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Optimization of Dosing Methodof Hybrid Filler (Cellulose/MgAl LDH) in Biopolymers Using Micro-Compounder for Preparation of Bio-Composites

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Optimization of Dosing Method of Hybrid Filler (Cellulose/MgAl LDH) in Biopolymers Using Micro-Compounder for Preparation of Bio-Composites

Sajid Naseem, Sandra Heckel, Martin Zahel and Andreas Leuteritz[1]

Abstract: With growing environmental concerns about using conventional plastics in daily life, the demand for bio-based polymer products is increasing. Natural and biodegradable raw materials are alternatives for making plastic products more sustainable. Cellulose-based fibers have gained attention in preparing biodegradable polymer composites because of their biodegradable nature, bio-based origin, low cost and low weight compared to synthetic fibers (glass and carbon). In this research, hybrid fillers based on cellulose and hydrotalcite were used in biodegradable polymers such as in PLA and blend of PBAT/PLA to prepare bio composites. The loading of hybrid filler (cellulose/LDH) was done using a small-scale compounding machine. Hybrid fillers were used in compounding machines in different forms (paste, freeze dried, PLA dissolved, PEG mixed, and sheet based) with PBAT/PLA. The dosing method of hybrid filler in polymer was optimized in this work. Morphological analysis of hybrid filler and the mechanical properties of bio composites were also done. The tensile modulus of PLA was increased by about 33% when sheet-based hybrid filler was added to the PLA composite.

Keywords: Biodegradable, Cellulose, Bio-Composites, Hybrid Filler, MgAl LDH, Polylactic Acid (PLA), PBAT

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Introduction

Plastic-based products produced by using petroleum raw materials are becoming a huge concern, as they are less environmentally friendly [1,2]. Global environmental safety issues and regulations encourage researchers to work on biodegradable products that could replace conventional plastic products [1,3]. Bio composites can be a good alternative for solving the problems that arise due to the use of non-degradable plastic products. Natural fillers and natural fibers are components used in many types of polymer composites to make them environmentally friendly products [4]. One of the important fillers is hydrotalcites [MgAl layered double hydroxides (LDH)] which are being used in many different polymers over the last few years and are available naturally and can also be easily synthesized [5-8]. The other common bio-based fiber is cellulose fibers, which are being used in polymers. The use of a combination of fillers such as mineral fillers with cellulose in polymers has gained special attention because they could improve the properties of polymers [3]. The improved form of cellulose and mineral filler is a hybrid filler, combining positive aspects of both when used in bio-polymers that may provide fully environmentally compatible products, as shown in Figure 1. These types of bio composites are getting attention but there is big challenge to mixing these cellulose based fillers in a given polymer matrix. The objective of this research is to optimize the loading method and mixing of hybrid filler (cellulose/LDH) in polymer matrices (PBAT, PLA) to make fully bio-compatible plastic products, as shown in Figure 1 below.

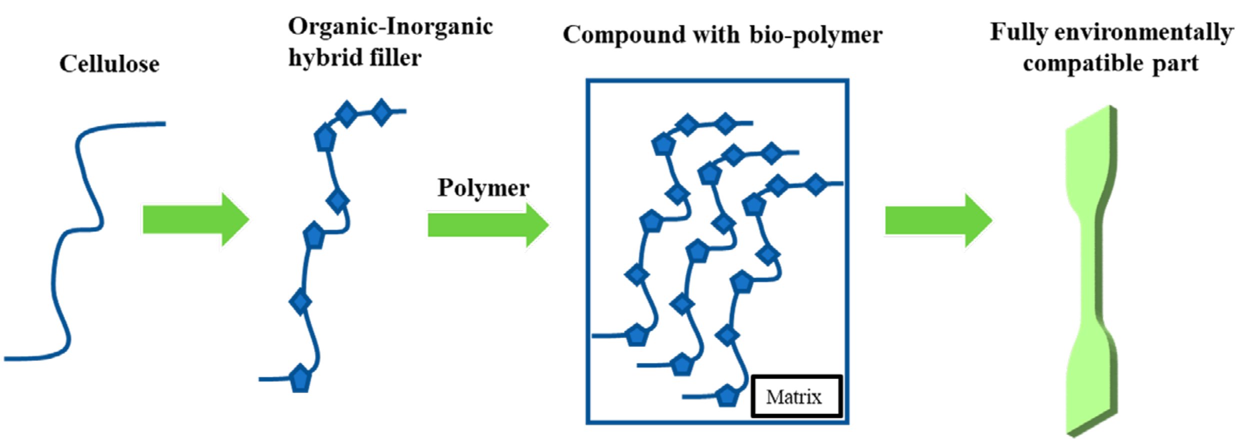

Figure 1. Schematic representation of hybrid filler/polymer bio-composites.

Materials and Methods

Hybrid fillers of cellulose and hydrotalcite [MgAl layered double hydroxides (LDH)] were supplied by Papiertechnische Stiftung (PTS), Heidenau, Germany. PLA (PLA: NW Ingeo 3251 injection molding grade), PBAT (Ecoflex F1200 film grade) (BASF), PLA (BioFed) (supplied by BioFed Germany), poly(ethylene glycol) (PEG) (BioUltra 10K) (Sigma Aldrich), dichloromethane (Acros Organic now Thermo Scientific), and distilled water were used in this work.

Preparation Methods of Bio composites

Preparation of bio composites was done using a micro-compounder (X-plore, The Netherlands), as shown in Figure 2, which contains a compounding part and an injection molding part. Hybrid filler (cellulose/LDH) and PBAT, PLA were mixed with different techniques, as shown in Table 1. The dosing method of hybrid filler in matrix was optimized using 5 wt.% loading in polymer matrix.

Figure 2. Micro-compounding machine and injection molding setup used for preparation of hybrid filler/PBAT/PLA bio-composites [9].

Table 1. Description of composition of hybrid filler/PBAT/PLA bio-composites and types of hybrid filler dosing system.

Sr. No.	Form of hybrid filler	Hybrid Filler (wt. %)	Matrix (37 % PBAT + 63 %PLA (3251)) or PLA (BioFed) (95%) (wt. %)
1	Paste filler	5	95
2	Freeze dried filler	5	95
3	Solvent mixed PLA filler	5	95
4	PEG mixed filler	5	95
5	Sheet based filler	5	95

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The pure PLA (BioFed) and the mixture of PBAT and PLA (3251) were used here as a matrix in this research, as shown in Table 1. The mixture of hybrid filler and polymer was compounded for 10 min at 100 rpm speed at a temperature of 190°C. The amount of hybrid filler used was 5 wt.% in each form of dosing system. The mixture was then delivered from a micro-compounder to a piston device for preparing samples for mechanical testing.

Characterization

SEM images were taken with a Zeiss Ultra Plus to visualize the hybrid filler of cellulose and MgAl layered double hydroxide (LDH). Tensile properties of bio-composites were measured according to DIN EN ISO 527-2/1BA/50 with a Zwick 1456 (Ulm, Germany). The Charpy impact strength of bio composites was measured using the standard ISO 179/1eU. The results of bio composites were averaged over five measurements for each sample for the tensile and Charpy impact testing.

Results and Discussion

Scanning Electron Microscopy (SEM) Images of Hybrid Filler

Figure 3 shows the SEM images of hybrid filler sample, which contain cellulose fibres and MgAl layered double hydroxide. The MgAl LDH particles are attached to the cellulose fibers, as can be observed in the SEM images. The hexagonal shape of MgAl LDH is also visible in Figure 3, which shows the well-ordered structure of MgAl LDH present in hybrid filler and attached to the cellulose fibers.

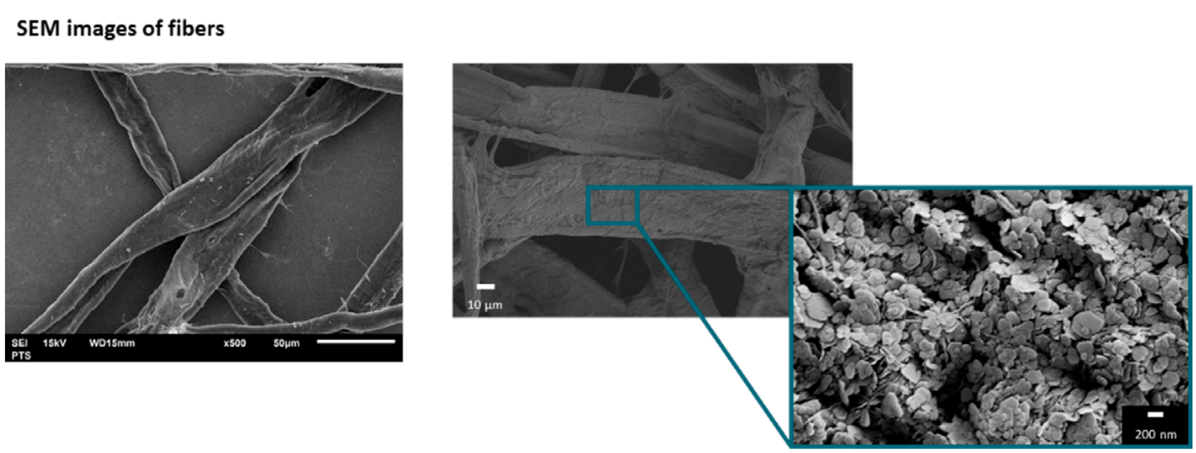

Figure 3. Scanning electron microscopy images of hybrid filler containing cellulose and MgAl layered double hydroxides (LDH).

Types of Dosing Systems of Hybrid Filler in PBAT/PLA Matrix

Figure 4 (a-e) show the form of hybrid filler that is used in the polymer matrix in the micro-compounding machine. The different forms of dosing are used here because the mixing of these hybrid filler in polymer was not easy. Initially, the hybrid filler in the form of paste (Figure 4[a]) was used during compounding. Freeze drying of paste (Figure 4[a]) was done and then used in the compounding machine to observe the mixing behavior. After freeze drying, the hybrid filler becomes fluffy and the volume of the freeze-dried hybrid filler (Figure 4[b]) increased. In the third option, freeze dried hybrid filler was first mixed in a solution of PLA (Figure 4[c]) and this mixture was then used in the compounding machine with the PBAT/PLA blend. In the fourth option, hybrid filler was first dispersed in PEG (Figure 4[d]) and then that PEG mixed hybrid filler was used in the compounding machine. Lastly, the sheet (Figure 4[e]) was made from the paste of hybrid filler and then used in the compounding machine with PLA(BioFed). All five dosing techniques were done to investigate which technique gives good mixing and good samples.

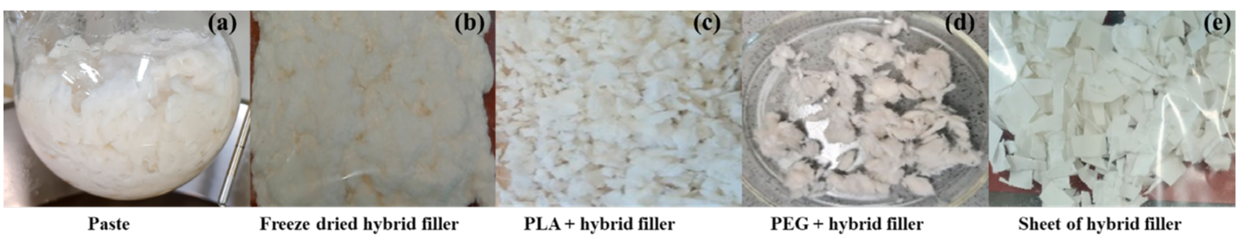

Figure 4. Hybrid filler dosing in different form (a) paste dosing (b) freeze dried filler dosing (c) hybrid filler dissolved in PLA (d) hybrid filler dissolved in PEG (e) sheet dosing.

Issues During the Dosing of Different Forms of Systems

Paste dosing was done with a polymer matrix in the micro-compounder and after mixing the polymer melt could not inject in the injector and in the end no sample could be made, as can be seen in Figure 5(a). The degradation of PBAT/PLA might occur during compounding in case of paste dosing due to the presence of water [10]. When freeze dried hybrid filler was used in the micro-compounder with PBAT/PLA, the filler was not mixed completely in polymer and some unmixed material was left in the mixing chamber, as can be seen in Figure 5(b). Due to the increase in volume and fluffiness of the hybrid filler after drying, the polymer melt could not infiltrate the hybrid filler. One reason might be the mismatch of surface properties leading to less interaction during mixing with PBAT/PLA. To overcome the issue of incomplete mixing of hybrid filler with polymer matrix, the freeze-dried hybrid filler was first mixed in the PLA solution and then dried that mixture. The dried mixture of hybrid filler/PLA was then used in the micro-compounder with PBAT/PLA. The mixing was done completely in this case but removing the sample from the mold was

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difficult and the sample broke in most cases, as can be seen in Figure 5(c). This might be due to increase in brittleness in the bio composite.

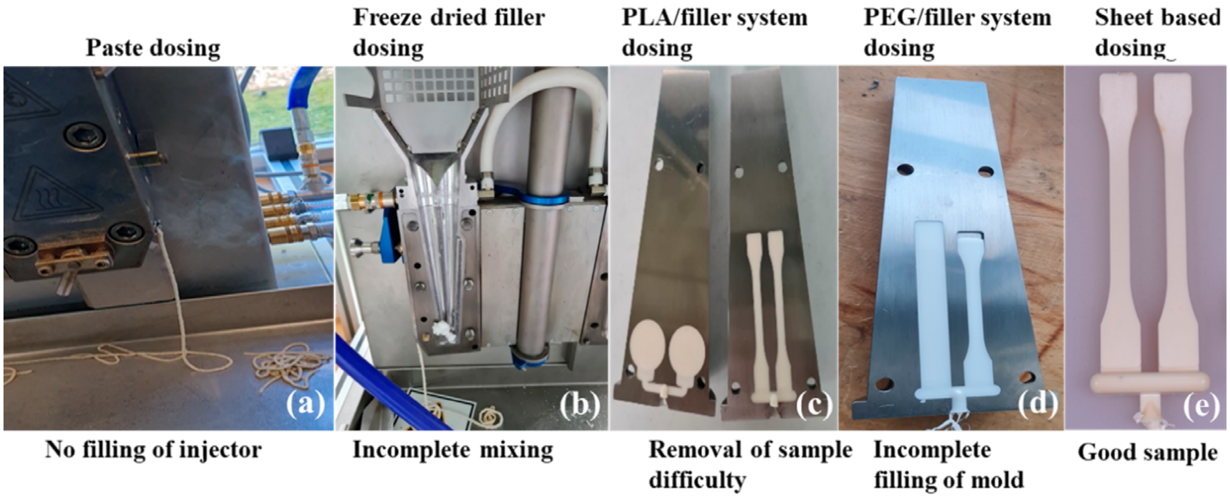

Figure 5. Different types of dosing system of hybrid filler (LDH/cellulose) in PBAT/PLA and issues during compounding process.

To overcome the issue of brittleness and broken samples after compounding, another option was used in which hybrid filler was dissolved in PEG and then used in PBAT/PLA in the micro-compounder. In this case, incomplete filling of the mold was observed, as can be seen in Figure 5(d). Lastly the sheet was made from hybrid filler paste in a press machine. The sheet was chopped and then used in PBAT/PLA. The mixing was relatively good and the sample was good in the end when compared to the other 4 methods of dosing, as can be seen in Figure 5(e). Finally, the sheet of hybrid filler was also used in PLA (BioFed) to compare the mechanical properties.

Mechanical Properties of Hybrid Filler-Based Bio Composites

The mechanical analysis was done on the sheet-based hybrid filler samples and is shown in Table 2. The bio composites of PLA (BioFed) were prepared using 5 wt.% of hybrid filler in PLA and the mechanical properties were compared with pure PLA. The tensile modulus and impact strength increased in the case of the hybrid filler samples. The tensile modulus in pure PLA was 2050 ± 152 MPa and in PLA composite was 2730 ± 230. The impact strength in case of pure PLA was 13.4 ± 1.18 and in case of composites was 19.1 ± 1.09.

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Table 2. Mechanical properties (tensile and impact testing) of hybrid filler/PLA(BioFed) composites in which sheet dosing was used.

Sr. No.	Hybrid filler (sheet) (wt. %)	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Impact strength [kJ/m²]
1	0	35.37 ± 0.43	2050 ± 152	6.4 ± 0.89	13.4 ± 1.18
2	5	31.02 ± 0.73	2730 ± 230	4.8 ± 0.55	19.1 ± 1.09

Conclusion

The dosing technique of hybrid filler was optimized in this work. Five types of dosing methods were used and various issues in each dosing system were observed. The sheet made from paste of hybrid filler showed optimum results as the compounding was good and the sample obtained was also good as compared to other dosing systems of hybrid filler. Mechanical properties (modulus and impact strength) were enhanced at 5 wt.% loading of hybrid filler in case of the sheet-based dosing system. The tensile modulus was increased about 37% at only 5 wt.% loading of hybrid filler, which shows the potential of this hybrid filler in the bio composites field. As the amount of hybrid filler used in this research work was only 5 wt.%, the increased amount of hybrid filler in the polymer matrix could lead to other mixing issues, such as reduced homogeneity. The ratio of layered double hydroxide (LDH) and cellulose in hybrid filler could also lead to different mixing issues. The optimization of amount of filler loading such as more than 5 wt.% and ratios of LDH/cellulose in hybrid filler could show different results while compounding and need to be further investigated.

Acknowledgments

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