REGENERATIVE AND BIO-BASED MATERIALS FOR SHEET MOLDING COMPOUNDS (SMC)

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ABSTRACT

In Europe, Sheet Molding Compound (SMC) has high market relevance in the field of glass fiber reinforced polymer composites (GFRPC) with a market share of almost 20% in terms of mass. SMC shows good mechanical properties that are comparable to aluminum while SMC-material is processed to net-shape components in compression molding process. Class-A surface quality and short cycle times of three minutes and less can be achieved. A conventional SMC semi-finished product mainly consists of a thermoset resin-paste, a variety of different additives, reinforcement fibers with a length of 24 to 48 millimetres, and different filler materials. The filler materials can be divided into non-functional and functional fillers, e.g. flame retardants. Calcium carbonate, with a density of about 2.7 g/cm³, is a commonly used non-functional filler material. Within this paper, the commonly used filler materials were replaced by regenerative and bio-based filler materials with a density of about 1.0 g/cm³. As bio-based fillers, different materials such as sunflower hulls, rapeseed meal and wood powder were used. By replacing the conventional fillers with bio-based fillers, same mechanical properties regarding tensile strength, Young's modulus and Charpy resistance could be achieved while reducing the density of the resin paste up to 18%. The partly bio-based semi-finished products showed same viscosity, storage behaviour and processability as conventional SMC semi-finished products.

1 INTRODUCTION AND MOTIVATION

Contrary to long and continuous fiber reinforced composites, SMC provides the ability of producing near-net-shape components in compression molding process at advantageous prices and short cycle times. With compression molding process, cycle times of three minutes and less can be achieved for the production of long fiber reinforced (24 till 48 mm) components with constant wall thickness and constant quality. By using different additives and formulations for the SMC semi-finished product, many different applications such as components with Class-A surface quality, insulating or flame-retarding behaviour can be achieved. Conventional SMC components show a density of 1.6 up to 1.8 g/cm³ based on the high filler content. SMC components are usually used for automotive or electrical applications. For automotive applications, SMC is used for components like fenders, trunk lids, mudguards, covering of loading areas. By reducing the weight of these components, a reduction of fuel consumption is possible.

Within this study, the use of regenerative and bio-based filler materials for SMC semi-finished materials was investigated. As bio-based filler materials different kinds of wood powder from hard- and softwood, sunflower hulls and rapeseed meal were investigated. These materials are not in competition with food industry and are available in industrial scale. Their density is between 1.0 and 1.2 g/cm³ and they have been tested to be processed into a SMC resin paste to produce SMC components. By replacing conventional filler materials with a density of 2.7 g/cm³, a reduction of the density of the resin paste of about 20 % is expected.

This paper should give a proof of principle for the processability of bio-based materials into a SMC compound. Therefore, different series of SMC compound were produced to show the influence of the

bio-based filler materials to processability and mechanical properties. All changes in the semi-finished product must not change the processability at all. The processing viscosity of the resin paste must be in between 15 and 30 Pa*s. The resin paste must be able to impregnate the glass fibers (typ: Owens Corning P204, 2400 tex, length: 1 inch) and transport them while processing. While processing in compression molding, no separation of fibers and resin should occur.

2 MATERIALS

Common SMC semi-finished products consist of a thermoset resin system, commonly unsaturated polyester (UP) resin (15 wt-%), a thermoplastic resin solved in styrene (9 wt-%), miscellaneous additives (6 wt-%), glass fibers (30 wt-%) and filler materials, which can be divided into functional and non-functional materials (40 wt-%), see Figure 1 [1].

At IVW, a SMC formulation which is robust for changes within the composition of the resin paste was developed. These changes can refer to resins, additives, filler materials, etc. This resin paste shows, compared to conventional resin paste, the same viscosity behaviour and the semi-finished material (produced SMC) shows same processability as conventional semi-finished products. Also the mechanical properties are comparable to those of conventional SMC materials.

The SMC-composition developed by IVW was the basis material for the presented study. The conventional non-functional filler material calcium carbonate ($CaCo_3$) was replaced by bio-based filler materials. As bio-based filler materials different by-products of wood- and food-industry were used. Therefore, different kinds of wood powder from hard- and softwood, sunflower hulls and rapeseed meal were tested in different pre-investigations regarding particle-size distribution, their influence to the viscosity of the resin paste and the moisture absorption [2, 3]. The density of the conventional $CaCo_3$-material is roughly about 2.7 g/cm³ [4], whereas the density of the bio-based filler materials is roughly about 1.0 g/cm³.

Based on the results of pre-investigation, different types of the filler materials were chosen. The filler materials, which show the overall best performance and are mostly comparable to the conventional filler materials, were used to be processed in a SMC semi-finished product. Therefore, semi-finished materials with a content of bio-based materials between 25% and 100% were produced.

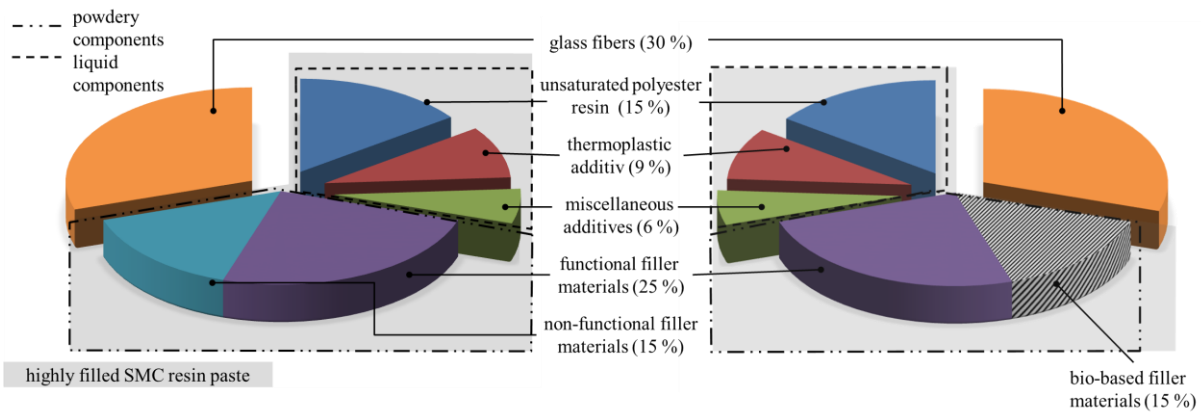


Figure 1: Mass fraction of the ingredients of a common SMC semi-finished product [2]

3 METHODS AND PROCESSES

3.1 Particle size determination

The particle size of the filler materials influences different properties of the SMC semi-finished product and the SMC part, e.g. fiber transport while press process, shrinkage compensation and viscosity drop while processing. There are different methods for the determination of the particle size available, for example: sieve analysis, laser diffraction analysis, dynamic light scattering, image particle analysis or sedimentation [5]. For this paper, sieve analysis on a vibratory sieve shaker (Typ: analysette 3 pro, manufacturer: Fritsch GmbH, Idar Oberstein) was used for the determination of the particle size distribution. Therefore, a stack of five different sieves with a mesh size between 25 µm

and 500 µm was used, see Figure 2. Hereby, the upper sieves have a bigger mash size than the lower sieves. The amplitude for vibration was 1.5 mm and the measuring time was 15 minutes.

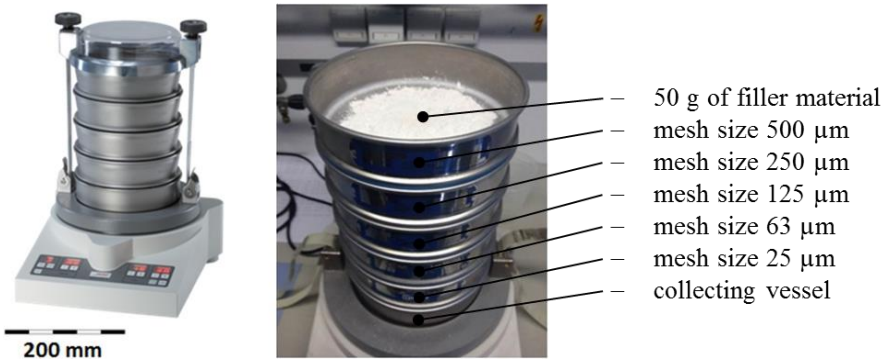


Figure 2: Left: vibratory sieve shaker; right sieves with different mesh size

3.2 Viscosity measurement

The viscosity of a liquid is a measure of its resistance to gradual deformation by shear or tensile stress. A fluid that has no resistance to shear stress is known as an ideal or inviscid fluid. Zero viscosity is observed only at very low temperatures in superfluid. All fluids have positive viscosity, which is higher than one at room temperature, see Table 1.

Material at room-temperature (25°C)	Viscosity mPa*s
Water	1.00
Olive oil	100
processable SMC resin paste	**30,000**
Honey	100,000

Table 1: Overview of viscosity values

A SMC resin paste with a variety of different filler materials acts as a non-Newtonian fluid with a thixotropic nature. Therefore, it is important to know the influence of the components of the resin paste to the viscosity behaviour. In this paper, the viscosity was measured according to EN ISO 2555:1999. Figure 3 shows the arrangement for the determination of the viscosity in laboratory scale. As the viscosity is very sensitive to temperature, all measurements were made at temperature of 25°C of the resin paste and thus, a double walled vessel was used. The vessel was flown through by tempered water, which was heated up to 25°C by a heating unit. The temperature of the resin paste was measured with a temperature sensor, which was inserted into the resin paste. The viscometer used was Brookfield LVDV II+ pro tools with spindle number 64, spindle type 7. This spindle was chosen for the measurement of the expected high viscosity in a range of 15 - 30 Pa*s. At the beginning of every measurement series, the viscometer was calibrated with a silicone calibration fluid.

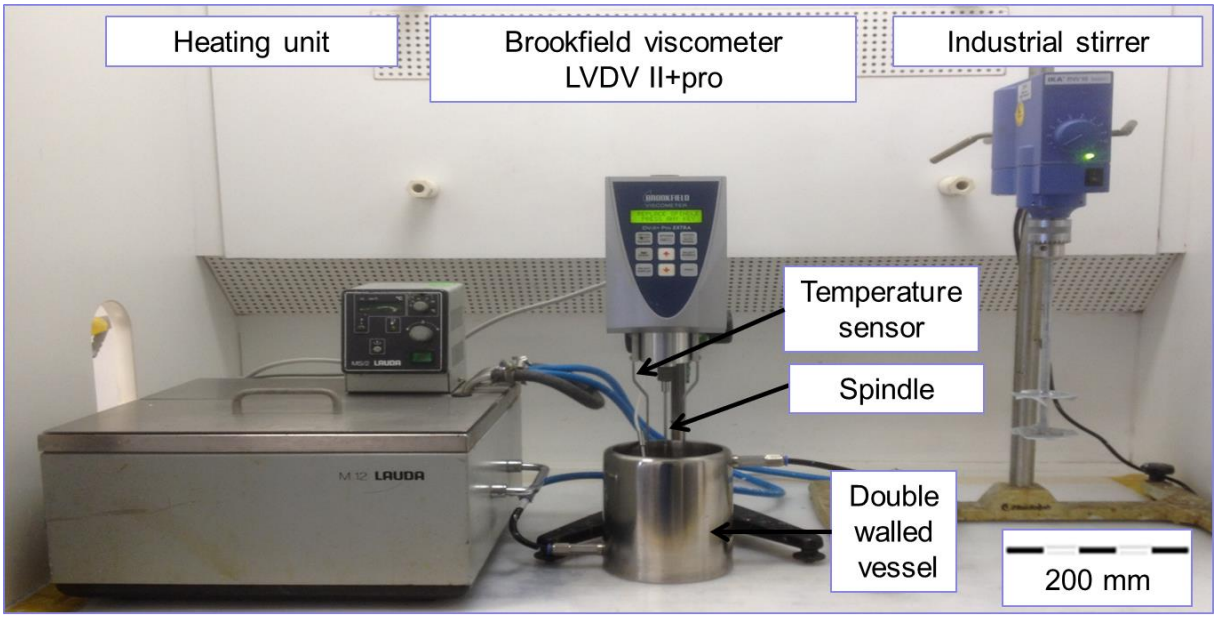


Figure 3: Arrangement for viscosity measurement

3.3 Density measurement

There are different methods for the determination of the density of a liquid component available. These are for example pycnometer, densymeter, areometer and ultrasonic pulse echo method. In this paper, the pycnometer was used for the measuring of the SMC resin paste's density. Figure 4 shows the pycnometer with a volume of 49.998 ml and the single steps which have to be made for the calculation of the resin paste density. At first the weight of the empty pycnometer (1) is determined with a scale with five decimal places. The pycnometer is filled up completely with the SMC resin paste (2) and subsequently the lid is closed by hand to a perfect fit (3). Within this closing process, superfluous SMC resin paste flows out (4). This resin paste has to be removed completely. After this process step, the weight of the fully filled pycnometer is determined again on a scale with five decimal places.

(1) (2) (3) (4)

Figure 4: Processing steps of density measurement with pycnometer

The density of the resin paste is calculated according to equation 1:

$$\text{Density of resin paste} = \frac{\text{weight of filled pycnometer} - \text{weight of empty pycnometer}}{\text{volume inside pycnometer}} \quad (1)$$

3.4 Production of SMC at laboratory scale

The SMC resin paste was produced in laboratory scale in a masterbatch of 800 g each with an industrial IKA stirrer (Typ: RW16 basic, manufacturer: IKA®-Werke GmbH & Co. KG, Staufen). Therefore, all the components, similar to the composition given in Figure 1, were mixed up in a defined order. In different master batches, the conventional filler materials were replaced by bio-based

filler materials in steps of 25%, starting from 0% and ending at 100%. The last component which is added to the recipe is magnesium oxide (MgO). After MgO is mixed up to the resin paste, a thickening reaction takes place and the viscosity of the resin paste rises from 1,000 to 30,000 mPa*s within 30 to 45 minutes, see Figure 5.

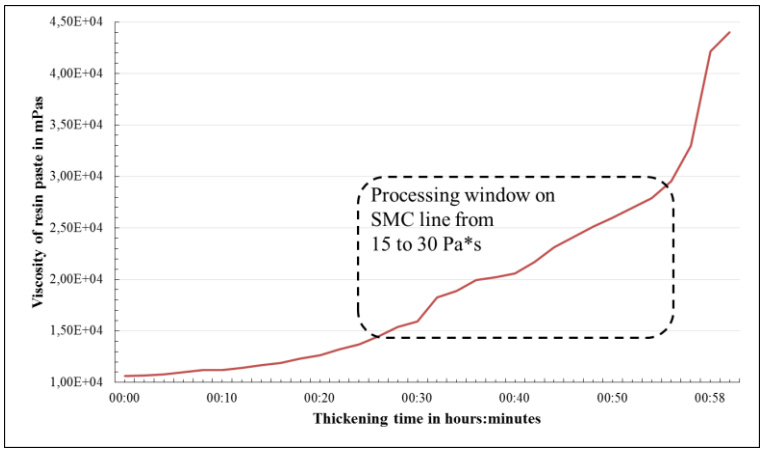


Figure 5: Viscosity of the resin paste after adding MgO

To produce a semi-finished SMC product within this time period the resin paste (1) is spread homogeneously with defined area weight on a styrene-proof carrier film (2). On top of the resin paste film, the pre-cut glass fibers are spread homogeneously on the half of the resin paste (3). Then the resin paste is folded to receive a stack of resin paste / fibers / resin paste. In the thumping unit of a conventional SMC production line the fibers inside the stack are impregnated by the resin paste (4). After this impregnation a processable SMC semi-finished sheet is achieved (5).

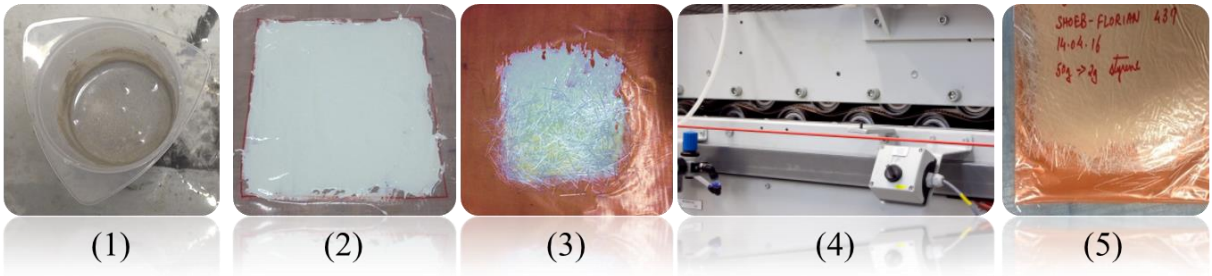


Figure 6: Processing steps of laboratory scale SMC

In the last step, the SMC semi-finished product was sealed styrene-proof and stored for 5 to 8 days in an air-conditioned and dark storage room. In that time maturing process proceeds and viscosity rises till 1,000,000 mPa*s. After maturing period, the SMC semi-finished product will be processed in a compression molding process.

3.5 SMC compression molding process

SMC semi-finished material is processed on a parallel controlled press by compression molding process. Therefore, the semi-finished material is processed on tools with sealing edges to large and partly high complex parts such as fenders, trunk lids, spoilers for automotive applications, and cabinets or lamp housing for electrical applications. Before the material is placed into the press, it is cut with CNC-controlled cutting machines to the required dimensions which occupy normally between 40 and 60 % of the mold surface. After cutting, the material is stacked to packages which are positioned very precisely in the mold. The temperature of the isothermal mold is set between 130 and 160°C, the pressure inside the closed mold is at about 100 - 120 bar. A standard cycle time for SMC-processing is three to five minutes [6]. While closing the mold, the SMC semi-finished material is heated up by the heated tool. The viscosity of the semi-finished SMC material drops and enables the material to flow and fill-up the mold completely. Based on the temperature of the mold, the curing of the semi-finished

material and thermal shrinkage compensation are initiated. After curing time, which is depending on the wall thickness (2 minutes per mm wall thickness), the part can be removed from the mold and be reworked.

For this study, a small laboratory scale press was used. The pressure inside the press mold was 120 bar, the temperature was 140°C, cycle time was five minutes and mold occupation was 60%. Figure 7 shows the process steps from the matured SMC semi-finished product till the pressed sample in laboratory scale.

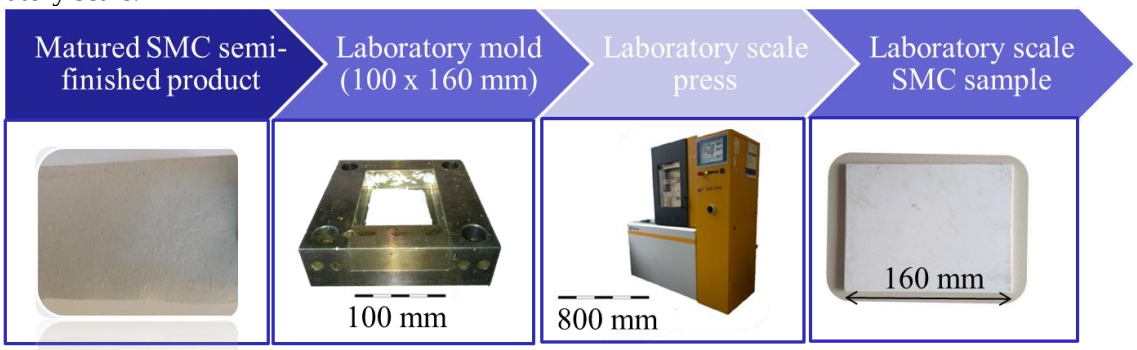


Figure 7: Processing of SMC semi-finished product on laboratory scale

3.6 Light microscopy

The dispersion, impregnation quality and the void content of the bio-based filler materials within the SMC samples were analyzed using a light microscope. Therefore, small samples (20 x 20 x 3 mm³) of the different processed SMC materials (standard SMC composition, 50 wt% and 100 wt% of bio-based filled SMC materials) were cut out of the pressed laboratory samples. The samples were cut out in the edge zones of the sample plates at the end of the flow front (in flow direction) with a distance of 10 mm to the edge. These samples were embedded into a cold curing EP-resin. After the curing of the resin, which takes about 8 hours, the samples were grounded and polished. Pictures of the cross section were made with different magnifications up till 500.

3.7 Mechanical properties

Tensile properties were measured according to DIN EN ISO 527-2 IBA 75x5 on a Zwick universal testing machine, type 1485 [7]. Specimen structure is a dog-bone structure. The specimen size is 70 mm x 10 mm, thickness 4 mm. A load cell with 10 kN maximum load was used.

Bending properties were measured according to DIN EN ISO 14125 on a Zwick universal testing machine, type 1485. Specimen size was 80 mm x 15 mm, thickness 3 mm [8]. A load cell with 10 kN maximum load was used.

Charpy impact resistance was tested according to DIN EN ISO 179-2 with unnotched specimens, type 2. Specimen size was 80 mm x 10 mm, thickness 3 mm, span L = 60 mm [9]. A 4 kN hammer was used.

For a statistical basis, at least seven tests were made for every test configuration.

3.9 Moisture absorption test

Moisture absorption test is very important for products with bio-based components. As the bio-based filler materials are derived from nature, they are hydrophilic. If they are not surrounded by the SMC resin-paste completely, they will take-up water and the SMC component starts to get moldy. In this paper the water-uptake from conventional SMC components and bio-based components was tested. Therefore, the samples were stored in a climate chamber (Typ: SB 22 160, manufacturer: WEISS Umwelttechnik GmbH, Reiskirchen-Lindenstruth) with controllable atmosphere. The temperature was set to 40°C and humidity to 80%. The weight of the samples was measured at the beginning of the test, after that the samples were placed inside the climate chamber for 16 days. Every day the weight of the samples was measured as a rise of the weight is an indicator for moisture uptake at all.

4 RESULTS AND DISCUSSION

4.1 Results of particle size distribution

Figure 8 shows the results of the particle size distribution of the different filler materials. As reference material CaCO3 (Millicarb) was used. It is clearly visible, that the particle size is between 25 and 500 µm. More than 75 % of particles are in a range of 63 to 125 µm. The bio-based filler materials generally show a similar particle size distribution than the reference material. In detail, sunflower hulls show comparable particle size distribution, more than 90 % of the particles are in the range of 63 to 125 µm. Rapeseed shows smaller particles (25 to 125 µm), wood powder shows much smaller particles, with more than 50 % are smaller than 25 µm. To avoid an unsought influence of particle size, sunflower hulls and rapeseed are used for further investigations.

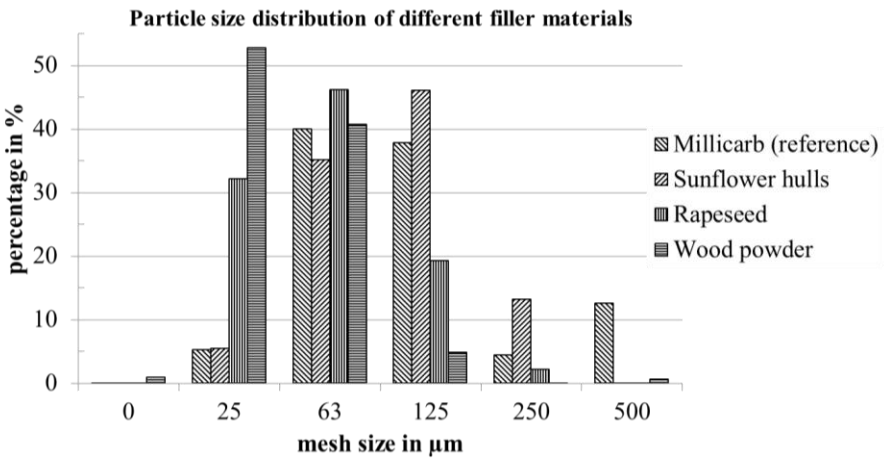


Figure 8: Results of particle size distribution of different filler materials

4.2 Results of viscosity measurement

Figure 9 shows the influence of the content of bio-based filler materials to the viscosity of the SMC resin paste. For a good impregnation of the glass fibers and the processability on the SMC line, a viscosity of the resin paste between 15 and 40 Pa*s should be gained. The standard SMC resin paste, developed at IVW, shows a viscosity of 20 Pa*s. There is almost no influence of the bio-based filler material up to a level of 75 %. By adding sunflower hull material as filler material the viscosity rises almost linear to the filler content till a level of 75%. In a resin paste with 75 % of bio-based filler materials the maximum impregnation viscosity and processability on a standard SMC line is reached. So sunflower hulls with a content of up to 75 % or rapeseed with a content up to 75 % are suitable for replacing conventional filler materials.

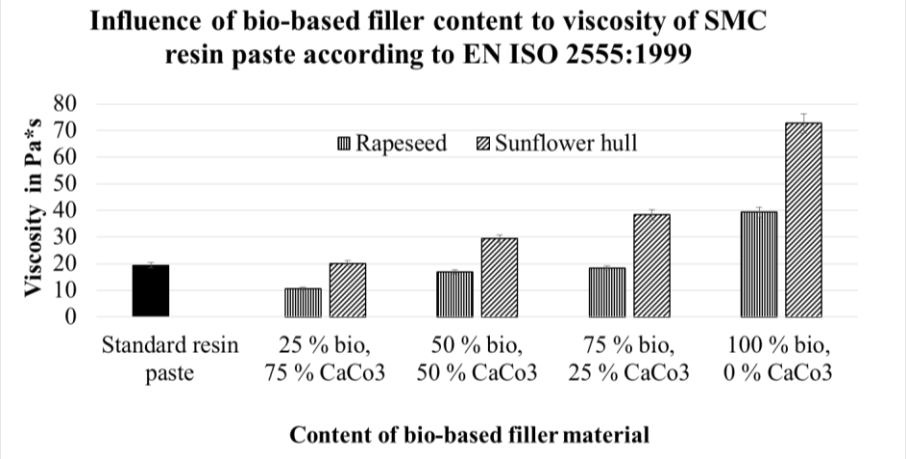


Figure 9: Influence of the content of bio-based filler to SMC viscosity

4.3 Results of density measurement

At first, the density of the IVW SMC composition including CaCO3 as conventional filler material was measured. The resin paste shows a density of 1.61 g/cm³. Based on this, a SMC semi-finished product with 30 wt-% glass-fiber content owns a calculated density of 1.86 g/cm³. Comparable standard SMC semi-finished products, which have same fiber mass content, hold densities of 1.6 to 1.8 g/cm³ [9], [10]. So, regarding density the IVW SMC composition is comparable with a conventional material.

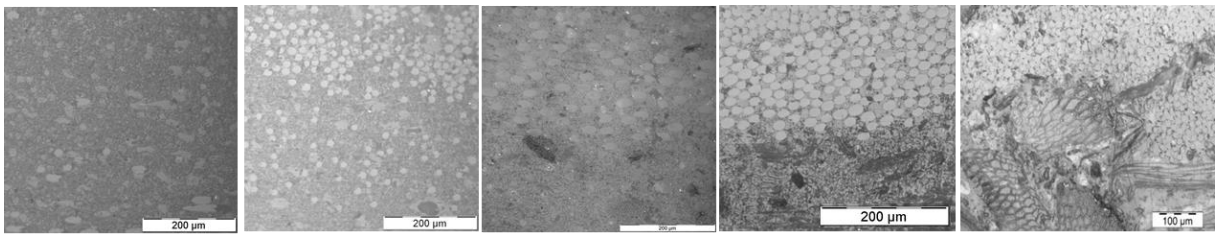
In a second step, the density of the resin paste with bio-based additives was measured. Therefore, standard filler materials were replaced in terms of mass by bio-based filler materials. With the use of sunflower hulls, the biggest decrease of density could be achieved. Table 2 shows the results of the density measurement. With a replacement of 50% of the conventional fillers by bio-based fillers, a reduction of the density of 13% could be reached. By replacing all filler materials by bio-based fillers, density could be reduced about 18%.

Content of bio-based filler materials [wt-%]	Density of resin paste [g/cm³]	Density of semi-finished product [g/cm³]
0	1.42*	1.80
50	1.23	1.59
100	1.17	1.51

Table 2: Results of density measurement

4.5 Results of light microscopy analysis

Figure 10 shows the results of light microscopy analysis of a SMC specimen with different content of bio-based filler materials. It is visible that with increasing bio-based filler content the homogeneous distribution of the reinforcement fibers tends to an island-like formation. This is based on an agglomeration of the bio-based filler materials at higher filler content. These agglomerations lead to lower mechanical properties. Furthermore, with increasing content of bio-based filler materials, pore content in the samples is rising. The agglomerates of the bio-based fillers are completely embedded with resin paste; a further reduction of the density of the semi-finished product could be reached, if the filler materials maintain their hollow structure



Reference 0 % bio-based filler material | 25% bio-based filler material | 50% bio-based filler material | 75 % bio-based filler material | 100 % bio-based filler material

Figure 10: Influence of bio-based filler content to pore content

4.6 Results of mechanical properties

4.6.1 Tensile test

The SMC materials with the bio-based filler materials (sunflower hulls and rapeseed) were compared to a reference material with a fiber mass content of 30%, see Figure 11 and Figure 12. The reference material was the IVW standard SMC material with standard filler materials. Up to a content of 75% of the bio-based filler material, the achieved results are better or even comparable to the values of the standard SMC material. More than 75% of bio-based fillers lead to a decrease of mechanical performance. A reason for this could be the high viscosity of the resin paste which leads to a worse impregnation of the reinforcement fibers.

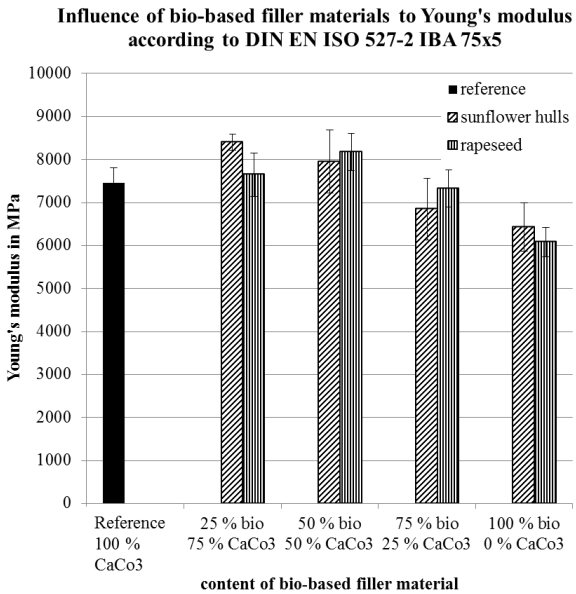


Figure 11: Influence of content of bio-based filler materials to Young's modulus according to DIN EN ISO 527-2 IBA 75x5

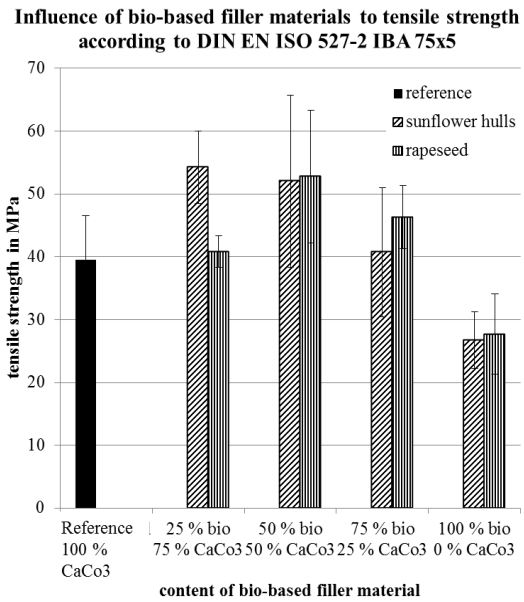


Figure 12: Influence of content of bio-based filler materials to tensile strength according to DIN EN ISO 527-2 IBA 75x5

4.6.2 Bending test

Figure 13 and Figure 14 show the results of three-point bending. It can be seen, that up to bio-based filler contents of 50%, the flexural modulus and flexural strength are comparable to the reference. At higher contents of bio-based filler materials, the mechanical properties drop down to less than 80% of the reference material values.

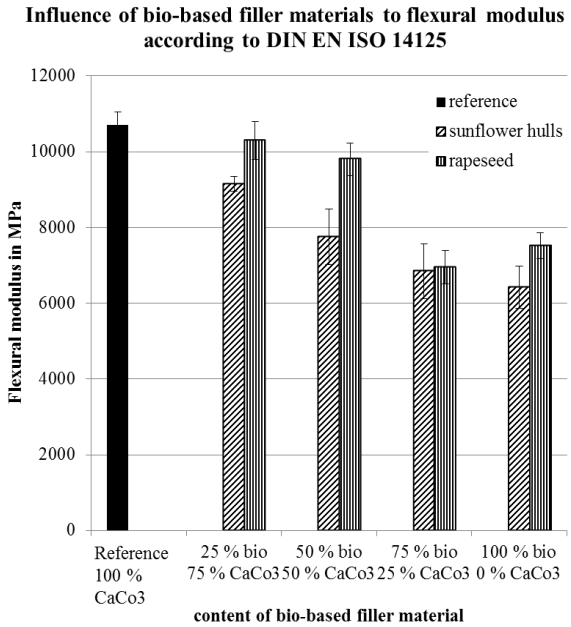


Figure 13: Influence of content of bio-based filler materials to flexural modulus according to DIN EN ISO 14125

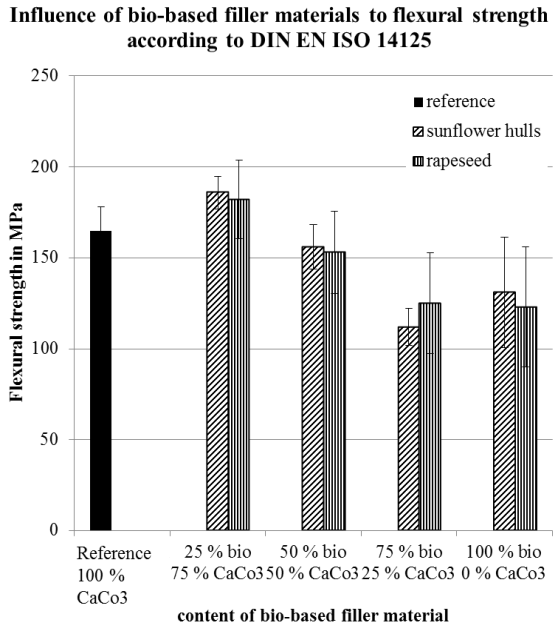


Figure 14: Influence of content of bio-based filler materials to flexural strength according to DIN EN ISO 14125

4.6.3 Charpy impact test

The impact strength of IVW material is comparable to conventional SMC material and shows an impact strength of 40 kJ/m^2. By replacing 50% of the conventional fillers with bio-based filler materials an increase of the impact strength of 41% could be achieved, see Figure 17. With increasing amount of sunflower hulls the impact strength decreased to 67% of the reference value. This can be explained by a strong hydrophobic behaviour which leads to a worse impregnation of the fibers and an increased number of pores within the fibers. Furthermore, agglomeration of the filler materials occurs.

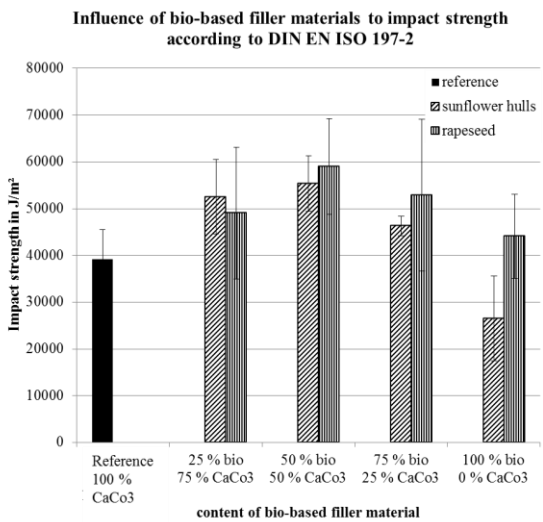


Figure 15: Results of Charpy test

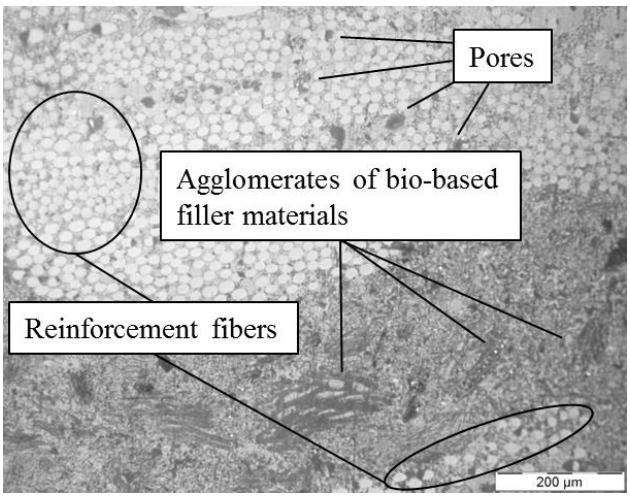


Figure 16: Pores and agglomerates based on bio-based filler materials

4.7 Results of moisture absorption test

As the developed resin paste includes a high content on bio-based filler materials, the moisture absorption is a very important test. Conventional SMC resin paste showed an increase of 0.2% weight

mainly during the first day, see Figure 17. After a short time, the material was saturated and there was no further water uptake recognizable. The SMC samples with the bio-based filler materials showed an almost constant water uptake for the first 14 days. After that period, water uptake was almost finished; the weight of the samples was unchanged for two days. It is recognizable, that the rapeseed filler showed a better water up-take behavior (0.4%) than sunflower hulls (0.5%). So changes in the formulation regarding water up-take will lead to better results also for higher contents of bio-based filler materials.

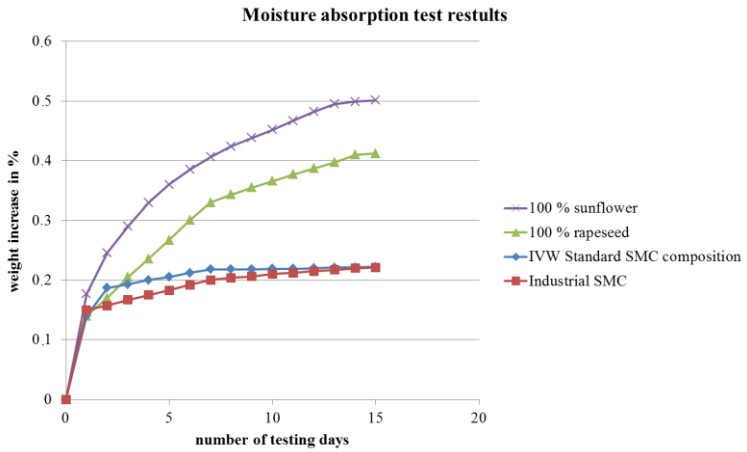


Figure 17: Results of moisture absorption test

5 CONCLUSION AND OUTLOOK

The aim of this study was to investigate the possibilities and use of bio-based filler materials in a thermoset SMC resin-paste and processing of these materials. The major criteria for the implementation of the bio-based filler materials are the processability of the semi-finished product without any changes regarding equipment and process technology. The developed resin paste shows the same processing viscosity as a conventional resin paste. By the use of bio-based filler materials the density of the resin paste could be reduced about 18%. The new bio-based SMC material shows comparable mechanical properties regarding tensile, bending, and charpy tests. Furthermore, the material can be processed in a conventional SMC process. The moisture uptake test showed that changes in the recipe have to be made to reduce water up-take by 50%. Further research regarding flame resistance and reducing moisture absorption as well as the processability of the bio-based SMC semi-finished product with the institute's own SMC line and an 800 t component press in industrial scale will be conducted.

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