

Feasibility Study of Biodegradation of Polyamide-6 and Natural Rubber Composite Materials

Alsu Dautova^a, Vladislav Yanov^a, Nail Mingaleev^b and Luybov Zenitova^a

^aKazan National Research Technological University, Kazan, RUSSIA; ^bKazan State Agrarian University, Kazan, RUSSIA

ABSTRACT

To obtain a biodegradable material based on fiberglass-filled (FG) polyamide-6 (PA-6) was used purified (NR-P), non-purified (NR-N), natural rubber (NR) of Vietnam and Malaysia production. When determining NR composites fungal resistance using *Aspergillus niger*, *Penicillium expansum* and *Fusarium oxysporum* filamentous fungi it was found out that major degradation of materials have undergone in the presence of *Fusarium oxysporum* fungi. For all samples were mentioned significant changes in technological and the physical and mechanical properties after accelerated environmental tests, more pronounced for samples with NR-N. It was found that the introduction NR, regardless of its purification, significantly reduces the water absorption of compositions based on fiberglass-filled PA-6.

KEYWORDS

Biodegradation, fungal resistance, natural rubber, polyamide, polymeric compositions

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Introduction

Plastics, widespread nowadays, are, usually, not biodegradable except few of them that are capable of biodegradation, but very slowly. Taking into consideration sharp increase in demand for polymers and their availability, there is a danger of ecological pollution with a lot of used polymeric products and their waste at disposal landfill. Recently, the possibility of destruction of synthetic polymers by microorganisms is regarded as one of the potential ways of their degradation (Ghosh, Pal & Ray, 2013; Chen et al., 2005; Harada et al.,

CORRESPONDENCE Alsu Dautova ✉ alsu_5572@mail.ru

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2006; Miller et al., 2004; Othmer, 1997; Syed et al., 2007; Tsuchii & Takeda, 1990; Linos et al., 2000; Mooibroek & Cornish, 2000; Sivan, Szanto & Pavlov, 2006).

NR is one of the polymers, capable of biodegradation. The fact that NR is not accumulated in nature but is produced by plants means that it is prone to microbial decay under the action of bacteria and fungi.

A sufficient number of studies to determine the biodegradation of NR (Cherian & Jayachandran, 2009; Berekaa et al., 2000; Roy et al., 2006; Chengalroyen & Dabbs, 2012; Kalinenko, 1938; Esuruoso, 1970; Kwiatkowska, 1980; Borel, Kergomard & Renard, 1982; Williams, 1982; Nayanashree & Thippeswamy, 2015; Tsuchii & Tokiwa, 2001) were carried out around the world.

In the study of E. Cherian & K. Jayachandran (2009) *Bacillus* sp. SBS25 - Gram-positive bacteria isolated from the soil, were identified as effective agents of natural latex biodegradation. Microorganisms were isolated from latex contaminated with soil, which was collected on rubber plantations. Researchers have shown basic compound biodegradation into three fractions with a low molecular weight.

M. Berekaa (2006) has isolated bacteria from a sample of old tires, made on the basis of NR, and determined that they belong to the actinomycetes of *Nocardia* genus. His investigations, carried out on samples of latex gloves, showed the possibility to use by *Nocardia* genus actinomycetes of rubber based on natural rubber as the sole carbon and energy source.

R.V. Roy and others (2006) conducted a comparative study of biodegradable of vulcanized and non-crosslinked natural rubber under the action of *Pseudomonas* sp. They showed rubber degradation under the influence of *Pseudomonas* sp. They observed a decrease in organic carbon content along with the changes in the tensile strength of the NR and rubber of NR. Reduction of tensile strength after five months study for non-crosslinked rubber and rubber, vulcanized with the use of dicumyl peroxide constituted 60.88% and 41.66%, respectively.

M.D. Chengalroyen & E.R. Dabbs (2012) studied sixteen soil samples for the presence of strains, degrading rubber. They isolated twenty-five strains. Identification showed that twenty-three of these isolates were of *Streptomyces* type, as well as single species of *Pseudonocardia* and *Methylibium* each. Scanning electron microscopy revealed that the isolates were able to colonize and penetrate into the vulcanized rubber gloves.

When examined the NR for fungal resistance, even V.O. Kalinenko (1938) reported the strains of *Aspergillus* and *Penicillium* fungi genus as an effective destructors of rubbers.

O.F. Esuruoso (1970) has isolated *Aspergillus fumigatus*, *Aspergillus Flavus* и *Aspergillus aculeatus* fungi from moldy rubber sheet found in Western Nigeria. Implantation of *Aspergillus fumigatus* and *Aspergillus flavus* on sterile rubber sheet showed evidence, similar to that observed initially regarding moldy rubber sheet.

D. Kwiatkowska (1980) conducted investigations of vulcanized NR sheets of specific composition, by keeping them in the soil for 91 days, resulting in significant weight loss up to 40% of the original. These authors have isolated

fungus strain *Fusarium Solani* from rubber surface, which caused its degradation.

M. Borel, A. Kergomard & M.F. Renard (1982) have isolated several fungi from mineral agar, containing NR powder as a sole substrate, as well as from the surface of the damaged material of the tire, which were reducing the rubber properties. Fungal strains *Fusarium Solani*, *Cladosporium cladosporioides* and *Paecilomyces lilacinus* were grown on the surface of the rubber after 20 days of incubation. It was found relative decrease of molecular weight up to 20% and an intrinsic viscosity of up to 35%.

G.R. Williams (1982) have isolated a fungal strain of *Penicillium variabile* in the result of destruction of the NR sample, placed into the soil. Spore suspensions were inoculated onto NR in the humidity chamber that resulted in biomass increase on the NR surface and was accompanied by the weight loss of rubber bands up to 13% after 56 days. Using solution viscosity measurement, the author has defined a 15% NR molecular weight decrease after 70 days.

G.B. Nayanashree & B. Thippeswamy (2015) have isolated microorganism - *Penicillium chrysogenum*, which effectively degraded NR, as well as identified the enzyme responsible for its degradation, using burial ground disposal of NR samples.

In the scientific literature, the majority of studies are devoted to the study of purified NR biodegradation or of pieces of NR rubber tires, but there are no studies of non-purified NR. When cleaning, the protein-lipid layer, contained on the surface of the rubber globules, is to the large extent removed. The use of NR-N in polymer compositions, in our opinion, should enhance the biodegradation of the material. In biodegradation process the non-rubber components due to the lower molecular weight, as compared to rubber molecules, are absorbed by microorganisms first, which leads to a change in structure of the material and accelerates the process of further degradation. Our investigations with the use of NR-N in polymer compositions are based on this assumption.

Materials and Methods

The object of investigation is a polymeric composition based on PA-6 filled with FG in the amount of 30% mass of brands PA 6-210 KS and NE PA 30-2T, manufactured according to OST 6-11-498-79 and TU2243-015-11378612-97, as well as filled with FG 50% mass, brand PA FG 50-1, manufactured according to TU2243-015-11378612-2005 of LLC NPP "POLYPLASTIC", Moscow. In the capacity of material, promoting degradation, was used NR, input to the composition in the quantity of 5 and 10% of mass, Vietnam made: NR-N; Malaysia made: NR-N of SMR-10 brand, exposed to cleaning, NR-P of RSS-1 and SMR-L brand.

Polymeric compositions were obtained on a laboratory twin screw extruder UR-TC of Rondol company with the temperature at extruder zones: at feed zone - 100 ° C, at the beginning of the cylinder - 200 ° C, in the middle part of the cylinder - 240 ° C, in the front part of the cylinder - 250 ° C and in the head - 260 ° C.

By injection casting on the device model 2 of Ray-Ran company were obtained samples in the form of the disks 40 mm in diameter and 3 mm thick for studies on water absorption, the blades 150 mm long, 10 mm wide and 4 mm thick for testing tensile strength; samples in the form of bars 80 mm long, 10



mm wide, 4 mm thick for Charpy impact test. Melt temperature at casting constituted 240-260°C. Formlining temperature of the hollow mold surface - 80-100 °C. When humidity content exceeded 0, 2% of mass the 4 hours pre-drying was carried out before material processing. Polymer compositions in the form of granules were kept, according to GOST 19599-90, at a temperature $(70 \pm 1)^\circ\text{C}$ in an oven LOIP LF series with circulating air until the actual absorbed moisture equilibration.

Determination of strength and elasticity modules was carried out on a universal testing machine 7000-AI-M in accordance with GOST 11262-80, at a clamps separation displacement speed of 25 ± 2 mm / min. Charpy impact strength was determined according to GOST 4647-80 on the Charpy machine GT-7045-MDL, melt flow rate measurement - according to GOST 11645-73 on the GT-7100-MIB automatic extrusion rheometer. Water absorption was determined in cold water according to GOST 4650-80.

Determination of structural resistance to weather conditions was carried out in the climatic test chamber with ultraviolet rays Accelerated Weathering Tester model QUV/spray with Solar Eye Irradiance Control of Q-LAB company (cycle G) on ASTM G 154. There were carried out 20 cycles 12 hours each. Each cycle consisted of UV irradiation - 8 hours at $T = 60^\circ\text{C}$, sprinkling with water - 15 minutes and water condensation - 3 hours 45 minutes at $T=50^\circ\text{C}$.

Fungal resistance of composite materials development was carried out according to GOST 9.049-91 under the action of three mold fungi: *Aspergillus niger*, *Penicillium expansum* and *Fusarium oxysporum*. Samples in the form of plates 0,148-0,318 mm thick were obtained by compaction on hydraulic molding press at $T - 240^\circ\text{C}$, molding pressure – 20 MPa, preheat time– 10 min, hold pressure – 10 min, cooling – 5 min. Composite materials plates of 2,5-3×3,5-4 cm were cleaned from external contaminants by immersing for 1 minute in ethanol and then dried. Samples of material were contaminated with fungal spores in Czapek-Dox medium containing (g / l): sucrose - 30 g, NaNO_3 - 3 g, KH_2PO_4 - 1 g, MgSO_4 - 1 g, $\text{MgSO}_4 \times 7\text{H}_2\text{O}$ - 0,5 g, KCl - 0 5 g, $\text{FeSO}_4 \times 7 \text{H}_2\text{O}$ - 0,01g. The surface of the samples was contaminated with a spore suspension of fungi by uniform spraying, avoiding merging drops. Infected materials were kept in the box till drops drying. Then, contaminated materials were inverted side down, were sprayed with a spore suspension on the other side and dried under the same conditions. Test materials were placed in glass Petri dish 9 cm in diameter. Materials, contaminated with spores of fungi, were kept in conditions, optimal for the development of fungi, followed by evaluation of the degree of fungal resistance by the degree of mold fungi development and (or) by change of characteristic parameters of materials properties. For this purpose Petri dishes were placed into thermostat at 30°C . The duration of the test was 84 days with an interim analysis on the 28th day.

Results and Discussion

Determination of water absorption

To reveal the possibility of polymer composition degradation with the addition of NR it was determined water absorption (χ) of fiberglass-filled PA-6 (brand PA6-210KS, PA-FG 50-1) and based on them NR-N and NR-P compositions (brand RSS-1). The results are given in Table 1.

Table 1. Water absorption of fiberglass-filled PA-6 and based on them composite materials with NR

Name	Rubber content, % mass.	x, %
PA FG 30%	0	1.05
PA FG 30% with NR-N	5	0.87
PA FG 30% with NR-N	10	1.10
PA FG 30% with NR-P	5	0.90
PA FG 30% with NR-P	10	0.97
PA FG 50%	0	0.74
PA FG 50% with NR-N	5	0.66
PA FG 50% with NR-N	10	0.65
PA FG 50% with NR-P	5	0.65
PA FG 50% with NR-P	10	0.65

It is known from the literature that PA-6, due to presence of intermolecular hydrogen links is a material with rather high level of water absorption (3% for 24 hours) (Karsakova & Kravchenko, 2008). As it can be seen from Table 1, compositions, containing FG, have lower water absorption. Thus, the greater the inputted NR, the smaller the water absorption of polymeric composition, as the fiber glass, present in the composition, is not able to absorb moisture. Introduction of non-polar NR to the composition further reduces the hydrophilicity of the material and also leads to a slight reduction of water absorption.

Introduction of NR into the polymer composition with 30 % mass of FG in an amount of 5% of weight reduces water absorption by 0.15-0.18%, regardless of the NR purification. With an increase of NR in the composition to 10% of mass, water absorption remains almost on the same level with the samples not containing NR.

In the compositions with 50% FG of mass due to the greater content of fiberglass, the water absorption is reduced to a lesser extent by 0.08-0.09% regardless of the quantitative content of NR and approximately equal for both samples with NR-N, and with the NR-P.

In general NR regardless from the type: purified or non-purified is not significantly affect the water absorption of the polymer compositions.

Study of change of physical-mechanical and technological performance after accelerated environmental tests

Accelerated environmental tests, imitating the devastating effects of prolonged exposure of polymeric materials by keeping the samples under conditions simulating the corrosive effects of weather, such as UV radiation, heat and humidity were carried out. When using fluorescent UVA-340 lamps were obtained emission in the spectrum centered in the UV wavelength range of 295 to 365 nm. Due to the temperature obtained through controlled heaters, in the climatic test chamber was provided forced water condensation. Changes in physical-mechanical and technological performance of PA-6 (brand PA6-210 KS, PA FG 50-1) and based on then polymeric compositions with NR-N (Vietnam made) and NR-P (brand RSS-1) after accelerated environmental tests are shown in Table 2.



Table 2. Changes in physical-mechanical and technological performance of PA-6 and based on it polymeric compositions with NR-N and NR-P.

Composition	Rubber content, % mass	Changes in the performance after accelerated environmental tests, %			
		Tensile strength at break	Elasticity coefficient	Charpy impact strength	MFI
PA FG 30%	0	-26	-42	-18	+10
PA FG 30% with NR-N	5	-30	-42	-29	+22
PA FG 30% with NR-N	10	-29	-37	-35	+30
PA FG 30% with NR-P	5	-31	-42	-31	+13
PA FG 30% with NR-P	10	-21	-41	0	+3
PA FG 50%	0	-23	-44	-12	-0.4
PA FG 50% with NR-N	5	-26	-33	-3	+9
PA FG 50% with NR-N	10	-25	-31	-12	+42
PA FG 50% with NR-P	5	-26	-35	+23	+9
PA FG 50% with NR-P	10	-26	-33	+15	+6

Significant changes in tensile strength at break and elasticity coefficient in the direction of reduction, are observed for all the samples, and are in the range from 21 to 31% and from 31 to 44% respectively. Reduction of tensile strength at break for samples containing rubber is more than without it: 3-5% for samples with 30% FG and 2.3% for samples with 50% FG. However, these changes are not significant.

PA G 50% of mass due to the larger content of FG is less ductile polymer as compared to PA FG 30% of mass. Their impact strength is 98 and 136 kJ/m², respectively. During aging PA FG 50 % of mass, it becomes more brittle and its destruction requires much less energy. By contrast, in the compositions of PA SW 50 % mass with NR - rubber serves as a plasticizing agent. This corrects the impact strength in compositions with FG 50 % of mass, shifting it towards increase.

Very essentially changes MFI for the samples, containing NR-N 10% of mass. The increase in MFI is observed for PA FG 30% of mass by 30%, for PA FG 50% of mass by 42% as compared with controls. Based on the results in sharp increase of MFI at NR input it is possible to assume that there is a significant decrease in the molecular weight of the polymer compositions.

Funginertness studies

According to the ability of materials to be oxidized by filamentous fungi it is possible to judge about their biological sustainability. Thus, after 28 days of incubation with filamentous fungi the weight of PA FG 30% and PA FG 50% of mass control samples are virtually unchanged and constitute from 99.8 to 100% of the original. The mass of samples containing rubber 10% of mass as filler decreased more significantly, being in the range from 97.1 to 99.5%. The most significant decrease in weight was observed when using PA FG 50% of mass with NR-N 10% of mass and NR-P 10% of mass samples.

The most significant weight loss of the sample PA FG 50% of mass sample with NR-N 10% of mass occurred under the influence of the fungus *Fusarium oxysporum*, decreasing to a value of 2.9%, and under the influence of the fungus *Aspergillus niger*, decreasing to a value of 2.1%. The most significant weight loss

of the sample PA FG 50% of mass with NR-P 10% of mass occurred under the influence of the fungus *Aspergillus niger*, decreasing to a value of 2.8%. Taking into account that the materials samples not containing rubber during incubation actually almost have not lost the weight, it is likely its decrease happened due to presence of rubber. However, the rubber content in the samples constituted about 10 % of mass, so the degree of degradation varied from about 10% to about 30% of weight.

A more significant degradation of the materials was observed at incubation for 84 days. Weight loss of the samples, reflecting biodestruction, depended both on the PA type, and on the added rubber filler, as well as on the type of micromycete. Mass of the samples without rubber decreased by about 0.5% when exposed to the fungi *Aspergillus niger* and *Penicillium expansum*, and by 1.7% in the presence of *Fusarium oxysporum*. The greatest destruction of materials had the materials in the presence of *Fusarium oxysporum*. Thus, for the sample of PA FG 50% of mass with NR-N 10% of mass the weight loss was 7.8%, for a sample of PA FG 50% of mass with NR-P 10% of mass – 5,6 %, that testifies that the presence of rubber filler in the sample contributes to enhanced degradation of the material (Dautova et al., 2015a). Other types of fungi - *Aspergillus niger* and *Penicillium expansum* - also caused degradation of the samples in the range of 2-3%.

In the result of the study it was found that the reduction of the mass of samples using NR occurs to a much greater extent than without it. The weight loss under the action of *Aspergillus niger* is from 2.0 to 4.5 times higher as compared with the samples without rubber, under the action of *Penicillium expansum* - 3.8 -5.4 times, and *Fusarium oxysporum* - 1.5 -5.2 times.

Microscopic pictures of the samples surface with *Fusarium oxysporum*, *Aspergillus niger* and *Penicillium expansum* after 84 days of incubation are shown in Figures 1-2.

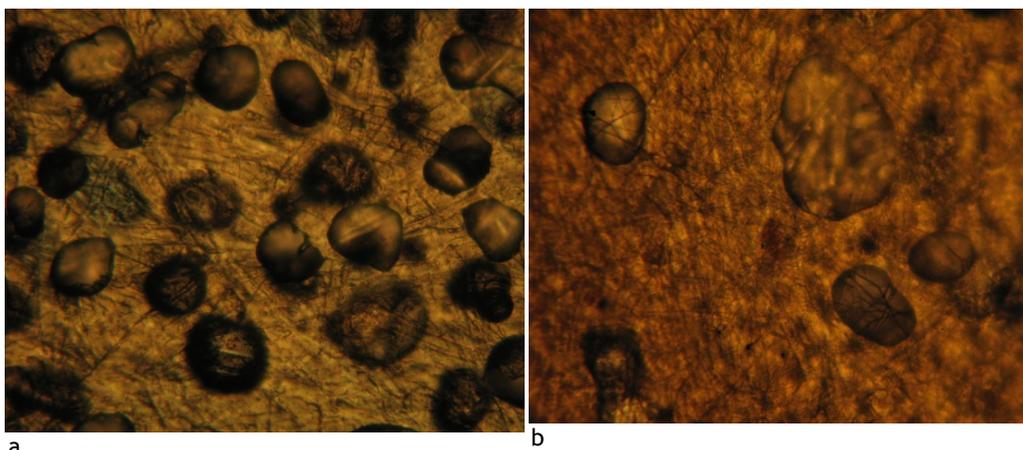


Figure 1. Microscopic pictures of the samples surface with *Fusarium oxysporum* (x250): a - PA 6-210 KS, b - PA 6-210 KS with NR-N 10% of mass (Vietnam made)

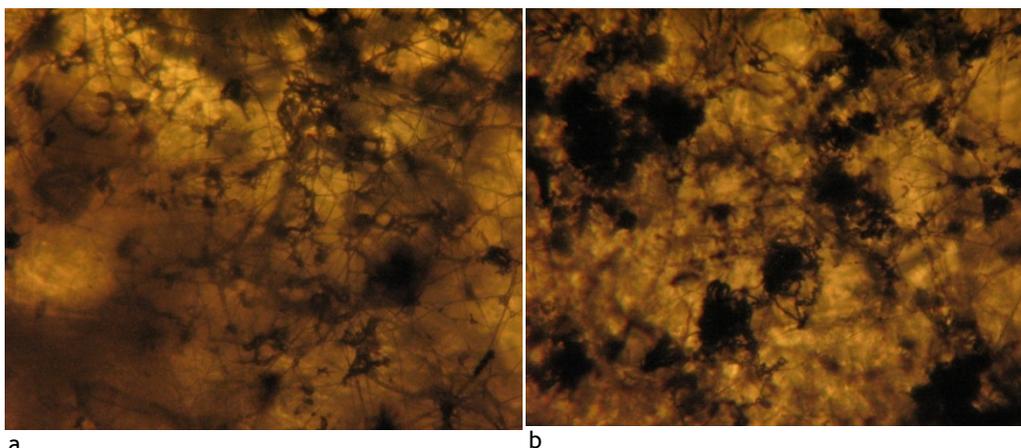


Figure 2. Microscopic pictures of the samples surface PA 6-210 KS with NR-N 10% of mass (Vietnam made) (x250): a – *Penicillium expansum*, b – *Aspergillus niger*

The pictures show the development of fungal mycelia on samples contaminated with their spores. Round-shape formations give evidence of material porosity.

Previous studies have confirmed the samples weight loss after 6 months in soil - from 3.2 to 5.8% for PA FG 30 % of mass and from 1.5 to 1.9% for PA FG 50 % of mass (Dautova et al., 2015b).

Conclusion

It was found that the introduction NR, regardless of its purification, not significantly reduces the water absorption of fiberglass-filled PA. The changes constitute 0, 08-0, 18 % of mass.

Changes in technological and the physical and mechanical properties after accelerated environmental tests for polymeric compositions based on fiberglass-filled PA with NR are greater than without it, at the same time for the samples with NR-N more than with NR-P. For all samples is observed decrease of tensile strength at break by 21-31% and elasticity modulus by 31-44%. Considerably increases MFI of compositions, containing NR-N, for PA FG 30 % of mass by 30 %, for PA FG 50 % of mass by 42 % as compared with controls.

In assessing the fungal resistance of fiberglass-filled PA compositions under the influence of fungi: *Aspergillus niger*, *Penicillium expansum* и *Fusarium oxysporum* after 84 days of incubation it was found out, that weight loss of samples using NR occurs to a much greater extent than without it. The weight loss under the action of *Aspergillus niger* is from 2.0 to 4.5 times higher as compared with the samples without rubber, under the action of *Penicillium expansum* - 3.8 -5.4 times, and *Fusarium oxysporum* - 1.5 -5.2 times.

Thus, the use of NR-N in fiberglass-filled compositions of PA-6, hardly exposed to degradation, is a factor contributing to greater destruction of the polymer in the process of recycling. Manufacturing of products with its addition to compositions will be the new solution to the problem of synthetic polymers disposal.

Disclosure statement

No potential conflict of interest was reported by the authors.

Notes on contributors

Alsu Dautova, junior researcher at the Scientific and technological center of chemistry and petrochemistry in Kazan National Research Technological University, Kazan, Russia.

Vladislav Yanov, associate professor at the department of the Technology of synthetic rubber in Kazan National Research Technological University, Kazan, Russia.

Nail Mingaleev, leading specialist at the Kazan State Agrarian University, Kazan, Russia.

Luybov Zenitova, professor of the department of the Technology of synthetic rubber in Kazan National Research Technological University, Kazan, Russia.

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