



The Surface Structure Of Polymer Composites Based On Recycled Polypropylene And Natural Components Of Vegetable Origin In The Process Of Biodegradation

Marina Viktorovna Bazunova, Renat Bayazitovich Salikhov, Ainur Radikovich Sadritdinov, Valentina Vitalevna Chernova, Vadim Petrovich Zakharov

Bashkir State University, 450076, Russia, Ufa, Validy Str., 32

Abstract

The effect of biodegradation on changing the hydrophilicity, the morphology and the topography of the surface of polymer composites based on recycled polypropylene and natural filler of plant origin (WF) was studied. For the purpose of studying biodegradation of samples of polymeric materials in soil, restored soil was tested. The morphology and surface topography of the samples of polymer composites were studied with the use of atomic force microscope Agilent 5500 AFM (USA). The hydrophilicity of the surface of polymer films was studied by measuring the wetting angle formed between the surface of the material and a drop of water. It has been found that when composite samples are exposed to restored soil in the laboratory conditions for four months, a significant increase in roughness and hydrophilicity of the surface is observed in samples with the maximum filling degree (30-50 pts. wt. of wood flour).

Keywords: recycled polypropylene, wood flour, round mean square roughness, wetting angle.

INTRODUCTION

Currently, to create plastic products with adjustable service life, biodegradable polymer composites with short life cycle are used, as well as composites that preserve operating characteristics for a long time only during the period of consumption, after which, under the action of environmental factors, undergo physico-chemical and biochemical transformation, and are easily included into the metabolism of natural biological systems [1, 2].

The large scale industrial production and wide use of polypropylene (PP) determines the relevance of creating biodegradable composites based on it [3, 4]. The problem of degradability of synthetic polymeric materials, including PP, may be solved by introducing mineral and organic natural fillers, such as vegetable fillers like wood flour or agricultural wastes (buckwheat husk, rice husk, chaff, etc.) into the material [5, 6].

Strong ability of microorganisms to assimilate fillers of plant origin determines intensification of their development on polymer materials, which is certainly an undesirable process during storage and use, but has a positive effect on the ability to biodegrade. It is important that all processes of materials' biodegradation under the action of environmental factors occur in the presence of moisture [7]. Therefore, when biodegradable polymer composites based on polyolefins are created, it is useful to fill the polymer with components of exactly vegetable origin, which contributes to hydrophilization of the surface, and increases the interphase contact, through which moisture and harsh chemicals can penetrate into the polymer. Also, adjusting the components' rate in the composition allows, by changing the morphology of the material and its surface topography, to adjust not only the operating properties, but the rate of biodegradation as well [8 -10].

Thus, this work is aimed at studying the influence of biodegradation on the changing wettability, morphology and topography of the surface of polymer composite materials based on recycled PP and natural filler of plant origin - wood flour (WF).

METHODS

Samples of recycled PP were used, which was the material obtained from crushed non-conforming products produced by molding under pressure.

The natural additional filler of plant origin was WF of grade 180 long fiber with the average particle size of about 0.17 mm, and containing 45-52% of cellulose, 35% of lignin, and 17-

23% of hemicellulose. The dosage of WF was calculated in weight parts (pts. wt.) per 100 pts. wt. of PP.

Polymer composites were obtained by melting at a laboratory station (plastograph) "PlastographEC" (Brabender, Germany) for 15 min under the load of 200 N at 180 °C, followed by pressing in automatic hydraulic press "AutoMH-NE" (Carver, USA) at 210 °C, and exposure to the pressure of 7,000 kgf for 3 min. The amount of loaded polymer was 25 g.

For the purpose of studying biodegradation of samples of polymeric materials in soil, restored soil was tested [11]. Soil for testing was made of horse manure, garden soil and sand taken in equal mass ratios [12]. The soil was placed in boxes, the thickness of the layer in this case was 30±5 cm. Soil moisture (not less than 60%) was monitored with moisture analyzer ETR-310. Acidity of the used soil was 6.2.

Boxes with soil were stored in laboratory conditions at room temperature. The method of testing consisted of immersing polymer samples vertically into the ground with subsequent exposure for 2, 3, 4 months.

At certain time intervals, the samples were removed from the soil, cleaned of soil and brought to constant weight at (80±2) °C. After that, weight loss was determined.

To shorten the experiment, and to avoid influence of abiotic factors (temperature, humidity) on the process, constant conditions of the experiment were maintained.

The morphology and surface topography of the polymer composites' samples were studied with the use of atomic force microscope Agilent 5500 AFM (USA). The samples were scanned in the air in the semi-contact mode using silicon cantilevers PPC-NCL-20 with the stiffness of 3.5 N/m and resonant frequency of 184 kHz (Nanosensors). Image processing and statistical processing of results were performed in the Gwyddion application.

The hydrophilicity of the polymer films' surface was studied by measuring the wetting angle formed between the surface of the material and a drop of water, using a digital camera with macrocapability, and further processing in CorelDRAW X3 (Corel Corporation, USA).

The results of the experiment were processed in the STATISTICA 10.0 software package.

RESULTS

It is known that adhesion of microorganisms to the surface of polyolefins increases with increasing hydrophilicity and surface roughness [9]. In this regard, changes in the surface topography and wettability with water of polymeric composite materials'

samples based on recycled PP and WF in the process of their biodegradation were studied.

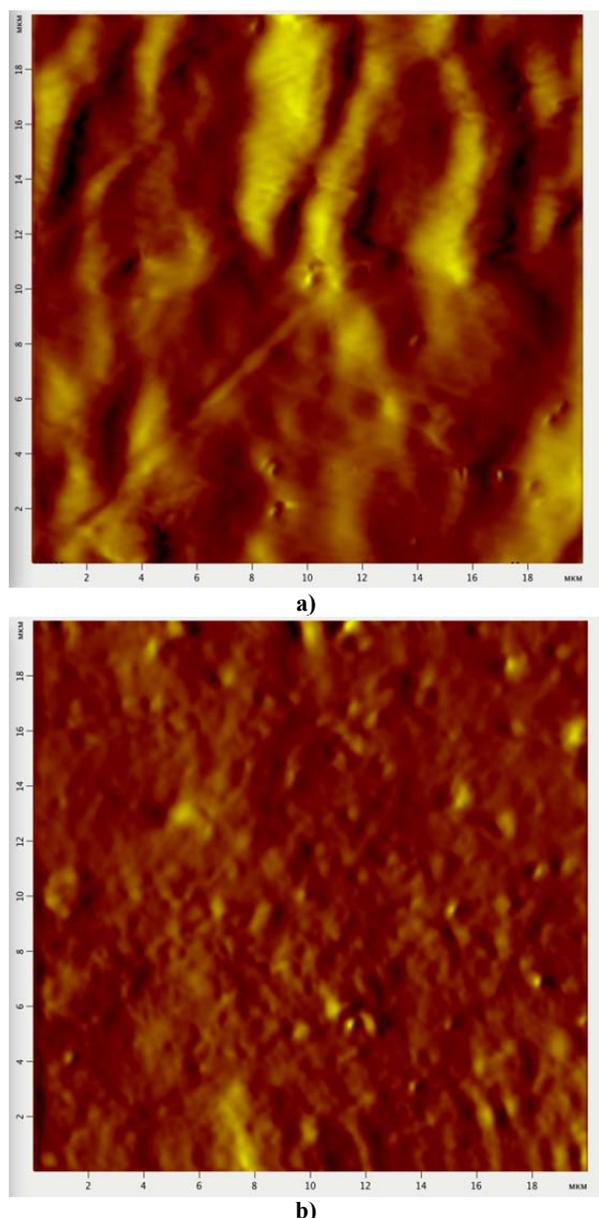


Figure 1. Phase-contrast AFM images of the surface of materials based on recycled PP without filler (a) and with filler - 5 pts. wt. of WF (b).

It is known that the structure of the polymer composite material is not only set by the conditions of mixing and forming, but by the shape and dispersiveness of the filler particles as well [13, 14]. Indeed, when comparing the surface morphology of the materials obtained based on recycled PP without filler and with WF filler (Figure 1 a and b), it was found that in the presence of WF particles, the surface of the composite material had granular structure, whereas unfilled material had ridgelike structure. This difference in the surface topography of materials may be explained by various conditions of crystallization: in the presence of fine filler, on the surface of its particles there are centers of crystallization, which, most likely, are the germs for forming crystallites of the polymer binder.

Therefore, there is no doubt that microorganisms' ability to bioassimilate polyolefins unfilled and filled with plant-origin components considerably varies.

In this paper, the process of biodegradation after composting in the soil has been studied in terms of three main issues:

- Assessing the weights' loss by the samples by weighing at regular intervals;
- Changes in the surface texture of the samples;
- Changes in the samples' surface hydrophilicity.

As it follows from the data in Table 1, one month after placing into restored soil, the first symptoms of weight loss were noted in samples with high degree of filling (50-70 wt. pts. of WF). 4 months after the start of the experiment, no visual changes in the samples placed in the soil were noted, only disappearance of gloss, however, weight loss was noted in all studied samples (up to 5% for samples with 70 pts. wt. of WF).

Low values of weight loss in the samples during the studied period of contact with the soil (4 months) may attest to the fact that at this stage only slight biochemical destruction of plant components occurs without chemical and mechanical degradation of the polymer binder.

Analysis of changes in the surface texture of polymer composites' samples based on recycled PP and WF during the process of biodegradation (Figure 2) showed that the beginning of substantial increase in the round mean square roughness of the sample surface correlated with the beginning of significant loss of their weight due to biodegradation. It has also been noted that while after two months of exposure to soil the round mean square roughness slightly depends on the content of WF, after four months of exposure, the round mean square roughness significantly increases with the increase of WF content. This is probably due to "etching" and washing away of part of the filler and to formation of quite deep depressions and protrusions (Figure 3).

Table 1. Weigh loss in samples of polymer composite materials based on recycled PP and WF after various time of contact with restored soil.

WF contents, pts. wt.	Weight loss after 1 month of contact with soil, %	Weight loss after 2 months of contact with soil, %	Weight loss after 3 months of contact with soil, %	Weight loss after 4 months of contact with soil, %
0	0	0	0.3±0.03	0.4±0.04
2	0	0.05±0.01	0.4±0.04	0.6±0.06
5	0	0.1±0.01	0.7±0.07	1.0±0.1
10	0	0.1±0.01	0.9±0.09	1.4±0.1
15	0.05±0.01	0.2 ±0.02	0.7±0.07	1.9±0.2
30	0.07±0.01	0.4±0.04	1.1±0.1	2.3±0.2
50	0.1±0.01	1.0±0.1	1.3±0.1	4.1±0.4
70	0.1±0.01	1.2±0.1	2.2±0.2	4.3±0.4

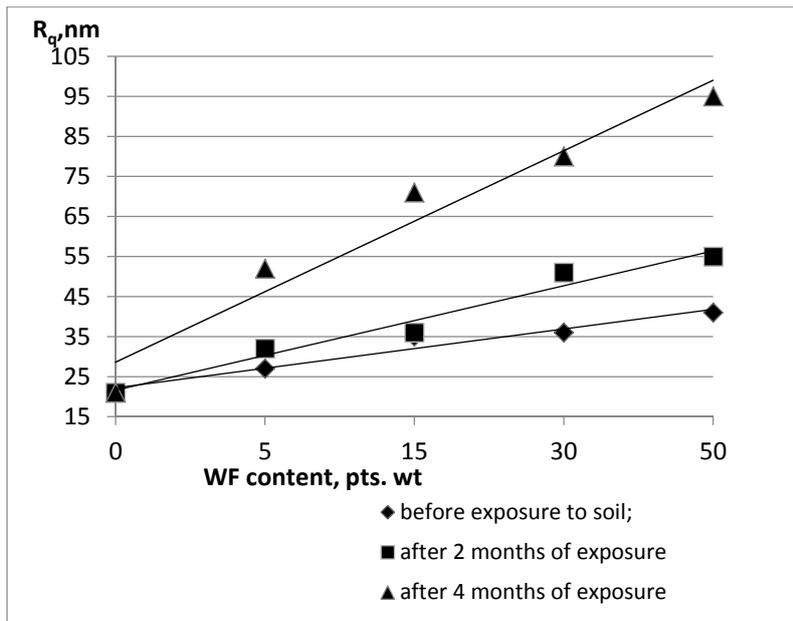
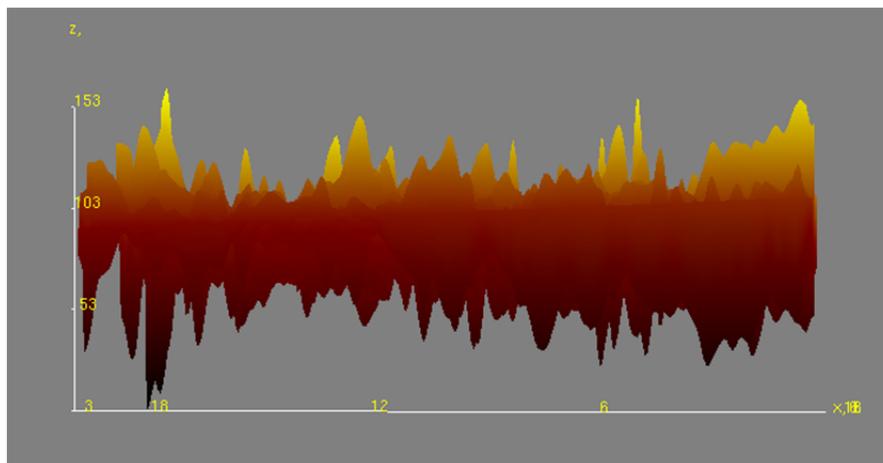
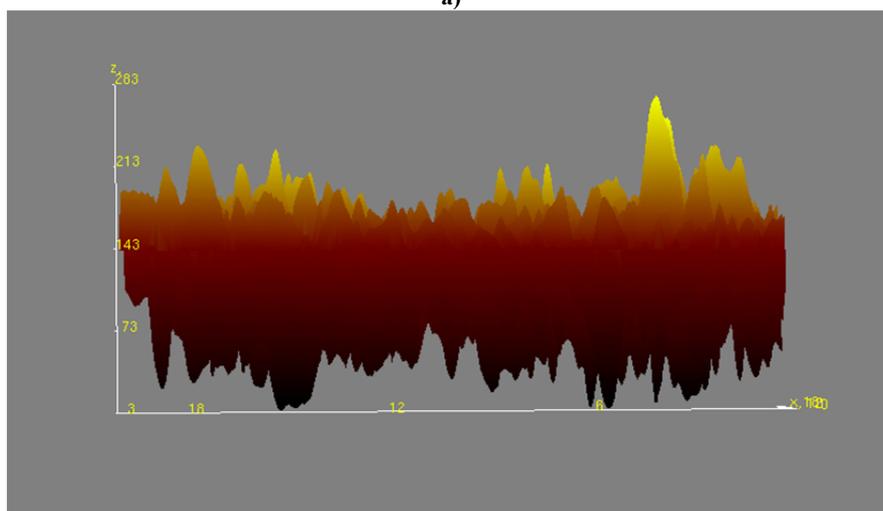


Figure 2. Dependence of the round mean square roughness of the composite material samples based on recycled PP and WF on the content of the filler before and after exposure to restored soil.



a)



b)

Figure 3. Two-dimensional AFM images of the surface of the composite material samples based on recycled PP of brand based on recycled PP and 5 pts. wt. of WF before exposure to restored soil (a) and after 4 months of exposure (b).

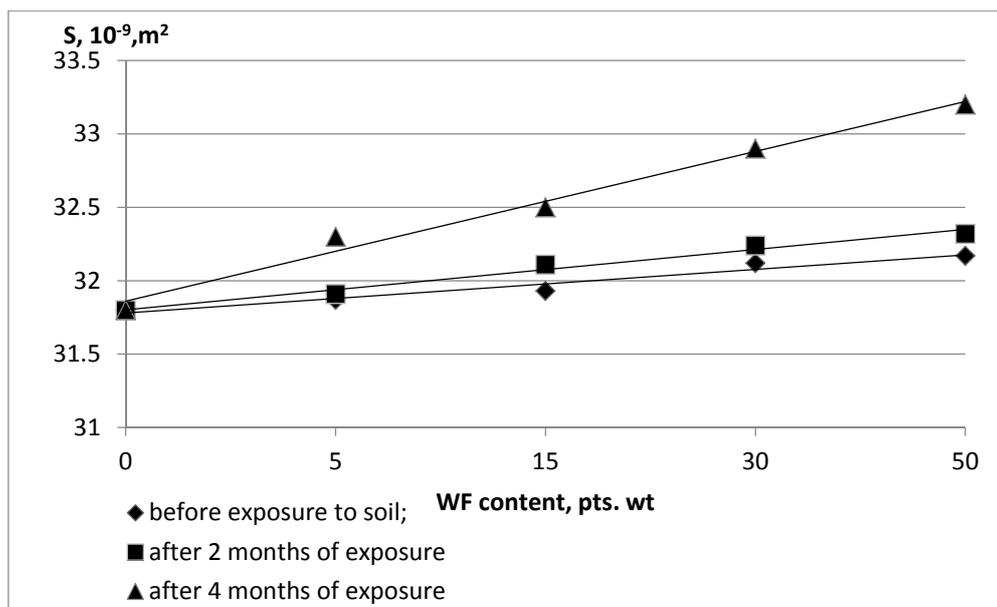


Figure 4. Dependence of the roughness of the composite material samples based on recycled PP and WF on the content of the filler before and after exposure to restored soil.

Table 2. Wetting angle values (Θ) in the composites based on recycled PP

WF contents, pts. wt.	Θ before contact with soil, deg.	Θ after 2 months of contact with soil, deg.	Θ after 4 months of contact with soil, deg.
-	72±4	72±4	70±4
2	71±4	71±4	69±4
5	70±4	70±4	68±4
10	69±4	68±4	65±3
15	65±3	63±3	59±3
30	64±3	60±3	53±3
50	61±3	56±3	50±3

The data about dependence of the surface area of the composite samples before and after exposure to soil shown in Figure 4 prove that the surface area also starts significantly increasing with increasing the content of the filler only after 4 months of exposure to soil.

Therefore, increasing the roughness and the surface area contributes to attaching soil microorganisms to the samples of polymeric materials and accelerating the processes of bioassimilation.

Another determining factor of bioavailability of polymer composites is hydrophilicity of the surface. To monitor changes in hydrophilicity of the surface, wettability of the surface of samples of the composite material based on recycled PP and WF, the wetting angle Θ was determined. The initial recycled PP is characterized by low values of the wetting angle (Table 2), which is characteristic of polyolefins. Introduction of WF slightly shifts hydrophilicity of the materials' surface towards increasing, which can be explained by the fact that the particles of the filler, though they are more hydrophilic than the polymer binder, are partially encapsulated in the polymer matrix even on the surface.

During the biodegradation, hydrophilicity of the surface increases (Table 2), and the wetting angle significantly changes for the samples of composite with high degrees of filling with WF and after 4 months of exposure to soil, i.e. for samples with the maximum roughness and surface area.

CONCLUSION

Thus, studying the evolution of the surface properties of polymer composite materials based on recycled PP and natural filler of plant origin, WF, during the biodegradation and being exposed to restored soil in the laboratory, showed a significant increase in roughness and hydrophilicity of the surface for the samples with the maximum degree of filling (30-50 pts. wt.), which contributed to consolidation of soil microorganisms on the polymeric materials samples and accelerating the processes of bioassimilation.

ACKNOWLEDGMENTS

The article was prepared within the framework of scientific research work at the FSEI HE The Bashkir State University with the financial support of the Ministry of Education and Science of the Russian Federation (Agreement No. 03.G25.31.0275).

REFERENCES

- [1] Fomin V. A. and Guzev V. V. Biorazlagaemie polimeri, sostoyanie i perspektivi ispolzovaniya. [Biodegradable polymers, state and perspectives of use]. Plastic masses, 2001; 2: 42-46.
- [2] Rogovina S.Z. Biodegradable polymer composites based on synthetic and natural polymers of various classes. Polymer Science, 2016; 58(1): 62-73.
- [3] Filonov, A. N., Maksimova N. V. Cnir I. N. and Mayer, E. A. Sostoyanie i vozmozhnosti razvitiya rossiiskogo rinka tkanih upakovochnih materialov iz polipropilenovoi plyonochnoi niti [The state and the possibilities of developing Russian market of woven packaging materials made of polypropylene tape yarn]. Plastic masses, 2004; 5: 30-34.

- [4] Buzunova M. V. and Prochukhan Y. A. Sposobi utilizatsii othodov polimerov. [Methods of disposing of polymer wastes]. Bulletin of the Bashkir University, 2008; 13(4): 142-156.
- [5] Mastalygina E. E., Shatalova O. V., Kolesnikova N. N., Popov A. A. and Krivandin A. V. Modification of isotactic polypropylene by additives of low-density polyethylene and powdered cellulose. Inorganic Materials: Applied Research, 2015; 7(1): 58–65.
- [6] Mastalgia E. E., Kolesnikova N. N. and Popov A. A. Faktori, opredelyayushchie biorazlagaemost kompozitsii na osnove poliolefinov i tsellyulozoderzhaschih napolnitelei. [Factors that determine biodegradability of the compositions based on polyolefins and cellulose-containing fillers]. Non-conventional materials, 2015; 9: 39-52.
- [7] Legonkova O. A. and Selitsky O. V. Mikrobiologicheskaya destruktziya kompozitsionnih polimernih materialov v pochvah [Microbiological degradation of polymeric composite materials in soils]. Soil science, 2009; 1: 71-78.
- [8] Rutkowska M., Heimowska A. and Krasowska K., et al. Biodegradability of polyethylene starch blends in seawater. Polish Journal of Environmental science, 2002; 11(3): 267-274.
- [9] Shan A.A., Hasan F. and Hameed A., et. al. Biologycal degradation of plastics: a comprehensive review. BiotechnolFdv, 2008; 26: 246-265
- [10] Stilman, M. I. Biodegradatsiya polimerov [Biodegradation of polymers]. The Journal of the Siberian Federal University. Series: Biology, 2015; 8(2): 113-130.
- [11] GOST 9.060-75. Unified system of protection from corrosion and ageing. Fabrics. The method of laboratory testing for resistance to microbial destruction. Moscow: The Publishing House of standards, 1975, pp. 11.
- [12] GOST 9.049-91. Unified system of protection from corrosion and ageing. Polymer materials and their components. The method of laboratory testing for resistance to mold fungi. Moscow: The Publishing House of standards, 1975, pp. 15.
- [13] Dikobe, D.G. Comparative study of the morphology and properties of PP/LLDPE/wood powder and MAPP/LLDPE/wood powder polymer blend composites. Express Polym Lett, 2010; 4(11): 729-741.
- [14] Galikhanov M.F., Ereemeev D.A. and Deberdeev R.Y. Electret effect in Compounds Polystyrene with Aerosil. Russian Journal of Appl. Chem. 2003; 10: 1651 – 1654.