BioPolyComp

Biochar polymer composites with specific properties for innovative applications in material technology

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Projektbeschreibung

Biokohle kann unter Anderem als Zusatzstoff für Polymere eingesetzt werden um deren Eigenschaften an bestimmte Anforderungen in verschiedenen Anwendungsfällen anzupassen. Dabei können einerseits die mechanischen, die thermischen und auch die dielektrischen Eigenschaften ghoezielt angepasst werden, andererseits können Reststoffe genutzt werden, die bei der Biomassevergasung anfallen und sonst im Allgemeinen entsorgt werden müssten.
Die Eigenschaften von Biokohle können sehr unterschiedlich sein. Der Rohstoff, die Vergasungstechnologie, das Vergasungsmittel, die Prozessregelung und andere Faktoren spielen dabei eine wichtige Rolle. Für die Anwendung von Biokohle als Additiv in Polymeren ist deren Verfügbarkeit mit einheitlichen Eigenschaften bzw. einheitlicher Charakterisierung notwendig.

Im Rahmen des Projekts werden zunächst 2 Arten von Biokohle untersucht bzw. eingesetzt:
1. Biokohle als Reststoff von Biomasse-Vergasungsprozessen
Die Mengen bzw. die Verfügbarkeit von Biokohle als Reststoff bei der Biomassevergasung und deren Eigenschaften werden untersucht. Ergänzend werden experimentelle Untersuchungen mit Vergasern durchgeführt um die Möglichkeit der Beeinflussung der Eigenschaften der Reststoff-Biokohle zu untersuchen und zu bewerten.
2. Biokohle als gezielt erzeugtes Produkt mittels Pyrolyse
Biokohle mit bestimmten Eigenschaften für deren Einsatz als Additiv in Polymeren wird im Labor- und Technikumsmaßstab produziert.

Die auf diese Weise gewonnene Biokohle wird sodann mit verschiedenen thermoplastischen Polymeren vermengt und entsprechend dotierte Materialen werden erzeugt. Diese werden in Hinblick auf ihre Eignung für verschiedene Anwendungsbereiche untersucht bzw. getestet. Dabei werden zwei Richtungen verfolgt:
1. Anwendungen bei der Produktion von Polymeren mit gezielten mechanischen und thermischen Eigenschaften für “nicht-elektrische” Einsatzbereiche
2. Anwendungen in der Elektrotechnik, insbesondere in der Hochspannungstechnik als Halbleitermaterial bzw. Material mit hoher Dielektrizitätszahl zur Potentialsteuerung in Kabeln und Gießharz-Isolatoren.

Abstract

Char originating from biomass can be used among others as a bio-filler in the production of bio-polymer compounds with enhanced characteristics. The advantage is twofold: firstly, improving the mechanical, thermal and dielectrical properties of composites and secondly, utilizing organic residues from biomass gasification processes. This approach could be extended to other biochar production technologies such as pyrolysis or hydrothermal carbonization when wastes are used as feedstock.

Chars are very different among each other. Initial feedstock, gasification technology, gasification agent and operating conditions strongly affect the final characteristics of the biochar. In order to assess the best set of properties for biochar to be used in biopolymer compound applications, the production of innovative biochar-based polymers and their preliminary characterization are fundamental.

Within the project firstly two types of biochar will be applied resp. investigated:

1. Biochar originating as a residue from biomass gasification processes

Amounts resp. availability of biochar and their properties will be analysed. In addition, experimental investigations with gasifiers will be carried out in order to analyse possibilities of targeted control of the gasification process to improve the properties of the biochar residues in the viewpoint of their application as carbon additive in polymers.

2. Biochar, intentionally produced for polymer-addition via pyrolysis.

Biochar with specific properties for the application as additive in polymers will be produced in laboratory scale.

The biochar will then be blended with different thermoplastic polymers resulting in different biochar-polymer composites, which will be characterized regarding their applicability for specific applications, whereby two fields of applications are targeted:

1. Applications in the production of biochar-polymer compounds with adequate mechanical and thermal properties in the “non-electrical” sector.

2. Applications in the high voltage (HV) technology as a semiconducting dielectric resp. a dielectrict with high permittivity with the option of targeted field grading in HV-cables and cast-resin isolators.

Endberichtkurzfassung

INTRODUCTION

Char originating from biomass can be used as a sustainable carbon additive in the production of polymer compounds with enhanced characteristics. The advantages are manifold: firstly, char addition may improve the mechanical, thermal and dielectric properties of the composites and secondly, the substitution of fossil carbon sources reduces the CO2-footprint of the composite production. Furthermore, utilizing organic residues, e.g. from biomass gasification-based CHP-plants, can improve the overall plant economy by generating a valuable side-product. Chars differ considerably depending on their origin. Indeed, initial feedstock, conversion technology, reactive agents and operating conditions strongly affect the final characteristics of the char. In order to assess the suitability of char in polymer composite applications, the investigation of the char, the composite production processes and the detailed characterization of the final products are fundamental. One objective of this work is to identify correlations between char characteristics and properties of the final composite to determine requirements on char as an BPC additive to achieve enhanced product qualities.

METHODOLOGY

Within the project, chars of different origin, 1) the solid residue from biomass gasification processes, 2) pyrolytic biochar, are sampled and analysed. Threshold values such as moisture content, volatile content, maximum particle size, enabling subsequent polymer compounding processes are identified. Char parameters like ash content, fixed carbon, elemental composition, particle density, particle size distribution, specific surface area, pore size distributions, structural constitution via Raman spectroscopy are determined to investigate possible correlations to polymer composite properties. Gasifier process conditions are varied in order to assess possibilities to improve the properties of the char residues considering their application as carbon additive in polymers. During the subsequent compounding process char is blended with various thermoplastic polymers resulting in different char-polymer composites. These polymer composite samples are characterized regarding their applicability for specific assignments. Two fields of application are targeted: 1) production of char-polymer composites with adequate mechanical and thermal properties for 3D-printing applications and 2) functionalized utilisation in high voltage (HV) technology as a semiconducting dielectric or a dielectric with high permittivity for targeted field grading in HV-cables and cast-resin isolators.

RESULTS

Producing, collecting and characterizing chars

A first screening of available chars from pyrolysis (own test facility) and gasification processes (6 commercially operating plants) and carbon black as a commonly used reference additive, showed significant differences in parameters that are assumed to have an impact on composite materials properties and/or composite manufacturing performance, such as content of ash and volatiles, the specific surface area and particle size distribution.

Ash contents in chars are overwhelmingly defined by the input materials and varied widely between 2 and 20 m.%. The volatile matter of biomasses (~ 80 m.%) was reduced to 6 to 9 m.% in chars from biomass gasification, but remained at considerably high level of 20 to 33 m% in samples from the pyrolysis pilot plant. Based on that they were excluded for further use as a polymer additive due to their degassing effects during composite compounding. Further tests were carried out with gasification derived chars, produced at different temperatures (795 to 900°C) and applied to different post-treatment (milling, washing, sieving).

This allowed to highlight the differences and the impact of char characteristics and pretreatments on polymer composite properties.

Compared to all tested gasification chars, Carbon Black shows the lowest ash content (0.93%), the highest C content (99.0%), the lowest VM content (1.8%) the highest FC content (96.9%), the highest surface area (1069 m^2/g) and the highest pore volume (2.19 cm^3/g). As expected, CB and char are two different materials: the first one is made on purpose to reach high carbon content and surface area, the second one is a by-product of the gasification process and thus is considered as a waste. Highlighting the similarities between the two materials can foster the exploitation of char and its valorisation in industrial applications.

Controllability of biochar properties in biomass gasifiers

Beside the investigation of produced and collected chars, the effect of gasifying agent (nitrogen or carbon dioxide), temperature (500 °C, 700 °C and 900 °C) and heating rate (10 °C min^{-1} , 30 °C min^{-1} or 50°C min^{-1}) on the characteristics of the char collected downstream the process has been assessed. In particular, char yield, carbon content, higher heating value, surface area, pore size and pore volume were considered.

All the investigated process conditions (gasifying agent, temperature, and heating rate) have a statistically significant influence on the char yield. The highest char yield (28.7%) was achieved in oxidative atmosphere, at low temperature (500 °C), and low heating rate (10 °C/min), while the lowest (10.7%) at 900 °C, 50 °C/min in oxidative atmosphere. Temperature affects the char yield more than the heating rate. In fact, high temperature accelerates the biomass thermal cracking. Similarly, high heating rates favour the depolymerization and fragmentation of biomass. This can be explained by the fact that the secondary reactions dominate over the primary reactions, an effect promoted by low temperatures rather than high temperatures.

As far as the carbon content is concerned, the carrier gas does not seem to play a major role, while an increasing trend with the temperature can be recognized in accordance with the fact that the carbonization process is accelerated by increasing the temperature (Table 1). Only at 900 °C, char obtained under N_2 shows a higher carbon content (94.43% at 50 °C/min) than the one obtained in CO_2 (91.68% at 50 °C/min), since high temperatures enhance the thermal conversion of the feedstock and thus, the impact the oxidizing agent. Regarding HHV, values are generally higher for the pyrolysis chars than for the chars obtained with CO_2 gasification reaching the maximum value of 33.5 MJ/kg at 700°C and 10 °C/min .

Since BET surface area (S_{BET}) shows an increasing trend versus the heating rate for some temperatures and a decreasing one for others, without a common behaviour among the different carrier gases only the dependency of S_{BET} from temperature and carrier gas was considered. Data shows that S_{BET} increases with temperature under both atmospheres and that this trend is more pronounced in the case of CO_2 , which also corresponds to the highest S_{BET} values measured (673 m^2 /g).

Melt Compounding of chars and thermoplastic polymers, 3D-Printing and requirements of biochar quality

First screening tests showed that the general processability of char as polymer additive producing filaments for 3D-printing can be achieved, considering boundary conditions regarding the char properties such as content of volatiles, particle size, and char to polymer ratios.

During the extrusion moisture and volatile organic substances can be released. Furthermore, a maximum particle size must not be exceeded, to avoid mechanical obstacles in downstream process units (e.g. 3D-printing). The analysis of physical/chemical properties and melt compounding tests permitted to define the following requirements for biochar:

Granulometry: particle size lower than 250 µm

Moisture content: lower than 3 %

Content of volatiles: lower 10 %

With the defined restrictions in biochar properties melt compounding tests of blending chars and thermoplastic polymers were performed successfully. Composite pellets and filaments were produced by employing identified optimal process extrusion parameters (barrel- and molding temperature, injection pressure and time) and further processed by injection molding to study the feasibility of the process. The overall workability of the compounds was very good compared to carbon black benchmark. In fact, these biochar samples showed very good metering in feeder and flow in hopper, produced very low fume emission from vent port and affected only slightly the viscosity of the melt. From the analysis of monitored screw torque and die pressure over biochar content it is clear that the biochar samples tested produce a limited change of the polymer rheology (TPU Estane and PE Eraclene) in particular if compared to the effect of carbon black. From workability point of view little or no differences were noticed among the different biochar samples.

All samples were pre-dried in a vacuum oven and then test specimen with different geometries were printed by injection molding: dog-bone specimen for mechanical and disk-shaped specimen for electrical characterization related to different high voltage application fields. Charpy specimens were also printed for further uses.

Industrial tests by 3D printing

All compound samples based on TPU matrix showed an overall good printability compared to the neat polymer in contrast to the results achieved with blends based on PE. In the latter case the extrudability was good but the presence of biochar does not improve the well-known problems that limit the use of polyethylene in FDM 3D printing like adhesion and dimension stability.

The printability of the TPU based compound was good also at industrial scale and comparable to the printability of neat TPU. In particular it showed good adhesion to the bed and interlayer adhesion. A tiny tendency to stringing, known from working with neat TPU, was observed.

A special field grading element was successfully printed for further tests of field grading effects using biochar-added polymer-elements in cast resin parts.

Mechanical properties of (produced) composite samples

In an attempt to assess the influence of added biochar on the mechanical properties of polymers, tensile testing was performed on suitable dog-bone-samples. The observed stress-strain-curves are typical for a soft elastic polymer such as

TPU. The ultimate tensile strength of the five samples tested was between 80 and 100 MPa. The samples experienced significant strain when the mechanical stress was increased. Samples elongated by a factor of 4 – 8 before fracturing. The loading rate influenced the mechanical behaviour, however, no clear trend was discernible. Considering this and the observed scattering of results different sample geometries shall be used in future tests.

Dielectrical properties of (produced) composite samples

Various measurements on polymers and cast resins containing different amounts of biochar as well as Carbon Black have been performed. In total, 23 different polymer composites and 16 cast resin samples were tested. The overall aim of the investigations was to examine the extent to which biochar as a powdered filler changes the dielectric properties of polymers.

When used in TPU, the material's relative permittivity rises from ε r ≈ 6 to ε r ≈ 12 for f = 50 Hz, when the char content is increased from 0 wt% to 15 wt%. Additionally, conductivity can be influenced by 10 orders of magnitude when the char content is increased from 0 wt% to 30 wt%. The associated percolation threshold is reached in the range of 15 – 20 wt% biochar. Especially for low biochar contents, conductivity is influenced significantly by temperature.

Compared to TPU, the dielectric properties of PE are influenced to a much lesser extent by the addition of biochar. Regarding the substitution of Carbon Black for conductive polymer composites, it was found that higher biochar contents are needed to achieve similar dielectric properties.

With the help of biochar fillers, it was also possible to significantly influence the dielectric properties of epoxy resin samples. Only minimal temperature dependencies were observed. Depending on the type of biochar, addition of 6 m.% biochar led to an increase in relative permittivity by a factor of 4 – 7 (at f = 50 Hz). With a biochar content of 10 m.%, it was possible to increase conductivity by 9 orders of magnitude.

The investigations performed show that the dielectric properties of polymers can be varied within wide limits using biochar additives. This offers the possibility of tailoring the material properties specifically to the intended application. In addition to studies on the ageing behaviour, future research shall in particular investigate the processing of these materials using modern production technologies.

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