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Carbon fibre recycling from milling dust for the application in short fibre reinforced thermoplastics

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Abstract

A new approach to reuse accruing chips and dust from milling operations of carbon reinforced plastics (CFRP) is studied, showing how CFRP milling dust, in comparison to primary and pyrolysed fibres, can find application as a filler material in thermoplastic granulates. Recent examinations show an overall better handling of milling dust when separating it into different classes of fibre lengths reaching up to 600 µm, which typically occur while machining reinforced plastics. Furthermore, the carbon reinforced polypropylene granulates have improved material properties, e.g. increased rigidity and tensile strength in dependence of their respective filler content towards non-reinforced plastics.

Peer-review under responsibility of the scientific committee of the 1st Cirp Conference on Composite Materials Parts Manufacturing

Keywords: fibre reinforced plastic; recycling; lifecycle

1. Introduction

Due to the focus on reducing the fuel consumption without influencing the integrity of structural parts in the aeronautical and automotive sectors, lightweight strategies are being pursued continuously [1]. Thus, these industries are processing almost 50 % of the global market share of CFRP [2]. The advantages over common lightweight materials like aluminium and magnesium alloys include its low density and its high tensile strength [3]. The demand for CFRP is growing steadily, which causes a predicted global usage of approximately 116,000 t in the year 2022 [4]. However, until today there are no standardised processes available for recycling CFRP to ensure a further use of fibre and matrix after reaching the end of its material lifecycle.

Moreover, even with near-net shape manufacturing techniques like Resin Transfer Moulding, trimming, deburring or drilling is still necessary. These post-processing steps lead to accruing chips and dust. This production waste disposal, which is estimated to be over 30 %, ends up in landfilling and incineration processes [5, 6]. This is mainly due to the inherent characteristic of thermosets, commonly used as the matrix for CFRP, not being fusible. Yet, changes in legislation, especially in the EU, make material recycling necessary [7]. One alternative way is the use of pyrolysis to dispose of CFRP, however this process is non-economic without reutilizing the carbon fibres [8, 9]. In terms of sustainability and a closed material cycle, new and environmentally friendly approaches with regard to this issue have to be found. A promising possibility is the application of CFRP waste in the form of milling dust or chopped material as a filler or additive in thermoplastics. In this study an attempt is implemented for injection moulding on polypropylene (PP). Besides the aspect of regaining material, better mechanical properties can be achieved. This is tested for different variations of filler content and fibre length to produce preferred variants for specific use cases. In addition to validating the performance of milling dust filled PP, primary and secondary (pyrolysed) fibres are also examined.

On the basis of sizing analyses, optical examinations and mechanical stress tests, a new material combination is being described in this paper.

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Nomenclature

Latin symbols

A	amplitude
CF	carbon fibre
CFRP	carbon fibre reinforced plastics
d_f	fibre diameter
E	Young's modulus
F_{max}	maximum force
I	interval
l_f	fibre length
l_E	clamping length
m	mass
M	mesh size
PP	polypropylene
q_m	mass flow
RTM	resin transfer moulding
SFRP	short fibre reinforced plastics
Shore D	hardness
t	time
t_T	testing time
T_p	pyrolysis temperature
v_T	testing speed
w_m	mass fraction
w_f	filler content
w_{fb}	fibre content

Greek symbols

ε	strain
ε_B	elongation at break
σ	stress
σ_{max}	ultimate tensile strength

2. Fibre sourcing and characterisation

2.1. Raw material overview

To investigate new applications of CFRP waste as a filler material in reinforced thermoplastics, three different carbon fibres were compared. They are defined as follows:

- Milling dust
- Primary fibres
- Secondary (pyrolysed) fibres

The sourcing itself was realised in cooperation with CarboNXT GmbH, Wischhafen, Germany. The initial shape of the raw material was provided in milled form, thus leading to better processing in the subsequent injection moulding trials. The milling dust represents industrial waste from machining semi-finished CFRP products. The dust itself predominantly consists of fibre bundles embedded in epoxy resin due to their adhesive forces. Depending on the used process parameters, the typical fibre lengths range from l_f = 10 µm to l_f = 1000 µm. The primary and secondary fibres on the other hand are not compounds, but comprise only of carbon fibres with an average length of approximately $l_f \approx$ 500 µm according to company information. Primary fibres are typically used for textile processing and afterwards for the production of CFRP. These fibres are coated with a bonding agent for better interface connectivity, whereas secondary fibres can be seen as a recycled variant of primary fibres.

These secondary fibres underwent a pyrolysis. In this thermo-chemical process, the organic compound of CFRP is separated, disintegrating the epoxy resin and leaving a pure carbon fibre behind. The surface of secondary fibres as well as their mechanical properties are strongly dependent on the process temperature, which should range from T_p = 500 °C to T_p = 550 °C for epoxy resins [10]. By using this process, it is possible to recycle the fabric as a whole. An overview of the appearance of all fibre types is given in Fig. 1.

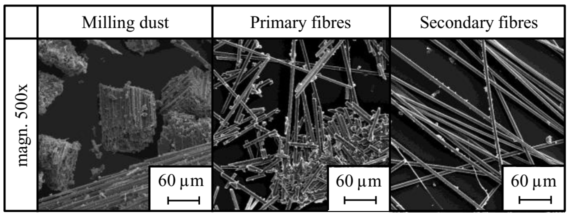


Fig. 1. SEM-images of the used fibre variants; (a) Milling dust; (b) Primary fibres; (c) Secondary fibres

2.2. Sizing and optical inspection

To differentiate the particle distribution of the carbon fibres within the supplied raw material, a classification of its length was conducted. Thus, a better prediction of the material properties was possible. First sieving tests with the different fibres were conducted with a test sieve shaker EML 200 from HAVER & BOECKER OHG, Oelde, Germany. The test sieve shaker has a closed system to reduce the dust exposure in the ambient air.

After first sieving trials with a mass of m = 100 g for each fibre variant, mesh sizes up to M = 710 µm were defined to display the fibre distribution, see Tab. 1.

Tab. 1. Applied mesh sizes in descending order

Pos.	1	2	3	4	5	6	7	8	9
Mesh size M in µm	710	600	150	125	106	75	45	32	20

The materials within mesh sizes M > 600 µm were mainly foreign matter or previous process-related parts related to carbon fibres. Only mesh sizes finer than M = 600 µm showed a homogenisation of the chip shape itself, making the dust more representative. Optical examinations as shown in Fig. 1 were conducted within the sieving trials for each fibre variant. Fig. 2 shows an exemplary overview of the sieved milling dust.

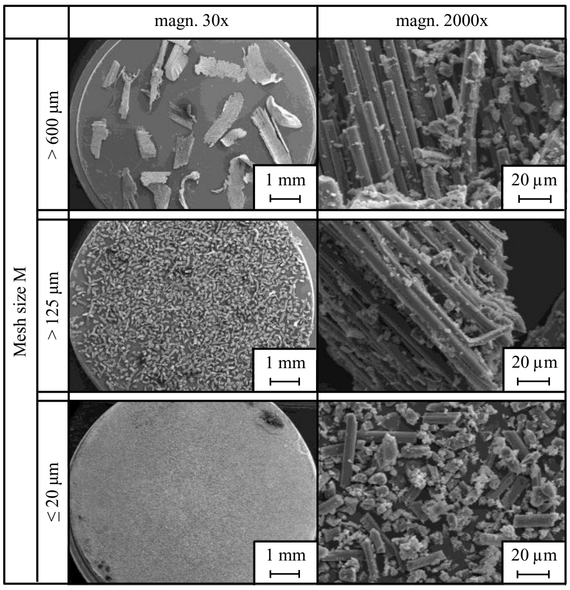


Fig. 2. SEM-images of the milling dust on exemplary mesh sizes

Wider mesh sizes up to M = 600 µm resulted only in particles with embedded fibres in its respective resin matrix. No separated fibres were available although they can be seen on the boundary layers of the particles. With mesh sizes below M = 45 µm, smaller fibre groups of 10 or less connected fibres can be seen. The occurrence of single fibres could only be apparent with mesh sizes M < 32 µm. But even at these small sizes epoxy resin was still attached to the fibre surface. In addition, the epoxy resin was also separated from the fibre, leading to impurities within the filler material. Furthermore, a sharp distinction of fibre lengths while sizing was not completely achievable. This is due the interaction of the fibrous geometry within the sieve shaker. The alternating amplitude leads to an inclined or perpendicular positioning of the fibres and thus allows them to fall through mesh sizes finer than their respective lengths. The best sizing results were achieved with the parameter given in Tab. 2.

Tab. 2. Test sieve shaker process parameter for m = 100 g

Parameter	Unit	Value
t	min	30
I	s	10
A	mm	1,2

Fig. 3 shows the distribution of the mass fraction of milling dust in the preliminary tests. It is noticeable that approximately 40 % of the test samples are within the range of M = 150 µm to M = 710 µm. This is because of foreign particles, which are unsuitable for use as a filling material. The peak at M = 150 µm is based on the wide range up to M = 600 µm. A finer gradation would lead to a more homogeneous mass distribution as it can be seen between M = 125 µm and M = 32 µm. Moreover, most fibres tend to be either long or short with fibre lengths of $l_f \geq 150$ µm or $l_f \leq 20$ µm. This is probably due to the milling process. While cutting the longer fibres, smaller carbon fragments occur as well.

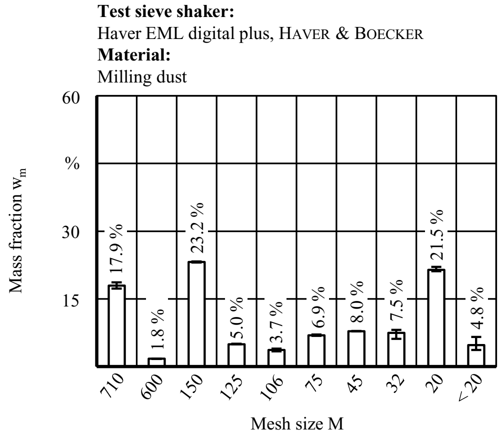


Fig. 3: Mass fraction of milling dust depending on the mesh sizes

The mass distribution also varied when sieving independent batches of the supplied milling dust. This is a sign of different used process parameters within earlier production processes. The three fibre classes were defined with a focus on an overall equal mass distribution, see Tab. 3. These fibre classes were the basis for investigating the impact of fibre lengths regarding the mechanical properties of carbon fibre filled polypropylene.

Tab. 3. Defined fibre classes

Classification	Range of fibre lengths l_f
Coarse	150 µm … 600 µm
Intermediate	75 µm … 150 µm
Fine	≤ 75 µm

For the use of carbon fibres in thermoplastic compounds and the subsequent injection moulding tests, the generation of a sufficient amount of filler material was required. To achieve this, a two-staged sieving process was implemented. The reason was the insufficient output performance of the test sieve shaker. Before sieving the material into its classes, a pre-sieving process was established with a Piccolo Sizer, Co. Mogensen GmbH, Wedel, Germany. Its operating principle is similar to the test sieve shaker with a higher mass output q_m. As shown in Tab. 4, sufficient raw material could be produced.

Tab. 4. Output performance of the used sieving machines

Parameter	Unit	Test sieve shaker EML 200	Sieving machine MOGENSEN SIZER
m	kg	0.25 kg	2.00 kg
t	min	60 min	20 min
q_m	kg/h	0.25 kg/h	6.00 kg/h

As mentioned before, the primary fibres, which were milled from continuous filaments, were coated with 5 wt.%

bonding agent in its initial condition. Unlike the milling dust, primary fibres had the strong tendency to agglomerate and interlock with each other mechanically, see Fig. 4. Therefore, the sizing even with sieving aids or compressed air was not successful. Another option like the deposition of different fibre lengths via cyclonic separation requires the raw material to be soluted in water. This is not very efficient due to necessary downstream drying processes.

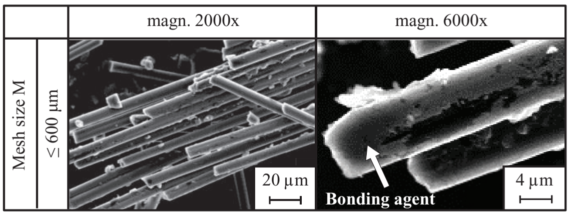


Fig. 4. Agglomerated primary fibres with bonding agent

Similar effects were ascertainable while sieving the pyrolysed fibre. Although disposing of pure surfaces, agglomerations within the raw material took place. Therefore, fibre lengths differed from its respective mesh size, having longer fibres predominantly in smaller meshes, see Fig. 5.

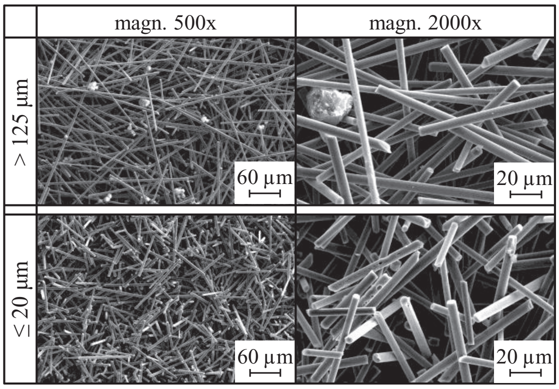


Fig. 5. Insufficient sieving results

In consequence, primary and secondary fibres were both used as mixed compounds without a length classification. For a better comparability of the tests, a mixed compound of milling dust with fibre lengths below the mesh size M = 600 µm was also defined.

3. Granulate production

The fibre variants given in Tab. 5 were used as filler material for PP. To study the influence on the mechanical properties, the filler contents w_f ranging from w_f = 10 wt.% to w_f = 30 wt.% in increments of 10 were also examined. This led to an overall variance of 19 material combinations including the PP without filler content as a reference material. The matrix material used for the compounding process was the polypropylene Ducor 2600 M, Co. Ducor Petrochemicals B.V., Rotterdam, Netherlands. For a better connectivity of fibre and thermoplastic, the bonding agent SCONA TPPP 9212 GA, Co. BYK-Chemie GmbH, Wesel, Germany with w_f = 2 wt.% was used.

Tab. 5. Overview of all tested materials

	Granulate variants
a)	Coarse milling dust
b)	Intermediate milling dust
c)	Fine milling dust
d)	Mixed milling dust
e)	Primary fibres
f)	Secondary fibres
g)	Non-reinforced polypropylene

For the granulate production a twin-screw extruder ZSK 26 Mc, Co. Coperion GmbH, Espenhain, Germany was available. The insertion of the filler material was especially important to reduce material damage within the extruder, as shear forces can lead to fibre breakage [11, 12]. To achieve this objective, the filler was only inserted later in the process during kneading when the PP was in a liquid phase.

4. Results and discussion

To analyse the generated material specifications with regard to their mechanical performance, multipurpose test specimen according to DIN EN ISO 3167 were produced with an injection moulding process. The mechanical tests included the recording of the Young’s modulus, ultimate tensile strength and elongation at break with a universal testing machine Z150 as well as the Shore hardness with a hand held durometer 3116, both from Co. Zwick GmbH & Co. KG, Ulm, Germany. The mechanical tests were conducted with 3 trials for each material variant according to DIN EN ISO 527.

4.1. Young’s modulus

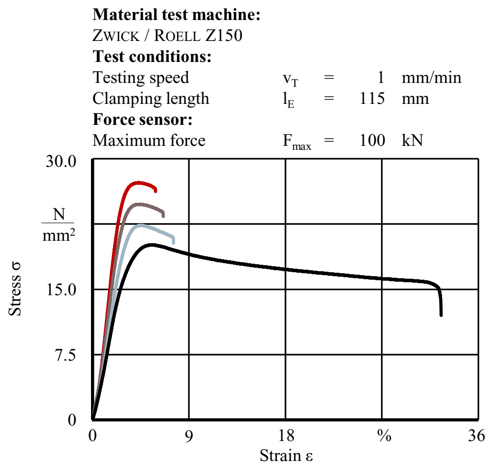
In general, it can be stated, that the filled polypropylene variants dispose of an increase in rigidity due to the embedded carbon fibres, see Tab. 6.

Tab. 6. Young's modulus of all granulate variants

Granulate variants	Filler content w_f			
	0 wt.%	10 wt.%	20 wt.%	30 wt.%
	E in N/mm²			
a)		844.3 ± 32.7	966.7 ± 7.8	1108.2 ± 15.9
b)		812.2 ± 10.2	1068.3 ± 0.7	1268.8 ± 9.9
c)		828.0 ± 11.2	1000.6 ± 18.8	1191.7 ± 9.8
d)		823.5 ± 4.9	1001.6 ± 22.6	1179.8 ± 0.9
e)		1463.4 ± 37.8	1875.6 ± 70.2	1661.8 ± 28.0
f)		1542.9 ± 30.2	2110.4 ± 5.3	1741.6 ± 11.9
g)	647.3 ± 5.8			

When looking at the classified milling dust, no clear dependence on the fibre length is visible, yet there is an average increase of nearly 27.8 % (average of granulate variant a to d) at $w_f = 10$ wt.% compared to non-reinforced polypropylene. Better results were achieved with primary fibres (granulate variant e) with an increase of 126.1 % and pyrolysed fibres (granulate variant f) with 138.6 % at $w_f = 10$ wt.%.

To display the dependency of the filler content on the material properties, the mixed milling dust (granulate variant d) is exemplary displayed on a stress-strain curve in Fig. 6. The main factor for increasing the Young's modulus is to increase the filler content of the respective fibres. Yet this increase in rigidity is to the detriment of ductility. Thus the flow behaviour results in a smaller strain capacity more known to semi-brittle materials. Furthermore there can be a direct proportionality attested for milling dust up to $w_f = 30$ wt.%, yet the rigidity of primary and pyrolysed fibres seems to decrease with a higher filler content of $w_f = 30$ wt.% as shown in Tab. 6. Probably this is due to the exceeding of a maximum filler content within polypropylene and will be investigated further.

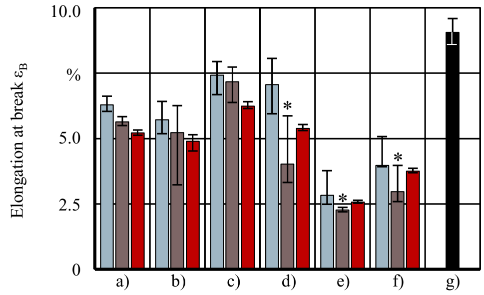


		E in N/mm²	t in min
PP	0 wt.%	647.2	47.8
PP/CF	10 wt.%	823.5	11.2
PP/CF	20 wt.%	1001.6	9.8
PP/CF	30 wt.%	1179.8	8.7

Fig. 6. Young's modulus for the mixed milling dust variant with its corresponding filler contents

4.2. Elongation at break

Polypropylene generally provides a high fracture strain, but carbon fibres as filler material reduce this particular material property. Conclusions can be drawn regarding the fibre-matrix-interface and its adhesion, see Fig. 7. With the increase of filler content, there is a degression in ductility as the carbon fibres itself tend to be more brittle. With a percentage reduction of 18.7 % in ductility compared to non-reinforced polypropylene, fine milling dust at $w_f = 10$ wt.% (granulate variant c) performs the best in terms of ductility. Furthermore, primary and pyrolysed compounds seem to have the best adhesion with PP due to the low elongations at break. However these material variants behaved differently at $w_f = 20$ wt.% than presumed. This is because of cavities within the test specimen, which led to a reduced cross-section. Therefore the test specimens performed worse than material with higher filler content. This failure is suspected to depend on the parameter choice of the injection moulding process.



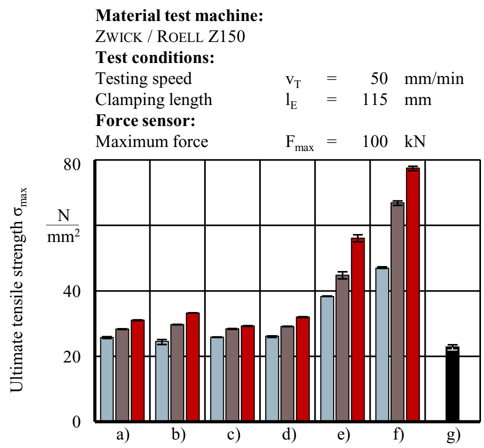
		ε_B in %						
		a)	b)	c)	d)	e)	f)	g)
PP	0 wt.%							9.1
PP/CF	10 wt.%	6.3	5.7	7.4	7.1	2.8	4.0	
PP/CF	20 wt.%	5.6	5.2	7.2	4.0	2.3	3.0	
PP/CF	30 wt.%	5.2	4.9	6.2	5.4	2.6	3.8	

* Fractured surfaces showed cavities

Fig. 7. Elongation at break for all compound variants with its corresponding filler contents

4.3. Ultimate tensile strength

An overall improvement of the ultimate tensile strength can also be stated for every compound variant, see Fig. 8.



		σ_{max} in N/mm²						
		a)	b)	c)	d)	e)	f)	g)
PP	0 wt.%							22.9
PP/CF	10 wt.%	25.8	24.6	25.8	26.1	38.3	47.0	
PP/CF	20 wt.%	28.3	29.7	28.4	29.1	44.8	66.9	
PP/CF	30 wt.%	31.0	33.2	29.3	32.0	56.1	77.5	

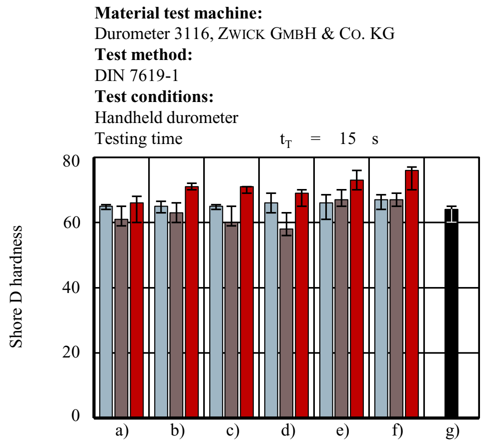
Fig. 8. Ultimate tensile strength for all compound variants with its corresponding filler contents

However, a clear distinction for milling dust between the different fibre lengths cannot be made as they perform very similar in their respective classes.

The maximum increase of milling dust was achieved with the intermediate variant and a filler content of w_f = 30 wt.%. Similar to the Young's modulus, the ultimate tensile strength is more dependent on the used filler content than on the fibre length. Still primary and pyrolysed fibres performed best with maximum tensile strength increases of 145 % and 238 %. When comparing them with the mixed milling dust, the reason for the difference in performance is due to the better fibre connectivity to the matrix. The purer surfaces of primary and pyrolysed fibres dispose of a better adhesion to the polypropylene. As shown in the SEM-images in Fig. 2, most of fibres are bundled and mainly covered in residues of epoxy. As a result, the mass fraction of milling dust is lower in comparison to primary and secondary fibres with an average fibre content of $w_{fb} \approx 50$ wt.% [13]. This ultimately leads to withstanding less tensile load.

4.4. Hardness

Due to dealing with a more rigid thermoplastic, Shore type D was applied for measuring the hardness. As a hand held measurement was utilised, there are not negligible error margins which had to be taken into considerations. Fig. 9 displays the Shore D hardness for each material variant and filler content w_f. The results show that there were no improvements towards the material hardness verifiable. This is probably due to the insufficient fibre lengths, not providing a reinforcement effect. Similar to the elongation at break ε_B, it is presumed that the fibres are being pushed during the instrumented indentation as they are too short to give resistance against penetration.



	Shore D hardness						
■ PP 0 wt.%							64
PP/CF 10 wt.%	65	65	65	66	66	67	
PP/CF 20 wt.%	61	63	60	58	67	67	
PP/CF 30 wt.%	66	71	71	69	73	76	

Fig. 9. Shore D hardness for all compound variants with its corresponding filler contents

5. Conclusion and outlook

The application of CFRP milling dust as a filler material in polypropylene shows a performance increase regarding rigidity and tensile strength to the detriment of the ductility. Still the performance does not achieve the material properties of primary and secondary fibre filled polypropylene due to impurities like residues of expoy resin.

However, on the basis of sustainability of CFRP machining the approach to consider milling dust as an additive for reinforcement purposes is one of many possibilities to close the material cycle of used carbon fibres. Yet further research has to be conducted focusing on rheological and electrical aspects of the compound granulate. Also the fibre orientation within the injection moulding process plays an important role in the forming of anisotropy and the resulting mechanical properties of short fibre reinforced thermoplastics. Thus, these aspects should be examined as well.

Acknowledgements

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