USING A SPOUTED BED SPRAY GRANULATION PROCESS TO STUDY THE INFLUENCE OF ASPECT RATIO ON FRACTURE TOUGHNESS IN COMPOSITES

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Abstract – In this work the fracture toughness of copper-composite materials was studied. The volume fraction of copper was between 69 and 76 %. The study was carried out with two types of composites. The first type were composites containing spherical copper particles. The second type were composites with copper particles, which were rolled before they were pressed to a bulk material. The analysis of fracture toughness shows, that the composites with spherical particles have a mean fracture toughness of 1.69 MPa·m$^{1/2}$. The composites with higher aspect ratios of particles have a fracture toughness of 2.66 MPa·m$^{1/2}$. It corresponds to an increasing of approximatively 55 % for the toughness referred to composites with spherical particles.

INTRODUCTION

In nature there exist materials, which consist of one component, and also materials, in which two and more components are arranged in a particular way. Such materials with different components are named composites. Composites can be man-made or created by the nature. Naturally occurring composites consist mostly of ceramics and polymers (Gao, 2006), (Barthelat & Espinosa, 2007). Thereby ceramic particles are uniformly distributed in a polymer matrix and the content of ceramics is significantly higher than that of the polymer. The ceramic content in a polymer matrix is important for the reinforcement of the polymer. The polymer content is responsible for the ductility of the materials. There exist many natural composite materials. One of the best investigated natural materials is nacre. Nacre consists of small ceramic platelets, which are surrounded by a polymer matrix (see fig. 1). Although nacre consists of brittle ceramic and soft polymer, nacre has good combination of mechanical properties like stiffness, strength and toughness. The good mechanical properties could be achieved by arrangement of particles and polymer in an intricate way (Barthelat, 2007). On the one hand ceramic content in nacre is about 95 vol.%. On the other hand ceramic particles have a high aspect ratio and are organised in several hierarchical levels. Due to such a structure nacre has good mechanical properties.

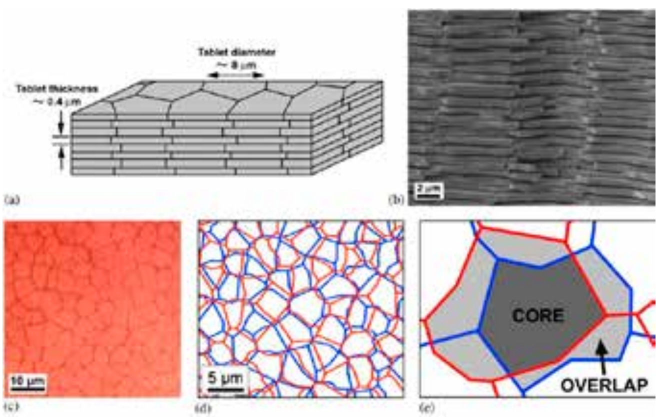

Fig. 1. Structure of nacre. (a) Schematic of the tablets arrangement in nacre; (b) scanning electron micrograph of a fracture surface in nacre; (c) top view of tablet tiling in nacre; (d) reconstitution of the arrangement of the tablets from one layer to the next; (e) core and overlap areas in the tablet arrangements (Barthelat et al., 2007).

Beside nacre more natural composite materials with hierarchical structure are known. These are for example elk antlers and toucan beak (Chen et al., 2008). The natural composite material with highest known tensile strength are limpet teeth. The strength of the teeth is 3-6.5 GPa and also the modulus of elasticity with 120 GPa is very high (Barber et al., 2015), (Lu & Barber, 2012). The good and sometimes extremely good mechanical properties of natural materials in spite of relative weak components gave an impulse to reproduce the natural structures. Therefore, in recently years, many attempts have been made to reconstruct the structure of the natural material and to achieve good mechanical properties. There exist some possible process routes to fabricate composite materials, but not every route can be applied for hierarchical materials. The problem in fabrication of hierarchical materials could be partially destroying of the existing hierarchical level during the build-up of the next level. This can happen due to the choice of an inappropriate solvent for example. One possible route for the reproduction of natural hierarchical composite materials is the spouted bed spray granulation process. The usage of the process has allowed achieving of high ceramic contents in composite materials (Wolff et al., 2014) as well as reproducing of the hierarchical structure (Brandt et al., 2013).

Spouted bed is a special form of fluidized bed with many applications in particle technology, such as drying, granulation, coating and sometimes also agglomeration. Spouted bed can be used for different type of particles. The spouted bed technology was investigated as alternative to fluidized beds for operating of coarse particles (Epstein & Grace, 2011). A fluidized bed has a process chamber with a constant cross section. Therefore, all particles are fluidized under similar conditions in such a bed. A spouted bed has, by contrast, an increasing cross section area of the process chamber. The form of the process chamber in a spouted bed can be conical as well as prismatic. Process air comes through a hole or through two slits in the chamber and particle-air spout forms in the middle of the chamber. As result only particles in the middle of the chamber are in the spouted state. So the energy consumption is significantly lower thereby. This is especially important for the application of coarse particles. Nevertheless, the spouted bed technology has also found application in processing of fine particles nowadays. Spouted beds are used also for cohesive and nonspherical particles (Epstein & Grace, 2011). For processing of fine and cohesive particles a special spouted bed was designed. As it was mentioned above, it has been already successfully applied for fabrication of highly-filled and hierarchical ceramic-polymer composites (Wolff et al., 2014), (Brandt et al., 2013).

Beside of the high-filling degrees and hierarchical structure of composite materials, high aspect ratio plays an important role for good mechanical properties of composites. This can be seen in the structure of natural occurring composite materials (Chen et al., 2008). Additional to the structure of natural composites Gao (Gao, 2006) postulates a theory about the influence of the aspect ratio on mechanical properties. Some attempts were made to reproduce structure of nacre. For example Behr et al. (Behr et al., 2015) tried to mimick the structure of nacre by sedimentation of particles, which are about 10 µm in diameter and 300 nm thick.

In this contribution we study the influence of the aspect ratio on the toughness of composite materials. The spouted bed was used for particles with mean size of 200 µm, which are still outside the typical application range of conventional spouted beds. Instead of ceramics or pre-structured particles, copper particles were used.

MATHERIALS AND METHODS

For the fabrication of composites, copper particles Rogal GK 100/250 (Schlenk, Germany) were used as filler. The particles have a density of about 8.9 g/cm³ and a modulus of elasticity of between 100 and 130 GPa. The particle size was measured with a Camsizer XT (Retsch Technology). The matrix polymer was polyvinyl butyral (PVB) Mowital B 30 H, which was provided by Kuraray Europe. The polymer has an elastic modulus of approx. 2.5 GPa and a tensile strength of 34.8 MPa. PVB is soluble in ethanol and has a very good adhesion to hydrophilic surfaces. The complete approach for the fabrication of composite materials contains spouted spray granulation, hot pressing of coated particles and characterisation of mechanical properties. The detailed description of the approach was done by (Eichner et al., 2017). But for the study the influence of the aspect ratio on composite materials properties, a further process step had to be added to the approach. The particles, which were coated in the spouted bed, were spherical (aspect ratio about 1). For achieving of higher aspect ratios, particles had to change the form. By the additional step, rolling, the form could be changed from spherical to platelets.

Before processing in the spouted bed polymer solutions were prepared. For the preparation, PVB in quantities between 10 g and 25 g was dissolved in ethanol with a constant concentration of 4 wt.%. In the first step the ethanol was heated up to a temperature of 30 °C and PVB was slowly added under stirring (magnetic stirrer, Witeg, Germany). For spraying-in of the solutions into the spouted bed a two-fluid nozzle (model 970, form 3 S1, Schlick, Germany) in bottom-spray configuration and a peristaltic pump (TU 200, Medorex, Germany) were used. A fill consisting of 500 g of copper particles was used in each experiment. Figure 2 shows the geometry of the used apparatus.

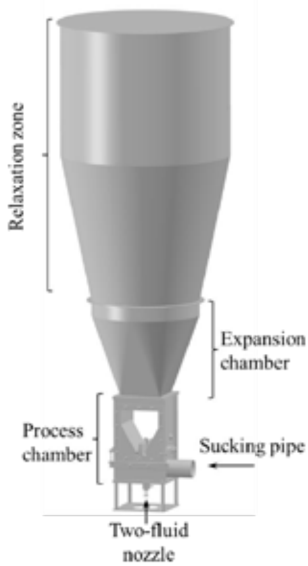

Fig. 2. Spouted bed for coating of fine particles.

This geometry is especially designed for the spouting of fine particles. The apparatus consists of a relatively small prismatic process chamber with two adjustable gas inlets, two conical parts and a cylindrical part. The bed is operated at under-pressure conditions. The air enters the apparatus through a sucking pipe, where it is heated up to the required temperature. From the pipe the air attains a wind box and then enters the prismatic process chamber through two thin horizontal slits, which height is adjustable. For a given air volume flow, the height of the slits specifies the gas inlet velocity. In the process chamber two air streams change the flow direction from horizontal to vertical by a profile in the middle of the process chamber and unite to a single gas jet. The gas transfers momentum to the particles and they follow the air flow within a turbulent spout. Particles carried by the gas jet pass the conical spraying zone. In the spraying zone, particles are coated by the polymer-solution, which is sprayed in by the two-fluid nozzle. After coating, the particles enter the conical expansion zone and the cylindrical relaxation zone. In these zones, the gas velocity is significantly lower. The particles become decelerated, change finally their flow direction under the gravity and slide downwards along the apparatus wall back in the process chamber. Hence the particle circulates in the apparatus, which is a characteristic attribute of the spouting process. During the period between leaving the spraying zone and the re-entry into the process chamber, the solvent from the polymer solution has to be evaporated in order to avoid agglomeration resulting in formation of large lumps occur.

For the usage of fine particles in a spouted bed, it has to be properly designed. The process chamber should be relatively small in comparison to large expansion and relaxation zones. The expansion and relaxation zones have to be large, because the strongly accelerated fine particles need a large height to be decelerated and to change the moving direction under the influence of the gravity. In this way elutriation of particles from the apparatus can be avoided (or at least strongly reduced). The major parameters for stable processing of fine particles are the air flow rate and the processing temperature, as well as the polymer content in the solution and the spraying rate of the polymer solution. Air flow rate has to high enough for a stable spouting, on the other hand it must not be too high, to avoid elutriation. Processing temperature, polymer content and spraying rate are responsible for evaporation of solvent from the solution and from the occurring of agglomeration accordingly. The appropriate parameter range should be found individually for each particle-solution system. For the used system the temperature in the prismatic process chamber was controlled on 30 to 40 °C. The volume flow of the spouting air was set to 25 - 30 m³/h at the beginning of the process. At the end of the process, the flow was increased up to 80 - 85 m³/h due to agglomeration of particles, which could not be completely avoided. The spraying rate of the solution was set to 5-10 ml/min.

After the granulation process, the granulated and partially agglomerated particles were hot-pressed, when toughness of composites with particles aspect ratio about one were measured. For increasing the aspect ratio of particles the rolling step was added. For the forming of particles a rolling mill W40 (Dinkel Maschinenbau, Germany) was used. The coated particles were rolled and as result small platelets were formed. The rolling step is shown in figure 3.

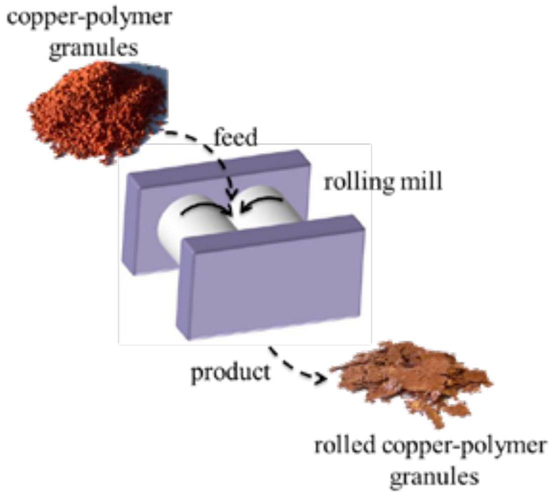

Fig. 3. Rolling step of coated copper particles.

After rolling formed platelets were aligned in a press die and were pressed to tablets using an automatic press PWV 300 (Paul-Otto Weber GmbH, Germany). Initially the die temperature was increased by a rate of 10 K/min to the final temperature of 160 °C at a small pressure of 40 MPa. After achieving of the final temperature, particles were pressed for 1 hour under isotherm conditions and at a pressure of 500 MPa. Not rolled particles were pressed directly after coating under same conditions. After pressing, the compact was grinded to get a smooth surface. The fabricated composite was cut in specimens with a rectangular cross section (size approximately 3-4 x 2 x 40 mm³ (height x width x length)) with a diamond saw Brillant 200 (ATM GmbH, Germany).

After pressing, the composition of the bulk materials was determined by measuring the geometrical density of the sample and by thermogravimetric analyses (TGA). For TGA 100 - 200 mg of the material m_{samp} were heated to the temperature of 450 °C (temperature higher than the decomposition temperature of PVB) and kept isotherm for 90 minutes. Nitrogen atmosphere was used in order to avoid an oxidation of copper at high temperatures. The complete calculation of the sample compositions can be found in Eichner et al. (2017).

Fracture toughness of the fabricated composite materials was studied by the measurement of crack resistance curve (R-curves) in load-displacement tests. For the measurements, three-point bending tests were carried out in a highly stiff loading device. The support rolls were mounted in a rigid metal frame. The distance between lower supports was 20 mm. The upper support was positioned in the middle between lower supports. For the measurements, an initial notch was produced with a razor blade (Kübler, 1997). In composites containing particles with increased aspect ratio, the initial notch was produced perpendicularly to the aligned particles. The measuring scheme with the initial notch is shown in figure 4.

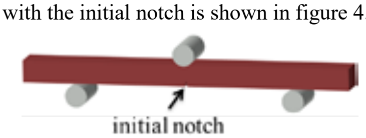

Fig. 4. Scheme of measuring device for R-curve determination.

The crack length was measured optically with a high resolution camera. The determination of crack resistance curves is based on crack-length and load measurement. On the basis of R-curve, the critical stress intensity factor K_{Ic} of composites was calculated.

The equation for the calculation of the stress intensity factor from three-point bending measurements can be found in (Fett & Munz, 1997):

$$K_{Ic} = \frac{3F \cdot L}{b \cdot h^2} \sqrt{a} \cdot \Gamma_M(\alpha) \tag{1}$$

$\Gamma_M(\alpha)$ is the geometry factor and it is calculated after following equation:

$$\Gamma_M(\alpha) = \frac{\sqrt{\pi}}{(1-\alpha)^{3/2}} \left[0.3738\alpha + (1-\alpha) \sum_{\mu,\nu=0}^{4} A_{\nu\mu} \alpha^{\mu} \left(\frac{h}{2L}\right)^{\nu} \right] \quad with\ \alpha = a/h \tag{2}$$

The factor L describes half distance between lower supports. The coefficients $A_{\nu\mu}$ are listed in Table 1:

Table 1. Coefficients $A_{\nu\mu}$ for the equation (2).

	$A_{\nu 0}$	$A_{\nu 1}$	$A_{\nu 2}$	$A_{\nu 3}$	$A_{\nu 4}$
$\mu = 0$	1.1200	-0.2387	0.4317	-1.7351	2.4145
$\mu = 1$	-1.8288	-0.2573	-4.9847	16.9047	-18.2883
$\mu = 2$	2.9741	0.2706	18.6767	-60.4912	59.9239
$\mu = 3$	-2.4280	0.5627	-27.3447	87.7078	-85.2405
$\mu = 4$	0.6712	-0.5184	13.5837	-43.5421	42.3503

RESULTS AND DISCUSSION

The fracture toughness was tested for different copper-polymer compositions. The results of the measured fracture toughness are presented in figure 5.

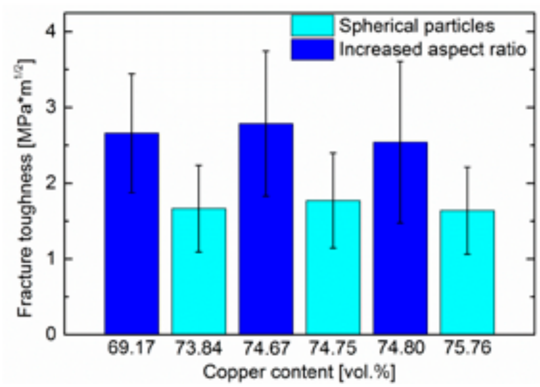

Fig. 5. Fracture toughness of different copper-polymer composites.

Figure 5 shows that the composites with spherical particles have lower fracture toughness than composites containing particles with increased aspect ratio. In the composites with spherical particles, the fracture toughness varies hardly despite of slight differences in composition. Also in composites with rolled particles, the fracture toughness stays relatively constant in spite of a stronger variation in composition in comparison to the composites with spherical particles. The measurements show a relative strong variation of fracture toughness values. The reason for this can be a relatively broad particle size distribution. During the crack propagation, the crack front is redirected and has to go around the particle. The surface of the crack, related to the crack growth, increases. The increase of the surface requires additional energy for the crack growth. So the elongation of the crack path increases the fracture toughness (Rösler et al., 2012). If a crack has to bypass a relatively fine particle, the surface increase and fracture toughness are relatively small. On the other hand, if a crack has to bypass a larger particle, the increase of surface is higher and therefore fracture toughness also grows.

In composites containing particles with increased aspect ratio, particles were aligned perpendicularly to the notch. For this reason, the crack path and fracture toughness increase significantly. But also the difference in crack path elongation between fine and coarse particles is stronger. The aspect ratio of particle with the same size can also vary. Although the particles were uniformly fed to the rolling mill, the slit between the rolls of the mills stayed constant and the rolls were rotated approximatively with a constant velocity, the amount and the size of the particles, which come at the same time in the mill, vary. The force distribution among the particles in the mill is changed and particles are deformed differently. So the aspect ratio of the particles can also vary with the same size. Due to the described possibilities, a stronger variation of fracture toughness values in composites containing particles with higher aspect ratios can be observed.

CONCLUSIONS

To sum up, in this work the influence of aspect ratio on fracture toughness was studied. Copper-polymer composites containing spherical particles (aspect ratio ~1) and containing particles with higher aspect ratios were produced and their fracture toughness was determined via three-point-bending tests. The results show that composites containing particles with higher aspect ratios have increased fracture toughness, even though the variation of fracture toughness values became stronger. The toughness of composites containing particles with increased aspect ratios is approximately 55 %higher than in composites with spherical particles and the mean value is 2.66 $MPa\cdot m^{1/2}$.

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NOTATION

L	half of the distance between lower supports, m	h	height of the beam, m
b	width of the bending beam, m	a	length of the notch, m
F	force, N		

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