2}}}. \tag{4}$$

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3. Results

In this study four composites of different particle volume fraction were studied. Firstly, this section presents the experimentally determined geometrical parameters of the embedded particles. Subsequently, the permittivities of the composites and a pure resin sample will be provided. At last, the aspect ratio of the embedded particles is given.

3.1. Composite – Geometrical Characterization

In this section the geometrical parameters required to model our prepared composites, in particular, of the particles were summarized. The particle's mean aspect ratio was calculated by dividing the particle's thickness by the area equivalent diameter.

Table 2. Particle characterization – mean area equivalent diameter, thickness, aspect ratio and circularity. Mean value and standard deviation.

Name	Area quivalent diameter [µm]	Thickness [µm]	Aspect ratio	Circularity
Iriodin 153	42 ± 10	0.9 ± 0.4	0.02 ± 0.01	0.69 ± 0.08

3.2. Composite – Permittivity

The permittivities of the prepared composites were determined using the cavity perturbation technique. The results, mean value and standard deviation are summarized in Table 3.

Table 3. Permittivities of the composites P01, P05 and P10. Measured at room temperature. Mean value and standard deviation. n=3.

Name	Permittivity
P01	2.57 ± 0.02
P05	2.78 ± 0.01
P10	3.05 ± 0.03

In addition, the permittivity of pure resin samples was measured as reference to verify the applied microstructure property correlation. The epoxy resin's permittivity was found to be 2.59 ± 0.01 (n=3).

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3.3. Microstructure Property Correlation – Estimation of the Measurement Accuracy

The properties of the composite depend on the direction of the applied field to the embedded particles. Figure 2 illustrates three possible orientations of the particles regarding the applied property field: particles with an orientation perpendicular to the applied field (z-axis), isotropic orientation of the particles regarding the applied field and particles with an orientation parallel to the applied field.

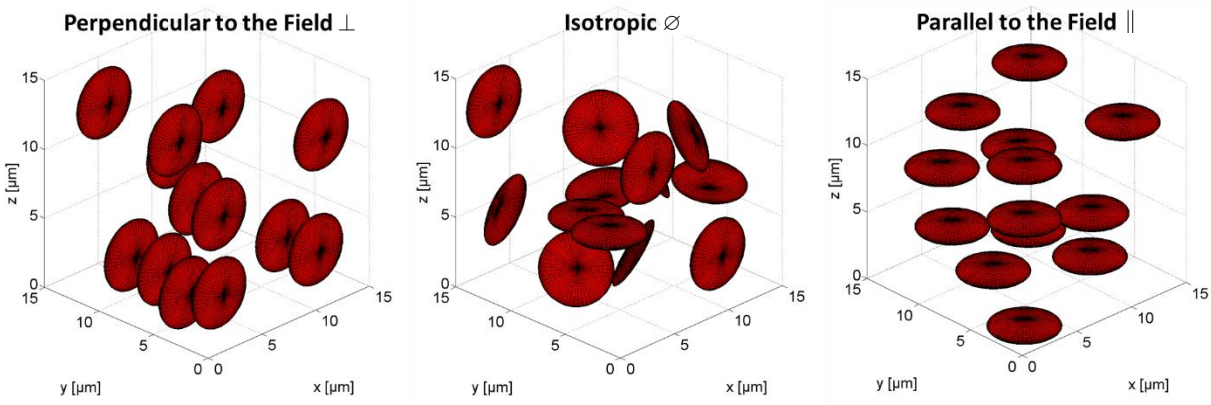

Figure 2. Schematical illustration of three particle orientations concerning the applied property field (direction of the z-axis): perpendicular (left; $\boldsymbol{\alpha_P} = 90°$), isotropic (middle; $\boldsymbol{\alpha_P} = 57°$) and parallel (right; $\boldsymbol{\alpha_P} = 0°$).

To investigate the influence of the particle orientation and their shape on the composite's permittivity a model composite made of alumina particles ($\boldsymbol{\varphi_P} = 9.1$) and an epoxy resin ($\boldsymbol{\varphi_M} = 2.5$) as matrix was used. Figure 3 a) illustrates the composite's permittivity as function of the particle volume fraction for three different orientations of disc shaped particles ($\boldsymbol{z/x} = 0$) and spherical particles ($\boldsymbol{z/x} = 1$). In addition, the difference between the profiles of different particle orientations and morphologies is given as function of the particle volume fraction, see Figure 3 b). In Figure 4 the same composite was investigated for different particle aspect ratios and orientations regarding the applied property field.

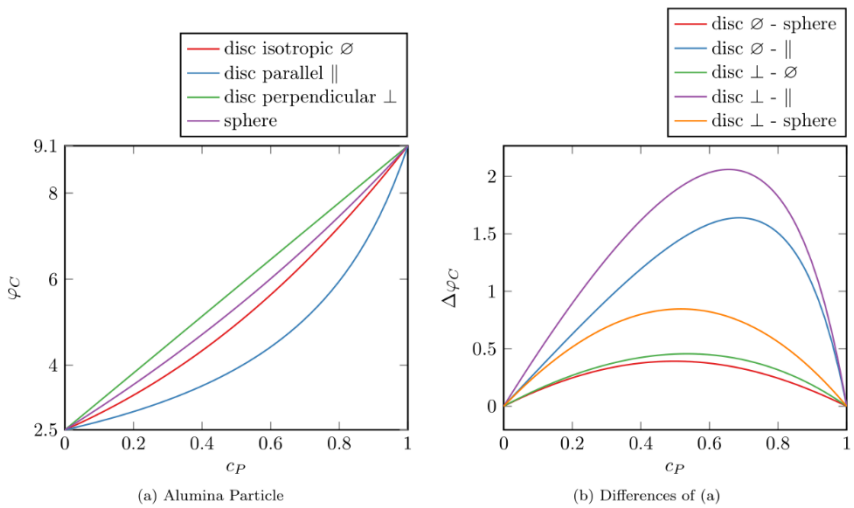

Figure 3. Left: Permittivity as function of the particle volume fraction for a model composite made of an alumina particle ($\boldsymbol{\varphi_P} = 9.1$) and an epoxy matrix ($\boldsymbol{\varphi_M} = 2.5$) for a sphere ($\boldsymbol{z/x} = 1$) and a disc ($\boldsymbol{z/x} = 0$) with different orientations concerning the applied property field. Right: Differences between different particle orientations and morphologies as function of the particle volume fraction.

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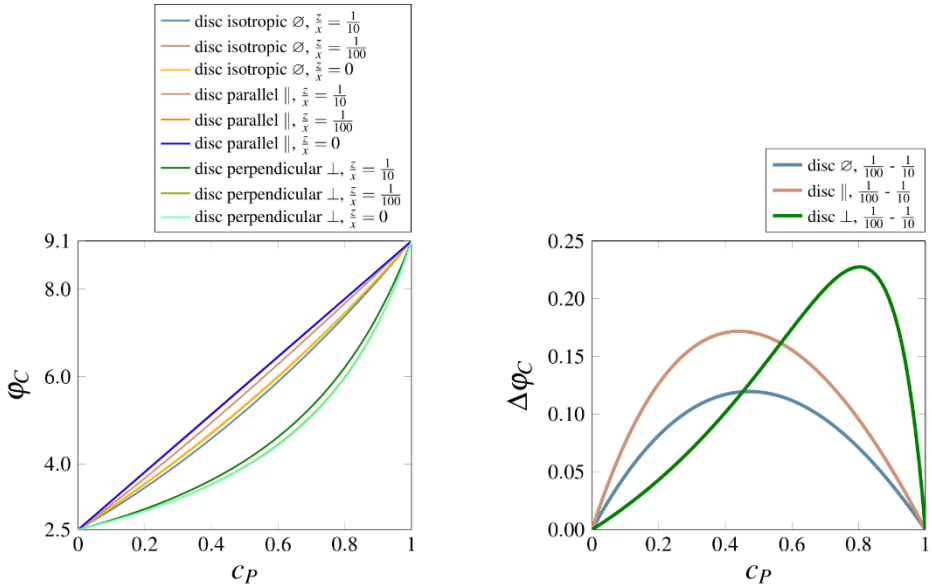

Figure 4. Left: Permittivity as function of the particle volume fraction of a model composite made of an alumina particle ($\boldsymbol{\varphi_P} = 9.1$) and an epoxy matrix ($\boldsymbol{\varphi_M} = 2.5$) for disc shaped particle morphologies of different aspect ratio ($\boldsymbol{z/x} = 0, 1/100$ and $1/10$) and different orientations concerning the applied property field. Right: Differences between different particle orientations and morphologies as function of the particle volume fraction.

3.4. Verification of the Microstructure Property Correlation

To test our hypothesis that the mean aspect ratio of the particles embedded into a polymer matrix can be determined via measuring the composites permittivity and the application of microstructure property correlations, the microstructure property correlation (Eq. 1) was fit to the measured permittivities. The fit was made assuming an isotropic particle orientation and a disc particle shape. Figure 5 shows the fit.

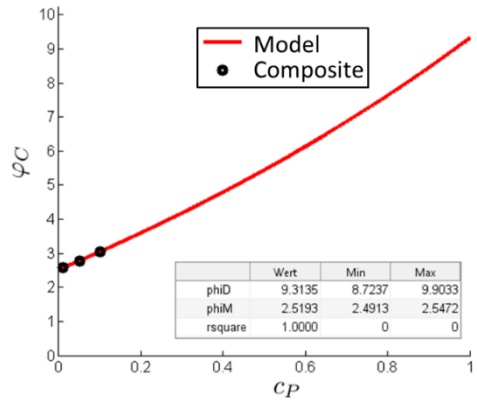

Figure 5. Fit of the composites' experimentally determined mean permittivities (black dots). The fit (red line) provides the permittivities of the epoxy resin (2.52±0.03) and the particles (9.31±0.59), the Pearson correlation coefficient of the fit (1.0) and the particles' aspect ratio (0.01±0.01).

The fit provided the particle's aspect ratio of 0.01±0.01. The permittivities of the epoxy resin and the particles were found to be 2.52±0.03 and 9.31±0.59, respectively.

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4. Discussion

The analysis of the SEM images in combination with the AFM images provided the particles' aspect ratio of 0.02±0.01. The fit of Eq. 1 to the composite's experimentally determined permittivities resulted in a particles' aspect ratio of 0.01±0.01. Thus, the hypothesis of this study can be considered as successfully tested. In the following a more detailed discussion of the obtained results will be given.

4.1. Microstructure Property Correlation – Estimation of the Measurement Accuracy

In Figure 3 a) and Figure 4 it was outlined that the orientation and the shape of the embedded particles affect the composite's permittivity significantly. The shape of the particles is only represented by one value – the particle's aspect ratio. An aspect ratio of one implies a spherical particle shape, an aspect ratio close to zero implies a plate-like particle shape and an aspect ratio close to infinity describes a fiber morphology. The comparsion of the profiles for different particle orientations shows that the composite's permittivity decreases with decreasing $\boldsymbol{\alpha_P}$ for disc-shaped particles.
The focus of Figure 4 was to study how a small change of the aspect ratio affects the composite's permittivity for different orientations. It is obvious that the composite's permittivity decreases only in a small extent in the case of a increasing aspect ratio – from 1/100 to 1/10, compared to a change of the particles' orientation. The difference between the different profiles, represented as an example by Figure 3 b), can be used to estimate the accuracy required to measure the composite's permittivity and to result in a statement about a potential change of the particles' aspect ratio compared to a control sample. These profiles show that the difference varies with the particle volume fraction, moreover, it has a maximum between 50 and 70 vol%. For particle volume fractions around this maximum the demand on a high accuracy of the permittivity measurement is reduced. However, the fact that the composite's permittivity strongly depend on the intrinsic permittivities of the raw materials (matrix and filler), the required measurement accuracy can be differ in a huge range.
In summary, this estimation shows that a high measurement accuracy is mandatory to prove a small change of the particles' aspect ratio. However, small changes in the particles aspect ratio can usually be tolerated in the manufacturing process, considering that in technical applications the particle size is a broad distribution.

4.2. Verification of the Microstructure Property Correlation

The aim of this study was to develop a method to monitor a composite in terms of a potential fracture of ssFPs induced during the embedding process. Figure 5 shows the fit of Eq. 1 to the composites' permittivities determined for different particle volume fractions. The fit provided the permittvities of the raw materials – the epoxy resin (2.52±0.03) and the mica particles (9.31±0.59), as well as the particle's aspect ratio (0.01±0.01). The permittivity of a pure epoxy resin sample was measured and found to be 2.59±0.01. As the reference for the permittivity of Iriodin 153 the permittivity of alumina was used, which is approximately 9 [8]. Thus, the permittivity of the resin as well as that of the particles match the values obtained by the fit. The particle's aspect ratio determined using the proposed method matches the aspect ratio obtained by the direct analysis of the particles via SEM and AFM images.
The fact that the permittivities used to determine the aspect ratio and the raw materials' permittivities are in the range of small particle volume fractions, lead to large confidence intervals (error) for the particle's aspect ratio as well as the particle's permittivity. To decrease these confidence intervals composites of high particle volume fractions need to be measured and included into the fit. It is expected that when a mode of dispersion is found where the aspect ratio is sufficiently preserved for high particle volume fractions that the same processing will also leave the particles intact at lower loadings. Another factor, which increases the confidence intervals is the number of parameters in Eq. 1. To decrease the number of parameters the permittivity of the matrix and the particles can be considered as verified and, thus, constant. However, in this study the raw materials permittivities were deliberately considered as parameters to use them as a benchmark for the proposed method. An additional uncertainty is the orien-

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tation of the particles, which was assumed to be isotropic, but this assumption was experimentally not verified. However, the samples were put in a tumble mixer during the curing of the epoxy resin to avoid the sedimentation of the particles and, thus, a preferred orientation of the particles is very unlikely.

The results of this study stated that the presented method is a promising method to determine the shape of flaky particles in a non-desctructive manner.

5. Conclusions

The analysis of the measured composites' permittivity demonstrates that a determination of the particle's aspect ratio is possible in principle. Thus, this technique provides a versatile non-destructive method to monitor a composite in terms of a potential fracture of ssFPs during the embedding process. As mentioned in section 4.2. there are still some uncertainties, such as the orientation of the particles and the permittivity of the particles. To eliminate these uncertainties a characterization of the composites' 3D morphology is presently underway, as well as a measurement of the particle's intrinsic permittivity.

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