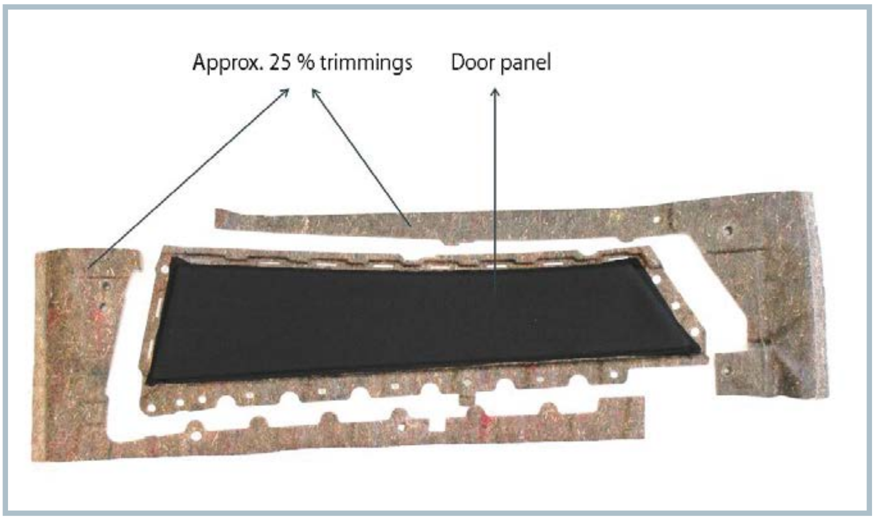
Filler with Lightweight Potential

Recycling of Natural Fiber-Reinforced Polymers to Sustainable Pyrolysis Char Filler

Mineral fillers are widely used in the automotive industry to enhance the performance of polymer grades. A recycling concept has now been developed, in which natural fiber-reinforced polymers are pyrolized to produce pyrolysis char as an alternative filler for thermoplastics.



Door panel trimmings of the Golf Sportsvan (© Volkswagen)

Mineral fillers such as talcum are widely used in thermoplastics for reinforced automotive components. Compared with virgin polymers, filled polymers have improved properties, e.g. stiffness and bending strength. Dimensional stability under heat is also improved by using talc. Disadvantages of mineral fillers are their high density as well as lower impact and tensile strength [1].

When used as filler in thermoplastics, pyrolysis char not only provides the same typical properties, but the composite's weight can be reduced due to the low density of char. Moreover, as a recycled product is used, no primary resources are required. Currently, this approach is being investigated by Volkswagen AG in cooperation with the Institute for Bioplastics and Biocomposites (IfBB) in Hanover, and the Rostock University. Since January 1, 2015 the ELV Directive specifies that at least 95 % of the mean weight of end-of-life vehicles must be recovered, and at least 85 % must be recycled or reused [2].

Closed Cycles

Because of the high demand for lightweight components in the automotive industry, natural fiber-reinforced plastics (NFRP) are finding increasing use. Compared with synthetic carbon or glass fibers, natural fibers such as hemp and flax have a low density and notable ecological advantages. NFRP components are produced by heating and pressure molding a hybrid fleece made of natural and polypropylene fibers. Excess material on the edges of the final part is removed by punching. These trimmings represent some 25 % of each component (**Title figure**) [3]. NFRP components are used e.g. in door panels of different vehicles, and consist of 50 wt.% polypropylene fibers and 50 wt.% natural fibers. It is estimated that some 3000 tons of trimmings are produced annually. This amount includes trimmings with comparable compositions from different vehicles and components produced by Volkswagen or its suppliers. At present, there is no practical alternative for producing NFRP components, so that edge trimming is still carried out. As a result, trimmings are thermally utilized, which means that a new recycling concept would be expedient. Moreover, the amount of scrap is certain to increase due to the growing use of NFRP in vehicles.

This article examines pyrolysis as a new recycling concept, in which pyrolysis char is created and used as filler for plastics, thereby ensuring a closed material cycle. Simultaneously, the lower density of pyrolysis char opens up the possibility of improved material properties, e.g. higher stiffness and better melt flow behavior.

Pyrolysis involves the thermal degradation of organic material into a carbon-rich solid (pyrolysis char) and volatile components in the absence of oxygen. The process is divided into three sections: low-temperature (up to 500 °C), medium-temperature (500 ... 800 °C), and high-temperature pyrolysis (above 800 °C), whereby the residence time can vary between minutes and several hours [4]. If volatile components condense, a mixture of liquid phase and non-condensable gases is created. All three mass flows (solid, liquid, and gas) that are formed by pyrolysis, exhibit different properties and possibilities for use [5]. With the NFRP examined here, the degradation of natural fibers in particular leads to the production of pyrolysis char [6, 7].

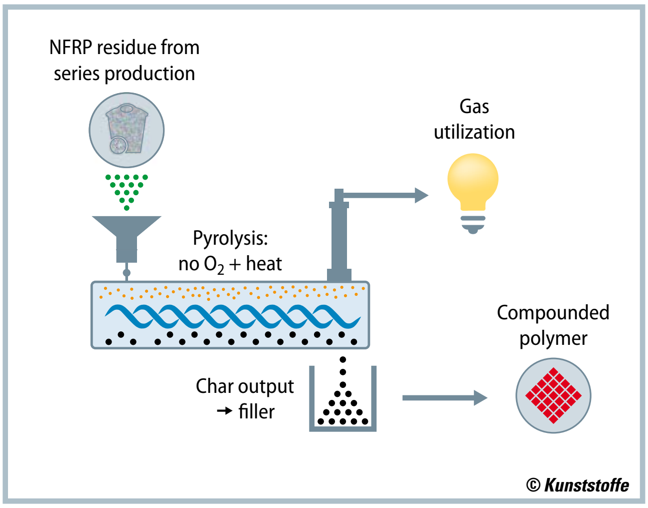


Fig. 1. Schematic of pyrolysis of NFRP residues into char, volatiles, and gases (source: Volkswagen)

NFRP Pyrolysis and Characterization of the Products

For these investigations, pyrolysis was conducted in a pilot plant (type: Ereka reactor, manufacturer: M.E.E.) with a burner for volatiles components and gases. **Figure 1** shows a schematic of the process. The trimmings are shredded in a cutting mill (type: MDS 410/200, manufacturer: Hellweg). Subsequently, the shredded material (sieve mesh size: 20 mm) is manually fed into the pyrolysis reactor. A thermogravimetric analysis was carried out first, to determine the pyrolysis parameters (nitrogen: 35 ml/min, heating rate: 10 K/min, **Fig. 2**). The process temperature is about 480 °C, and residence time is 10 minutes. Two screws transport the NFRP through the reactor during carbonization. The final char is discharged from the end of the reactor, and all generated condensates and gases are burnt for thermal use. Due to PP in the NFRP material, high-calorific gases and oils are produced. The total lower heating value of all products ranged between 4.3 and 5.1 MWh per ton of NFRP material (DIN 51900), so that the use as fuel is possible. Other options for use were not examined.

Figure 3 shows the shredded material and the pyrolysis char. The yield of solids ranged between 15 and 20 % of the raw material. Hereby, the carbon content increased from 62 wt. % in the raw material, to 79 wt. % in the char (TOC, DIN ISO 10694). Various investigations were conducted for a detailed analysis of the char. The specific surface of char is about 0.78 m^2/g (DIN ISO 9277), and a mesopore analysis (nitrogen isotherm at 77 K) showed that the char does not contain any pores smaller than 2 nm. However, optical methods (scanning electron microscopy and computer tomography) detected a few particles with small pores (**Fig. 4**).

Compounding the Pyrolysis Char

For an initial assessment of material development, different contents of char and various additives are compounded in a PP matrix (manufacturer: Borealis). **Table 1** shows an overview of all formulations. In addition, a bonding agent (manufacturer: BYK) and an impact strength modifier (manufacturer: Dow Chemical) are used. The bonding agent is supplied as a powder and is a PP grafted with maleic anhydride. The impact strength modifier is an ethylene-octene copolymer that increases the impact strength of thermoplastics. In order to analyze the influence of filler content, different proportions of char were compounded into the PP matrix. Compounding was done in a co-rotating twin screw extruder (type: ZE 34 Basic x 46D, manufactur- »

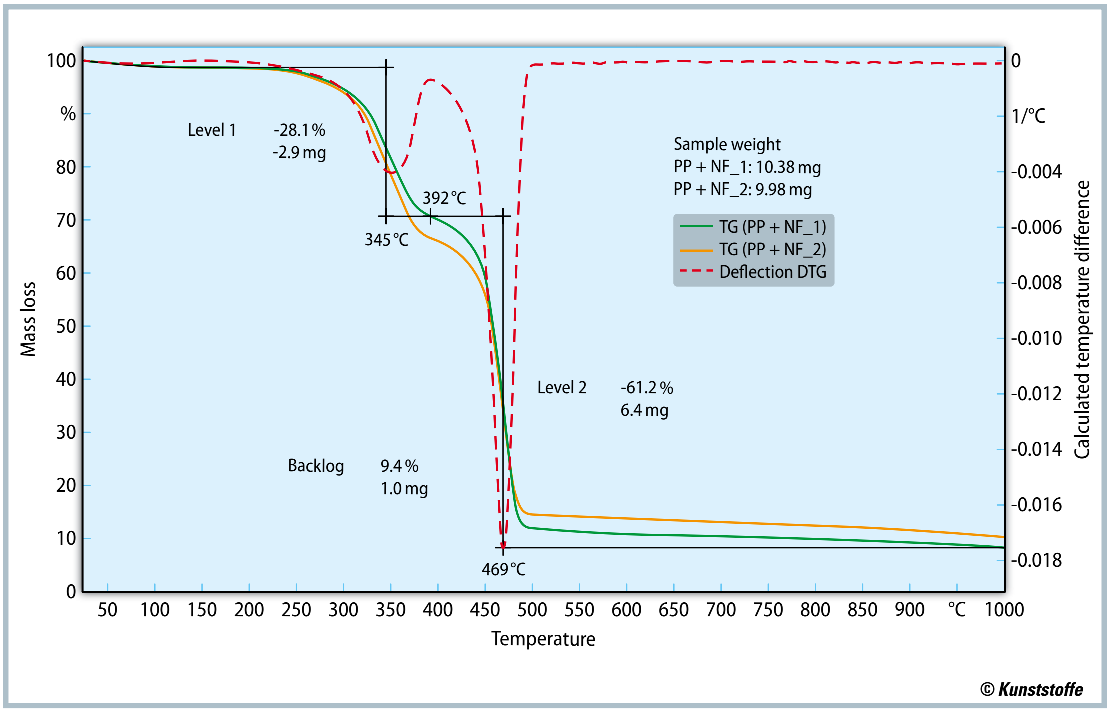


Fig. 2. Thermogravimetric analysis of raw material (NFRP) (source: Fraunhofer WKI)

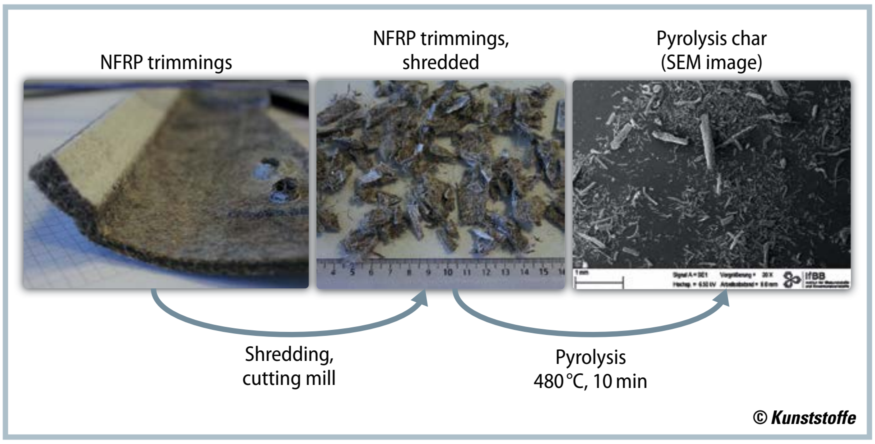


Fig. 3. Processing sequence – NFRP trimmings to pyrolysis char (source: Volkswagen)

Polypropylene [wt.%]	Char [wt.%]	Bonding agent [wt.%]	Impact strength modifier [wt.%]
100	-	-	-
90	10	-	-
80	20	-	-
77	20	3	-
72	20	3	5

Table 1. Overview of different material recipes in PP compounds (source: Volkswagen)

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er: KraussMaffei in Berstorff) at the IfBB in Hanover. Screw diameter is 34 mm with a length of 46D. For melting and fusing the matrix material and additives, the screws have a fusing zone with kneading block elements. This is followed by a feed zone for the char, including atmospheric back venting. The kneading blocks ensure that the char is homogenously compounded into the material. The feed zone also contains atmospheric forward venting and vacuum venting. After pressure build-up, the melt reaches the extruder's die head where the strands are produced. The test samples (type A) are produced with an injection molding machine (type: 50-180 AX, manufacturer: KraussMaffei). A tensile testing machine (type: Z020, manufacturer: Zwick) is used to determine the compound's mechanical properties.

Mechanical Properties of Recycled Filler

In general, the char has a compact structure. Laser diffraction (DIN ISO 13320) is used to analyze the particle size. The mean particle size is 34 µm (**Fig. 5**), whereby a bimodal distribution between 1...10 µm and 10...100 µm exists. The composition of the pyrolysis char is determined according to DIN 51732. The main constituent is carbon (79 wt. %), whereby oxygen (2.5 wt. %), hydrogen (7.08 wt. %), and nitrogen (5.18 wt. %) are also present. Ash content is 5.83 wt. % (DIN 51719) and in

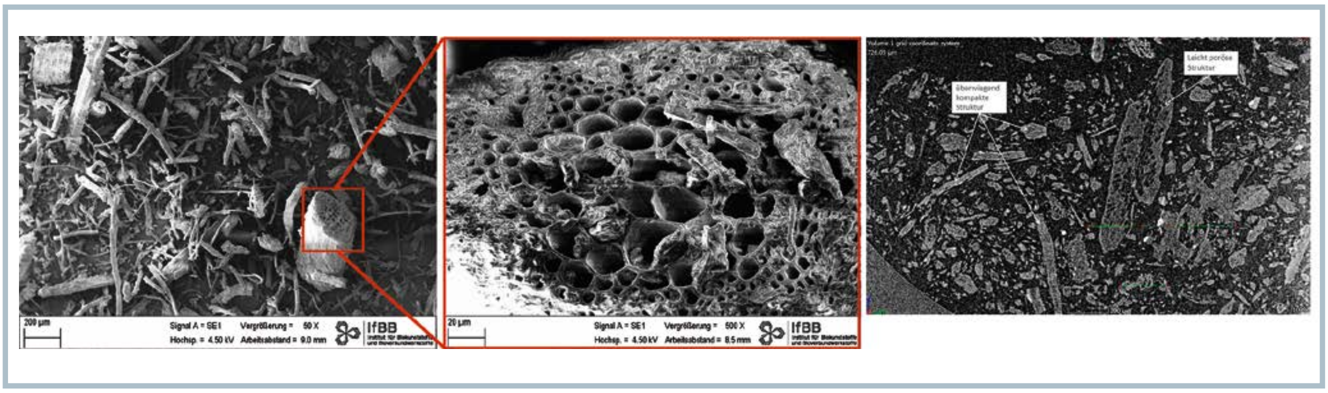

Fig. 4. SEM images (left 50x, center 500x) of char particles after pyrolysis, with pore structures from natural fibers. The CT image (right, in zy direction) of char particles shows several particles with pores (© IfBB)

particular, it contains the trace elements of the natural fibers.

Material development was focused specifically on the resulting processing and performance characteristics. The results of tensile testing (DIN 527), impact strength (DIN 179/1eA), heat deflection (DIN 75-1), melt flow rate (DIN 1133), and density are described below.

Figure 6 shows a network diagram with the results of different formulations. The values of pure PP are 100 %, and the other curves show the deviations due to the amount of char in the compound. It is clear that the addition of char results in a higher elastic modulus. The elastic modulus of the compound with 20 wt. % of char and 3 wt. % of bonding agent is about 1430 N/mm². On the other hand, tensile strength decreases slightly compared with pure PP. PP77/C20/BA3 has a tensile strength of 24.2 N/mm². Also the dimensional stability under heat (HDT-A) can be increased to about 60 °C by adding char, whereby compound density increases slightly with a higher filler content. Due to the increasing pressure of the different processing steps from extrusion to injection molding, char density varies. Based on the known constituents, char density can be back-calculated, so that density starts at 0.35 g/cm³ (DIN 53468) and increases to 0.73 g/cm³ after extrusion, and to 1.08 g/cm³ after injection molding. As some of the char particles still contain pores, they are compacted by the processing pressure. However, the density of the compound with 20 wt. % of char (DIN 1183-1, A) is about 10 % lower than the density of a compound with 20 wt. % of talcum ($\rho_{(PP+20\ wt.\%\ talcum)}$ = 1.04 g/cm³, $\rho_{(PP+20\ wt.\%\ char)}$ = 0.94 g/cm³).

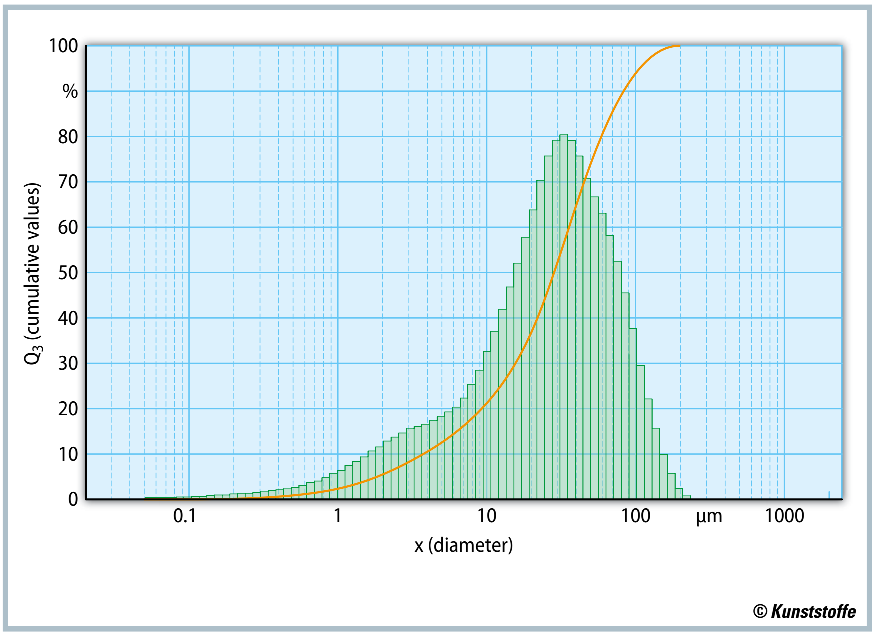

Fig. 5. Particle size distribution of pyrolysis char according to DIN ISO 13320 (source: Volkswagen)

Outlook

The investigations confirm that the innovative material has lightweight potential, although the properties have not yet reached the same level as talcum-filled PP. Moreover, the melt flow index increases with a char content of 20 wt. %, which improves the processing properties. However, this effect is slightly reduced by the use of additives, and usually becomes apparent only with higher char contents. Material brittleness due to the addition of carbon is still problematic, so that a few optimization steps will be necessary to obtain the required impact strength.

Consequently, a novel characteristic profile has resulted for pyrolysis char compounds. Possible applications in the automotive industry are being investigated, such as reinforced components in non-visible interior areas, which are currently manufactured with talcum-filled polymers. These include e. g. double-sided sunshades, where the carbon-reinforced material is used for the rear side. In general, further recipe improvements are necessary before the demands for series production can be met. ■

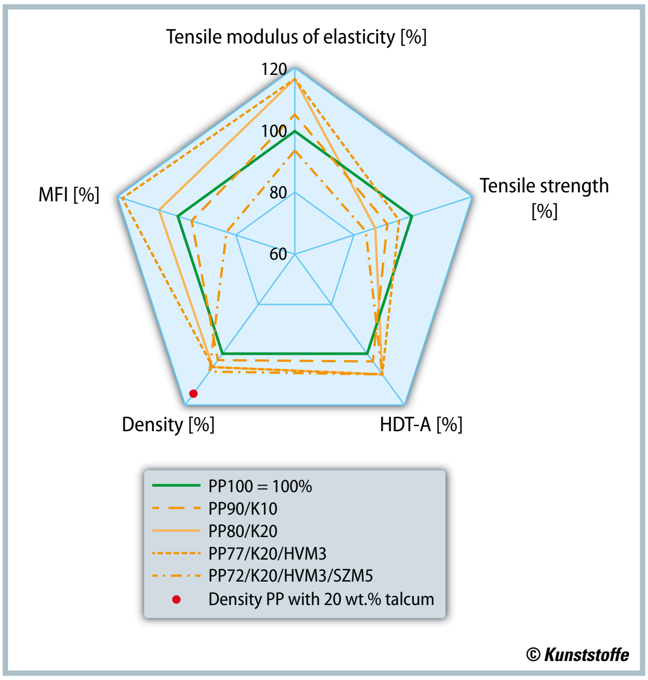

Fig. 6. Overview of the results – PP100 = 100 wt. %; other recipes are percentage variations (C = char, BA = bonding agent, ISM = impact strength modifier (source: Volkswagen)

To Dos until Series Production

- Pyrolysis optimization, and trials in a large-scale plant
- Preparation of char through milling for better dispersion in the polymer
- Further optimization of recipes, and compounding large amounts for material for mold trials
- Detailed ecological and economical evaluation