Biodegradation of natural reinforcing fillers for polymer composites

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Abstract. Twelve different natural raw materials were selected as possible fillers for eco-friendly biocomposites. The target was to find the most biodegradable ones. Two mycological tests were held: in the aqueous and agar media. It was found that two tests showed different results. In aqueous media, the fillers with a high content of water-soluble and easy-hydrolysed compounds demonstrated the most intensive biofouling. In agar media, the entire filler was exposed to biodigestion by fungi. Therefore, multi-compound fillers with a set of different macro- and microelements were more biodegradable than others.

1. Introduction
Among solid domestic and industrial waste, synthetic polymers, particularly polyolefins, are the most resistant to biodegradation by microorganisms that is due to their chemical nature and high hydrophobicity [1]. In view of this, developed countries are engaged in creating novel biodegradable polymeric materials. Adding natural fillers into synthetic polymers allows developing materials with enhanced biodegradability and partially replacing non-renewable petrochemical resources with renewable ones [2,3]. In such composite materials, the synthetic polymer provides optimal mechanical properties and recycling possibility [4]. In turns, the natural filler content in composites enhances the ability to bioassimilation by microorganisms [5,6]. The composite compound has the greatest effect on its biodegradability that proves the importance of filler kind choice and its investigation. The aim of this work is to determine the most effective natural fillers for developing biodegradable polymeric composite materials. The focus of this study was in determining the degradation and deterioration of a set of natural components used for filled composites due to the action of mold fungi cultures. Results interpretation emphasis is on the correlation between chemical composition and biodegradability of natural fillers.

2. Materials and methods
2.1. Materials
In deciding on a particular set of natural fillers initiating composites biodegradation, the following requirements were taken into account: low cost and affordability; ecological safety of biodegradation products; possibility of grinding on standard grinding equipment; high temperature of thermal destruction.
A set of natural components being waste products of various industries and rarely used for making polymer compositions were studied. The chemical composition of the fillers under investigation was analyzed according to literature data (table 1) [7-12].

**Table 1. Chemical composition of natural fillers.**

| Filler       | Cellulose | Hemicellulose | Lignin | Starch | Peptides | Lipids | Ash |
|--------------|-----------|---------------|--------|--------|----------|--------|-----|
| Oil flax     | 47÷58     | 5÷17          | 10÷21  | –      | 3÷9      | 2÷4    | 3÷12|
| Fibre flax   | 38÷40     | 14÷15         | 23÷24  | –      | n/a      | 2÷4    | 2÷8 |
| Wheat        | 40÷46     | 24÷32         | 6÷8    | 1÷2    | 4÷5      | 1÷2    | 6÷8 |
| Husk         | 31÷35     | 18÷19         | 27÷29  | n/a    | 3÷5      | 2÷4    | 3÷5 |
| Wood         | 45÷48     | 10÷13         | 28÷30  | 1÷2    | n/a      | 1÷2    | 1÷2 |
| Leaves       | 24÷26     | 3÷5           | 33÷35  | 2÷3    | n/a      | n/a    | 5÷7 |
| Banana       | 7÷12      | 6÷8           | 6÷10   | 13     | 9        | 13     | 3÷8 |
| Hay          | 35÷49     | 10÷15         | 23÷27  | 1      | 10÷11    | 2      | 12÷14|

The analyzed fillers include oil flax straw (oil flax) (grade LM98), winter wheat chaff (wheat) (grade Krasnodar-99), fir wood flour (wood), product of keratin hydrolysis of bird's feather (oligopeptides), fibre flax shive (fibre flax), sunflower husk (husk), sodium lignosulfonate (SL), banana skin (banana), birch leaves (leaves), mixed herbs hay (hay).

As reference fillers, powdered cellulose (hereinafter cellulose) (Polycell PCC, TU 5410-029-32957739) and corn starch (starch) (GOST R 51953) having a fixed chemical composition and widely used for development of biodegradable composite materials based on synthetic polymers were studied.

Fillers were preliminary dried for 3 hours at (80 ± 2)° C, crushed in an electric mill with a rotary knife, and screened by means of a sieve analyzer.

### 2.2. Methods

The effectiveness of natural fillers as additives accelerating the biodegradation of polymers was determined by growth intensity of mold fungi. To assess the effect of the input materials on the development of the test cultures, experiments were carried out on aqueous and agar media with filler particles in accordance with GOST 9.049 [13] and ISO EN 846 [14]. In the experiment, test cultures of mold fungi *Aspergillus niger*, *Aspergillus terreus*, *Penicillium chrysogenum* from the collection of Mycology and Algology Department of Lomonosov Moscow State University were used.

For the experiment on aqueous media, the substrate was a solution of bidistilled water containing 10 wt.% of milled filler. For the experiment on agar media, a solution of bidistilled water with 2 wt.% of dry agar was prepared, after sterilization of the solution 10 wt.% of milled filler was added thereto. The substrates were exposed to detention for 1 day and autoclaved at a pressure of 1 atm. at a temperature of 121° C for 30 minutes. After that, the substrate was poured into test tubes and Petri dishes for experiments on aqueous and agar media, respectively. The media were inoculated by spores of pure fungal cultures with a prick method. Bistillated water and Czapek's medium without saccharose were used as control substrates for experiments in aqueous and agar media, respectively.

Incubation of media contaminated with the test cultures was carried out under conditions of relative humidity over 90% and a temperature of (25±2)° C. The incubation period for agar and aqueous media was 28 and 14 days, respectively, with monitoring after 2, 5, 8, 11, 14, 21 days.

For aqueous media, the biomass of micromycetes and change in the pH-index of the medium were determined. For biomass gain analysing, the grown mycelium of fungi was filtered on a shaker, dried and weighed. By the mass of the grown mycelium, the biodegradability of the water-soluble part of the material was determined.

After the incubation period on the agar media, the degree of mold fungi development was assessed
[14]: linear growth rate of fungal seed colonies, development of the aerial mycelium, and the onset of sporulation.

3. Results and discussion

Under the action of mold fungi, natural fillers degraded to carbon dioxide and water. As the experiment was conducted for 28 days, the total biodegradability was not reached. To assess the fillers’ biodegradation, biomass gain and growth intensity of fungal cultures were analysed.

Figure 1 shows total fungal biomass gain for aqueous media with different natural fillers after 14 days from inoculation, recalculated by 1 g of the filler. According to the results of this study, all used fungal cultures had a high ability of growth on natural fillers extracts. The main biodestructor of fillers was *Aspergillus terreus*, which is a universal destructor assimilating the majority of polysaccharides and polypeptides.

![Figure 1. Biomass gain due to fungal growth in aqueous media for different fillers.](image)

The aqueous media with additives of oil flax straw, oligopeptides and lignosulfonate had the maximum total biomass gain (12±0.5 wt.%). Less biomass accumulation was fixed for media with birch leaves, hay, wheat chaff and wood flour (total biomass gain is 8±1 wt.%). The media with fibre flax, banana peel and sunflower husk showed the lowest biomass growth of mold fungi from all the tested fillers, which is probably due to their low water solubility and nature of water-soluble compounds.

It can be seen (figure 2) that the character of biofouling is different for the fillers. The fibers of cellulose swelled up a lot in the water. They were fully covered by fungi, the main mass of fungi was into the liquid media. Oil flax, wood flour, oligopeptides and the majority of other fillers had a «hat» of aerial micellium at the interphase between liquid and air. Starch was degraded by combination of these two mechanisms – it had feculence of fungi into the volume and a small fungal «hat» at the interphase.

The regularities of mold fungi growth on agar medium with different fillers differed from the results of aqueous media test (figure 3). In this test the whole filler was exposed to biodegradation. The media with banana and hay were characterized by a high intensity of fungal development for the majority of mold fungi cultures (figure 4), which is apparently associated with a high content of peptide component and microelements. In fact, mixed herbs hay contains high amount of different components. Banana skin consists of different parts (external, intermediate and internal) with different
chemical composition. From the other side, the fillers include one or two main components (starch, cellulose, sodium lignosulfonate, fiber flax, and wheat chaff) were poorly degraded by micromycetes.

Figure 2. Several photographs demonstrating *Penicillium chrysogenum* development on aqueous media with 10 wt.% of fillers after 14 days from inoculation.

Figure 3. Assessment of growth intensity of *Aspergillus terreus* culture (in points) on agar media with 10 wt.% of fillers after 28 days from inoculation according to ISO 846.

Figure 4. Several photographs demonstrating *Aspergillus terreus* development on agar media with 10 wt.% of fillers after 28 days from inoculation.
4. Conclusion

Twelve different natural raw materials were selected as the most perspective fillers for biocomposites. Technical parameters of the filler (thermal degradation temperature, length to diameter ratio of the particles, low price, etc.) are important, but in this paper, the main focus was on biodegradation. According to this paper results, at selecting the right filler for initiating biocomposites biodegradation, two parameters should be noted. First, for high biodegradability a composite filler should be multi-compound or it may be a combination of different fillers. Second, a filler should have water soluble and easy-hydrolysed components.

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