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A direct process to reuse dry fiber production waste for recycled carbon fiber bulk molding compounds

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Abstract

Recycling concepts for composites are gaining importance facing constantly growing production rates in multiple sectors. Today, a high percentage of the carbon fiber waste is generated during production. The unimpregnated share of waste cannot be reused as high-performance non-crimp fabrics, since shape, size and orientation of the patches were changed during the previous production step. The approach presented here shows the direct processing of chopped dry non-crimp fabrics cutting waste to Bulk Molding Compounds. The manufactured BMC materials are able to compete with materials from state-of-the-art Sheet Molding Compounds produced using virgin carbon fibers in terms of mechanical performance.

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Keywords: recycling; reuse; carbon fiber; rBMC; BMC; SMC; direct process

1. Introduction

With the rising usage of CFRP in the Aerospace, Automotive and Energy sector also the environmental awareness and the management of the waste gain more momentum. The main drivers for recycling of carbon fibers is the EU Directive on Landfill of Waste (Directive 99/31/EC). Therefore, landfilling of composites is already prohibited in some countries of the European Union. The high price of carbon fiber is another motive to reduce production waste of these [1]. Recycling inverts waste, expensive to dispose into a potentially profitable recycled material [2]. The growing demand of CF [3] can partially be filled with recycled materials, for instance a 10% share of CFRP used in the BMW i Series consists of recycled material [4]. Here a new solution of fast and easily reusing dry fiber cutting waste, which is a big fraction of the production waste, is presented.

Nomenclature

CFRP	carbon fiber reinforced plastic
vCF	virgin Carbon Fiber
rCF	recycled Carbon Fiber
BMC	bulk molding compound
SMC	sheet molding compound

2. Recycling concepts

The typical lifecycle from raw material till deposition of CFRPs and the routes of waste are shown in fig 1. C-fiber waste generally appears in three different kinds. First of all during the cutting in the production process of textile intermediates, dry fiber waste is generated. In case of using preimpregnated carbon fibers (prepregs) as intermediate, cutting waste and outdated prepregs arise as waste. When a part is broken or no longer in use, end-of-life waste accumulates. A large fraction of waste is generated during the production process of high performance CFRPs [5]. This problem can for example be addressed with effective recycling techniques. Figure 1 shows typical automotive production routes of waste. For production purposes, new materials as well as recycled materials are used. During

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production, due to cutting waste of textiles, dry fiber waste is generated. Net forming of the parts generates impregnated waste. After the usage of the parts, end-of-life impregnated fiber waste and residual waste is left.

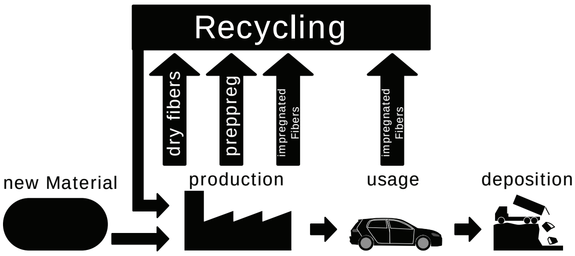


Fig. 1. Typical Process chain as used in the industry with illustrated path of waste generation and the role of recycling

The new approach shown in this paper only addresses the dry cutting waste, mostly generated in the production of high performance CFRPs. Other waste forms are mentioned but not explained as detailed as shown in Pimenta, Pickering, Oliveux and Seiler [6–9].

2.1. *Pre-preparation*

The first step in C-fiber recycling is the preparation of the waste as can be seen in fig 2. Here, the waste is cleaned and then shredded, crushed or milled into nearly same sized pieces [7]. This is necessary to ensure stable processing and easier handling of the material. Dry fiber waste also has to be cut due to the same reason.

2.2. *Generation of intermediates*

The second step of the recycling as shown in fig 2 is about regaining the pure fibers from impregnated waste and making an intermediate material available for the production step. Using impregnated end-of-life waste, the fibers have to be freed from the matrix. In this fiber regaining step, typically pyrolysis and solvolysis are processes of choice [9].

The dry fiber waste is mostly processed with mills or ground into different fiber length fractions, varying from powder like short fibers ($< 2mm$) to long fibers ($> 2mm$). After these processes both the dry and impregnated fiber waste are present as low density, so called ”fluffy” rCF that can be seen in fig 4 (c) and rCF ”powder”.

The short fiber and powder like rCF fractions are mostly used as filling material for injection molding composites. With these molding materials the fiber orientation distribution is mainly influenced by the flow that appears during the production of the part [10].

State-of-the-art recycling procedures for cutting waste use the ”fluffy” long fiber material as seen in fig 4 (c) to further process it to aligned textile intermediates of discontinuous long fibers [2,13]. For textile intermediates the long fiber fraction is cardined and stitched together to align and fix the fibers [2]. This process has the advantage that the fibers of these textiles can be oriented to obtain better mechanical properties in the oriented direction.

2.3. *Production*

Production processes of new parts made of rCFRP can basically be divided in loose material and textile rCF intermediates.

The textile intermediates like fleeces and mats can be reused for RTM processes where the textile has to be impregnated with resin to manufacture new parts. Also SMC intermediates can be produced by an impregnating step followed by press molding the part afterwards.

Most of todays reuse [14] and recycling [12,13] approaches emphasize the development of highly aligned, long fiber intermediates to maximize the mechanical properties. The here presented direct approach shown in fig 2 aims on shortening the processes and minimizing the needed machinery compared to other techniques to reuse carbon fiber production waste.

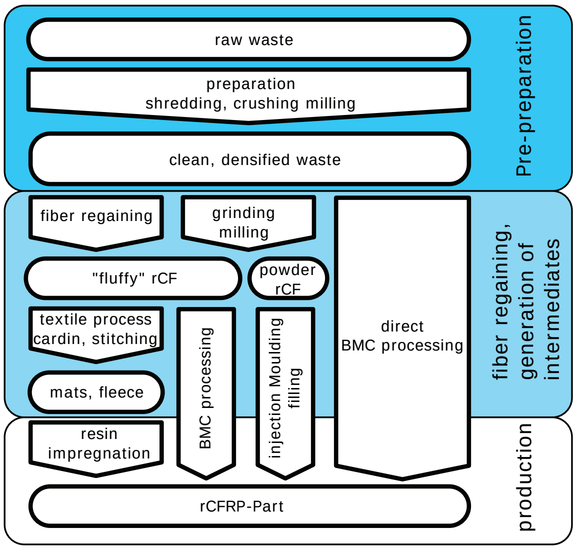


Fig. 2. General recycling concepts and sorting of the new shown direct BMC approach

3. The direct BMC process

Bulk Molding Compound (BMC) and Sheet Molding Compound (SMC) are typically polyester-based, glass fiber reinforced composite materials which are processed in a compression or injection molding process. These materials comprise around 25% of the total European production of glass fiber reinforced plastics [11].

The direct BMC process is depicted in fig 3 and is based on the conventional BMC production process. In the first step, the resin components are dosed to the formulation shown in table 1. To mix and homogenize the formulation a dissolver is used. This resin paste is then combined with the square cut rCF patches in a kneader. Finally, the compound is dosed by mass and packaged.

The fundamental structure of the BMC process chain is not changed with the new approach presented here. The innovative aspect of the direct BMC Process is to use cutted dry carbon fiber non-crimp fabric production waste instead of chopped vCF rovings. The production waste is cut into square patches

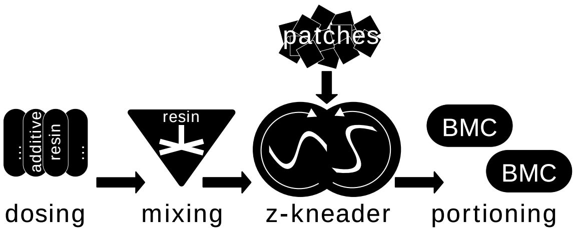


Fig. 3. the rCF direct BMC process

and directly fed into the BMC kneader (kneader type Fritz Meili Zürich). Hence, cutting such patches may be directly integrated in the preform cutting process of high-performance composite manufacturing. Patch size of 100 mm x 100 mm of the multi-axial Zoltek PX35 50K with polyester stitch were investigated as can be seen in fig 4 (a). A fiber volume content of 42% was chosen for all formulations.

As resin system, an unsaturated polyester - polyurethane hybrid resin (UPPH) was used. The same resin system was used for previous carbon fiber SMC investigations, so relevant comparison values from a state-of-the-art processing route are available. The resin formulation is shown in table 1.

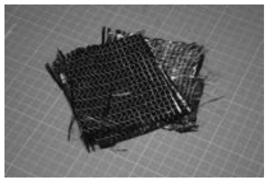
The ”fluffy” rCF material was produced and taken into account during production and microscopic investigations to compare to the state-of-the-art recycling process as reference to the novel approach. Due to the very low density of the ”fluffy” material, the aspired fiber volume content of 42% couldn’t be achieved and the material’s mechanical properties are not presented here. To underline the competitiveness of the new approach the mechanical properties were compared to virgin fiber made SMC produced in a state-of-the-art process using the same fibers, fiber volume content and resin system.

Table 1. Resin formulation

Type	Description	Parts by weight
Daron ZW 14142	Daron UPPH low viscosity	100
BYK 9076	Carbon Fiber Impregnation Additive	3
BYK 9085	Release and Flow Additive	2
BYK A-530	Air Release Additive	0.5
pBQ 10%	Inhibitor	0.3
Trigonox 117	Peroxide	1
Lupranat M20R	Isocynate	24.2

A Double-Z-Kneader with a capacity of approximately 7 kg was used for the BMC production. During the kneading process, the fiber patches were added gradually during the first minutes of kneading. In order to achieve an even distribution of the fibers and a disintegration of the stitched patches, a kneading time of 15 minutes was chosen for all samples. Due to the shear force in the BMC kneader, most of the fiber patches were quickly disintegrated. The resulting rCF direct BMC can be seen in fig 4 (b).

Figure 4 (d) shows an only partially disintegrated carbon fiber patch. It can be seen that the knitting yarn remains mostly intact. Due to the stretching of the patch, the single rovings are separated and can be torn out of their fabric structure. This leads to the conclusion that the knitting yarn does not break or rupture during the disintegration process of the fabric patch. After kneading, the compound is mass portioned according to the requirements of the molding process and stored for the maturation period of 7-8 days at 20°C. Sample plates were manufactured using a hydraulic press and a mirror-polished, chromium-plated compression molding tool of 458 mm × 458 mm . The process parameters can be found in table 2.



(a) cutted patches 100x100mm

(b) rCF direct BMC

(c) ”fluffy” rCF milled, 10 mm

(d) partially disintegrated patch

Fig. 4. Materials used in the shown new approach and in conventional recycling processes processes

Table 2. BMC Molding Parameters

Parameter	Unit	Value
Cavity temperature	°C	143.5
Molding pressure	bar	150
Molding time	s	112

The size of the initial charge for the compression molding process was approximately 25% of the total mold area, which is similar to the virgin carbon fiber SMC used, to allow for a comparison. It is remarkable that the required molding pressure for the BMC was twice as high as for the SMC. This effect can be explained by the higher degree of entanglement and interlooping of the BMC, which is caused by the kneading process. In contrast, the fibers of the vCF SMC material seem more bundled in the chopped roving strands after visual examination.

4. Testing procedures

In the following and if not indicated differently, *SMC* will refer to SMC produced with virgin carbon fibers whereas *BMC* refers to the rCF direct BMC. Mechanical properties of the material have been obtained by tensile, bending and impact (Charpy) tests to allow for a thorough comparison between SMC and BMC. The specimen geometries for all tests are depicted in fig 5 and were water jet cut, with specimen thickness according to the plate thickness of 3.00 ± 0.2 mm.

Table 3 lists the related standards as well as testing devices and testing speeds.

In addition to mechanical testing, microsections and scanning electron micrographs were taken. For the former, spec-

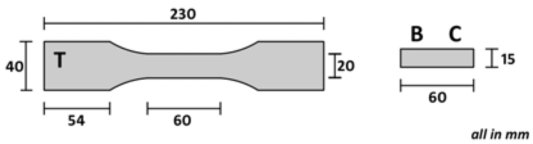
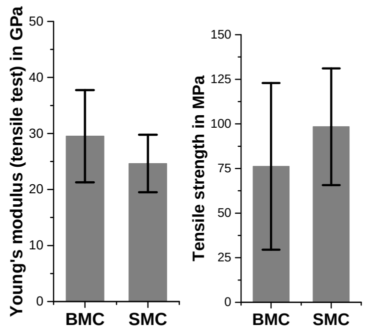


Fig. 5. Specimen geometries for tensile (T), bending (B) and Charpy impact (C) tests, with specimen thickness varying between 3.00 ± 0.2 mm due to the production process

Table 3. Overview of mechanical testing procedures

test mode		standard	testing device	testing speed
tensile	T	DIN EN ISO 527-4 [15]	Zwick 200kN	2 mm/s
bending	B	DIN EN ISO 14125 [16]	Zwick Z2.5	2 mm/s
impact	C	DIN EN ISO 179 [17]	Zwick HIT5.5P	2,9 m/s *

* according to machine manufacturer



(a) Young's modulus (b) Tensile strength

Fig. 6. Tensile test statistics for 23 BMC and 12 SMC specimens

imen were cut orthogonal to the plate surface, embedded in resin, ground, polished and investigated with a Leitz Aristomet light microscope. For the latter, fracture surfaces were sputtered with gold and a SEM of type EVO 50 by Carl Zeiss AG was used for investigations.

5. Mechanical Properties

In the following, the testing parameter and devices for each set of tests are presented and the results are listed. Later, a short resume and comparison of the results for BMC and SMC is given.

Specimens were cut from different positions and in two directions (0° and 90°). However, no significant influence due to region or orientation was found, so that the results of mechanical tests are grouped regardless of their position and orientation and comparison is conducted solely between BMC and SMC.

5.1. Tensile test

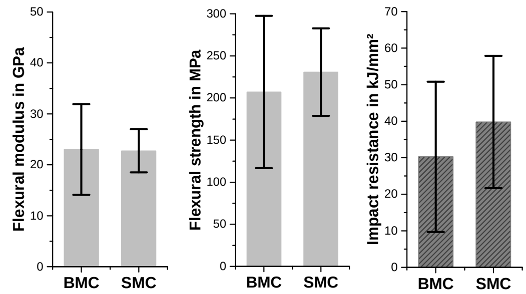
Tensile tests were performed on a Zwick/Roell 200kN with an incorporated 200 kN load cell and hydraulic grippers. The specimens were cut according to fig 5-T. Strain was measured using a mechanical extensometer with a measuring length of 60 mm. Figure 6 shows bar charts of tensile tests for rCF direct BMC and virgin SMC specimens represented by their mean values and standard deviations. Results include 23 BMC and 12 SMC test specimens. Taking the scatter of the data into account, no significant difference between the BMC and SMC material can be detected.

5.2. Bending test

Bending tests were carried out on a Zwick/Roell Z2.5 for specimens with a geometry according to fig 5-B. Flexural modulus was calculated as described in *DIN EN ISO 14125* [16] by

$$E_f = \frac{0.21L^3}{bh^3} \cdot \frac{\Delta F}{\Delta s} \tag{1}$$

with L being the support width in mm, h and b the thickness and width of the specimen in mm, Δs the deflection of the beam in mm and ΔF the difference of the force in N. Again, the results are given as bar charts (fig 7(a) and (b)) and again, the scatter of the data outruns possible differences between the two types of material. In total 118 BMC and 41 SMC specimens were tested in bending mode.



(a) Flexural modulus (b) Flexural strength (c) Charpy impact

Fig. 7. Bending tests, perfomed with a total of 118 BMC and 41 SMC specimens, and Charpy impact tests, performed with 49 BMC and 17 SMC specimens

5.3. Charpy impact test

A Zwick/Roell HIT5.5P testing device with a 5 J pendulum was used to determine impact resistance. Here, the unnotched specimens were shaped as shown in fig 5-C with a supporting width of 48 mm. Impact resistance was calculated according to

$$a_{cU} = \frac{E_c}{bh} \cdot 10^3 \tag{2}$$

with E_c being the work in Joule, and h and b the thickness and width of the specimen in mm. In fig 7, the impact resistance of BMC and SMC material is compared using bar charts. Charpy impact tests were run with 49 BMC and 17 SMC specimens. As for the other tests, the broad scatter overlays variations of the material and the difference is not significant.

5.4. Comparison of BMC and SMC

As aforesaid, the materials showed a high scatter in their mechanical properties which are expected to originate from the discontinuous fiber distribution of rather short fibers. The scatter could not be reduced by testing more specimens than required by the associated standards [15–17]. Thus, mechanical testing procedures are not able to significantly distinguish between the two material types, that is the virgin SMC, produced from new material, and the recycled BMC material, rCF direct BMC, from dry fiber waste. From a mechanical standpoint, material produced using the newly developed recycling process presented in this work is able to compete with its conventional analogon, a SMC made of new chopped fibers.

In addition to the resemblance in mechanical performance, this paper aims to demonstrate further analogies between the rCF direct BMC material and the vCF SMC material. To do so, materialographical investigations were carried out by comparing microsections of the material as well as scanning electron micrographs of fracture surfaces. In view of figures 8 and 9, a high level of accordance can be assumed: The microsections of the virgin and the recycled material appear quiet similar: In both materials, the fibers are packed closely together in bundles as they originate from dry roving material in which hundreds of single fibers are consolidated together. Thanks to the dense packing, high fiber volume contents can be attained in both materials. Opposed to this, fibers are only loosely packed in the composite if the rovings are separated in pre-processes like cutting or milling as described in paragraph 2 and fig 2. A BMC material using ground fibers is shown in fig 8 c), where the lower packing density of fibers can be seen, resulting in reduced fiber volume contents. Their mechanical properties are not under investigation here, as the fiber volume content that can be achieved is significantly lower than those of rCF direct BMC.

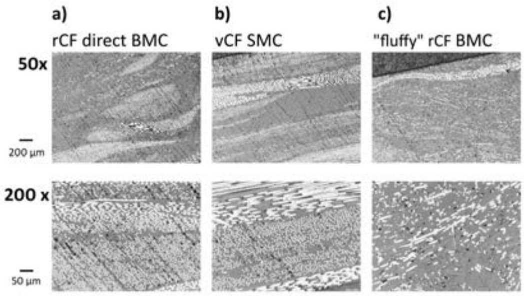


Fig. 8. Microsections of different materials in magnifications of 50 x and 200 x. While SMC and the BMC produced according to the here presented procedure resemble each other, BMC produced with ground fiber offcuts show a different appearance as most fiber bundles have lost coherence.

Similarities between recycled BMC and new SMC are also found when investigating fracture surfaces of tensile specimens as seen in fig 9. Again, bundles are visible for both types of material and fracture seems to appear mainly along the interface between fiber and resin. Visual examination of fracture surfaces suggest the assumption that fiber bundles oriented approximately orthogonal to the loading direction are weak spots and specimens are likely to fail there.

6. Discussion and further investigations

In contrast to conventional recycling processes the new rCF direct BMC process needs less processing steps with less machinery while the manufacturing process still remains stable. The shown mechanical properties are competitive to virgin made carbon fiber SMC.

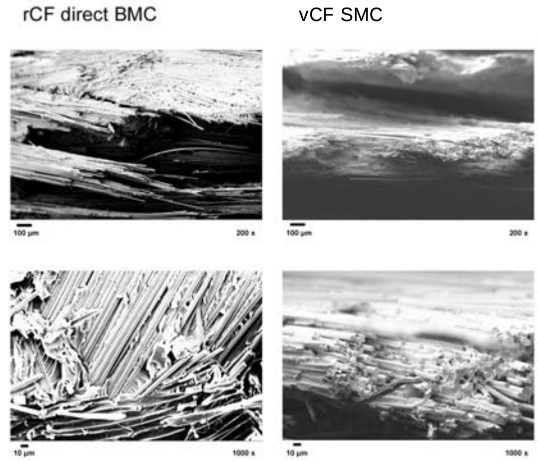


Fig. 9. Scanning electron micrographs of fracture surfaces of BMC and SMC specimens after tensile tests

The main difference in processing the material compared to vCF SMC is the higher pressing force needed, which is a negligible issue. By omissioning the step of milling the fibers, a simpler process is shown here and is able to substitute the conventional process of reusing textile dry carbon fiber production waste.

From a mechanical perspective, the newly developed rCF direct BMC material proves itself able to compete with vCF SMC material. Mechanical properties range in the same magnitude in standard tensile, impact and bending tests. Further, mircosections show high similarity in terms of bundle-like appearance and high packing densities. As given by SEM, fracture mechanisms appear similar, that is entire bundles are pulled out of the structure and/or the interface between fiber and resin is damaged. From this view, the presented rCF direct BMC route is comparable with vCF SMC material made of the same resin and fibers.

The main advantages of the presented process is the small amount of financial invest and negligible production interference to introduce this new recycling technique into an existing production environment. The short distances from waste generation to recycling and production in combination with small size and cost of the machinery to gain the rCF direct BMC material appear to be an interesting alternative, not only for high volume producer but also for smaller companies in the CFRP business.

Future works will exploit the process and mechanical behavior of different patch sizes, geometries, fillers, cutting angles and stitching yarns to investigate the stability and reliability of the shown approach.

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References

[1] Thielmann, A and Seeliger, W and Lerch, Ch and Günther, B. Wertschöpfungspotenziale im Leichtbau - und deren Bedeutung für Baden-Württemberg. Leichtbau BW Studie WSK

[2] Pimenta, S and Pinho, Silvestre T. Recycling carbon fibre reinforced polymers for structural applications: Technology review and market outlook. Waste Management. 2011. p.378-392;

[3] Sujit, D and Warren, Jh and West, D and Schexnayder, S M. National. Global Carbon Fiber Composites Supply Chain Competitiveness Analysis. Renewable Energy Laboratory NREL. 2016;

[4] Recycling SGL - ACF. http://www.sglacf.com/en/products/recycling.html, urldate. 2017;

[5] Lässig, R and Eisenhut, M and Mathias, A and Schulte, R T and Peters, F and Kühmann, T and Waldmann, T and Begemann, W. Serienproduktion von hochfesten Faserverbundbauteilen. Perspektiven für den deutschen Maschinen-und Anlagenbau. Studie Roland Berger. 2012;

[6] Pimenta, S and Pinho, S T. Recycling of Carbon Fibers. Book of Recycling. 2014. p. 269-283;

[7] Pickering, S J. Recycling technologies for thermoset composite materialscurrent status. Composites Part A: Applied Science and Manufacturing. 2006. p. 1206-1215;

[8] Seiler, E and Stark, A and Forberger, J. Recycling von Textilien aus carbonfaserverstärkten Kunststoff-Bauteilen und deren Produktion. Chemie Ingenieur Technik. 2016. p. 500-505;

[9] Oliveux, Graldine, Luke O. Dandy, und Gary A. Leeke. 2015. Current Status of Recycling of Fibre Reinforced Polymers: Review of Technologies, Reuse and Resulting Properties. Progress in Materials Science 72 (Juli): 6199. doi:10.1016/j.pmatsci.2015.01.004;

[10] Phelps, Jay H and Tucker, Charles L. An anisotropic rotary diffusion model for fiber orientation in short- and long-fiber thermoplastics. Journal of Non-Newtonian Fluid Mechanics. 2009. p. 165-176;

[11] Witten, E and Kraus, T and Kühnel, M. Composites - Marktbericht 2015 - Marktentwicklungen, Trends, Ausblicke und Herausforderungen. AVK Marktbericht. 2015;

[12] Longana, Marco L, Natalie O, HaNa Y, und Kevin D P. 2016. Multiple Closed Loop Recycling of Carbon Fibre Composites with the HiPerDiF (High Performance Discontinuous Fibre) Method. Composite Structures 153 (Oktober): 27177. doi:10.1016/j.compstruct.2016.06.018;

[13] Pickering, Sj, Z Liu, Ta Turner, und Kh Wong. 2016. Applications for carbon fibre recovered from composites. IOP Conference Series: Materials Science and Engineering 139 (Juli): 12005. doi:10.1088/1757-899X/139/1/012005.

[14] Manis F, Wölling J, Schneller A 2016. Ganzheitliche Recycling-Prozesskette für Carbonfasergewebe und Gelege. Lightweight Design 9 (5): 1419;

[15] EN ISO 527-4:1997, Kunststoffe Bestimmung der Zugeigenschaften. Teil 4: Prüfbedingungen für isotrop und anisotrop faserverstärkte Kunststoffverbundwerkstoffe (ISO 527-4:1997);

[16] DIN EN ISO 14125:2011, Faserverstärkte Kunststoffe Bestimmung der Biegeeigenschaften (ISO 14125:1998 + Cor.1:2001 + Amd.1:2011);

[17] DIN EN ISO 179-1:2010, Kunststoffe Bestimmung der Charpy-Schlageigenschaften Teil 1: Nicht instrumentierte Schlagzähigkeitsprüfung (ISO 179-1:2010);