

# [Mechanical, chemical structure and thermal properties of the environmentally frie...](https://assignbuster.com/mechanical-chemical-structure-thermal-properties-of-the-environmentally-friendly-biopolymer-composition/)

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## Abstract

The main aim of article is investigation of mechanical, chemical structure and thermal properties of the environmentally friendly biopolymer composition. To prepare composition used biopolymer as a filler and phenol – formaldehyde oligomer as a liason. As a biopolymer used nut shell. Firstly the phenol – formaldehyde oligomer was modified with dietilaniline. The main parameters of the modified oligomer have been studied. According to investigation biopolymer composition can be used as a environmentally friendly cover. Key words: Biopolimers, phenol – formaldehyde oligomer, modification, dietilanilin, fillers, binder, composite.

## Introduction

Thermal and mechanical indices of many bioplastics have similar, eventually even higher consumer properties in comparison with the ones traditionally obtained from thermoplastic products. It should be noted that the economic value of the finished product includes cost price, as well as disposal and consumer costs. In these terms bio crumbling polymers are more suitable: the resources necessary for their production and renovation are more efficient. It should also be noted that the high cost price of the material may be temporary, as far as the production of biopolymers is not mass and the value of bioplastics will be reduced over time, as a result, they will be affordable for lots of businesses. Biopolymers have various types widely used in medicine, food industry, agriculture and building construction. Coatings (approximately 50%), foam (approximately 20%), fibers, etc. are actually recycled biopolymers. It has been determined that compared to other polymers, biopolymers are environmentally friendly and safe not only for people, but for the environment as well (Naibova T. M., Musazade Z. M., 2016).

Currently, the research is being carried out in this direction on the basis of biopolymers. The main purpose of the presented research is to study nut shell composition as a biopolymer, its physical and mechanical properties and to use it as a filler in the preparation of the biocomposition. The components used in the preparation of the composition are biopolymer sample of nut shell applied as a filler and modified resol type phenol – formaldehyde oligomer used as a liaison. Having high physical, mechanical, and exploitation indices and being technologically easily obtained phenol – formaldehyde oligomer is widely applied in various industries. However, being fragile, containing more amount of ecologically poisonous free phenol (10-15%) and free formaldehyde (17%); having relatively low level of heat resistance and stickiness, to some extent inhibits the use of phenol – formaldehyde oligomer in some areas. To eliminate these disadvantages, phenol formaldehyde oligomer was modified with nitrogen-containing modificator and its main physical – mechanical properties have been studied

## Experimental section

To prepare a biopolymer composition, a resol type phenolic formaldehyde oligomer was used as a liaison and nut shell powder as a filler. To improve the physical-mechanical properties of the phenol – formaldehyde oligomer it has been modified with nitrogen-containing monomer. Modification process was carried out in the laboratory reactor. During the modification process 37% formaldehyde water solution (formalin) and 25% ‒ ammonia water as a catalyst were used. By modifying PHFO with nitrogen-containing carbamid its fragility was eliminated and heat resistance was achieved. Nut shell was crushed in the LZM type laboratory mill and sifted through 0, 090 mm- size sieve. Being one of the high molecular biopolymers nut shell can have molecular weight from about 500 • 103 up to a few million and mainly consists of cellulose and lignin. Nut shell taken as a filler leads to further improvement of physical – mechanical properties of the binder composition. The properties of nut shell have been studied by means of thermo gravimetric analysis (TGA) and infrared spectroscopy.

## Results

## Element analysis

The main part of the nut shell composition consists of (in %) respectively lignin – 49. 45%, cellulose – 36. 5%, oil and resins – 2. 8%, water-soluble ingredients 6. 3% and ash substances 0. 5%. Element analysis of a biopolymer sample has been carried out using LECO Truspec CHN – S Element Analysis device. Carbon (C), hydrogen (H) and nitrogen (N) have been determined by ASTM D 5373 – 02 standard test method and the sulfur (S) has been defined by the ASTM D 4239 – 05 standard test method. The results of element analysis are given below The results of the element analysis for the biopolymer (nut shell in %)Sample C H N S ONut shell 52, 32 5, 57 0, 44 ‒ 43, 75

## Physical – mechanical properties of components

Having investigated the level and the way of solution of the components in the solvent it has been concluded that the powder of nut shell best of all dissolves in the dimethylformamide. As nut shell powder contains mixtures, it has created slime in dioxane and metaxylene solvents, while phenol – formaldehyde oligomer is completely solved in acetone, dimethylformamide, dioxane and spirit. The comparative results of non-modified phenol – formaldehyde oligomer and phenol – formal-dehyde oligomer modified by carbamide are tabulated in accordance with the parameters in table 2. Table 2 The main data on resol type PHFO modified by carbamide and non- modified PHFOIndices PHFO MPHFOThe amount of nitrogen – 8, 6The amount of free phenol,% 13 – 15 0, 5 – 2, 0Free formladehid amount,% 9, 7 4, 6The amount of methylol groups% 11, 2 9, 8Carboxyl groups % 17, 5 15, 2Softening temperature (Ubbelode), ° C 56 75Viscosity (50% – solution) by VZ – 4 device, sec 40 52Heat resistance (by Vika device), ° C 105 180Hardness (according to Brunel), MPa 220 285Solidification rate,% 92 98, 8Stickiness, MPa 2, 2 4, 8The density of biopolymer sample, the non-modified phenol – formaldehyde oligomer used as a liaison. and modified phenol – formaldehyde was determined by pycnometer. Results The density of biopolymers and PHFOSample Nut PHFO MPHFOρ, kg/m3 1250 1120 1150

## DTA and TG Analysis

There have been carried out DTA and TG analysis of nut shell samples. The operating area of “ Perkin Elmer” 6000 STA device is 16 – 10000C, thermal processing speed is 5 –200C/ sec, PolyScience analyzer and “ digital temperature controller” type cooling system. The kinetic parameters have been determined using “ Pyris Manger” software program. In order to avoid the removal of product combustion from the system and to prevent condensation process the inert argon gas was used and given to the system with the speed of 20 ml /p. min. Here standard 177. 78 mg aluminum – oxide based sample was used. The results of DTA and TG analysis of biopolymer samples have proved the destruction process to be going on in two stages and the weight loss correspondingly making up 7. 237% at 67. 82 ° C; 36. 203% at 278. 97 ° C. DTA, TG, DSC analysis of the nut shellAs a result of the gasification reaction realized by biopolymer argon gas in the steam atmosphere the released mixture consists of H2, CH2, CO, CO2. In the first stage halocelluloze (hemicelluloze + celluloze) is expected to split. First of all hemicelluloze inside the polysaccharide starts crumbling. In the stage of hemicelluloze splitting as a result of ether compound breaking, CO2 gas is emitted. In the stage of cellulose splitting hydroxyl compounds and in the decomposition of ether groups the CO gas is released . In the process of CO emission, CO2 is expected to release as well. At the same time, at this stage CH4 gas is also released. The source of emitted CH4 is cellulose. In the first stage the separation of H2 occurs as a result of hemicelluloze, cellulose and lignin splitting. In the second stage aromatic compounds and lignin are expected to split. Methoxyl groups, inside the lignin make CH4 separate, and hydrocarbons stipulate CO and H2 to separate.

## IR Analysis

Along with compositions obtained on the basis of completed with biopolymers and modified phenol – formaldehyde oligomers, for comparison it has been analyzed non- modified PHFO and the filler by the IR spectroscopy methods. IR spectras have been determined with the help of the SPECORD M80 and NICOLET Is10 made in the Thermo Scientific firm in United States. The carried out analysis allows to determine the basic structure of the studied compound. Thus, functional groups included inside the sample molecule are identified and short relationships are identified. The investigated samples of spectra have been recorded with 2 sm–1 spectral precision in the mid-infrared 3500 – 500 sm–1 area spectrometer. The creation of the release and absorption spectra of the substances are closely connected with the change in the internal energy of their molecules and atoms.

In the IR spectrum of the phenol – formaldehyde oligomer, modified by carbamide 3399. 6 sm–1 indicates NH relationship existing the in combination and the group of peaks intermediate 3190. 86 – 2610. 19 sm–1 show the absorption zone of the OH valence oscillations in the carboxyl group. 1784. 70 sm–1 C = O, 1599, 79 sm–1 characterizes the aromatic rings, 1461. 93 sm–1 existence of CH, at 1261. 35 and 1106. 56 sm–1 CH2 and OH in the methyl group and 965. 28 – 758. 72 sm–1 , and 701. 81 – 625. 59 sm–1 peaks correspondingly characterize the CH2 and CH groups existing in the combination. IR spectral analysis of PHFO modified by carbamide In IR spectrum –3700 – 3100 sm–1 field wide range of absorption band of biopolymers is closely connected with the valence vibration of hydroxyl groups. It is known that the low frequency strip area νOH characterizes more powerful (intramolecular), while high frequency strip area characterizes a weaker (intramolecular) hydroxyl groups connected with hydrogen bonds.

IR spectral analysis of the nut shell powder and composition filled with nut shell (powder)It is evident from the IR spectrum of nut shell (fig. 3) that 654. 12 – 907. 23 sm–1 denotes CH bond, 1019 sm–1 compound ester groups, 1507. 12 sm–1 , C – CH3, 1606. 33 aromatic links 1646. 74 sm–1 NH2, 3648. 35 sm–1 absorption of strips of OH bond valence oscillation. While in the IR spectrum of the composite filled with nut shell powder 3675. 73, 3625. 25 and 3599. 82 sm–1 peaks denote OH, 3474. 67, 3361. 76 and 3227. 78 sm–1 peaks NH, 3012. 36 sm–1 CH bonds in alkyl groups, 1748. 54 sm–1 C = C, 1651. 87 sm–1 – HC = CH – group C = C bonds, 1593. 25 sm–1 aromatic rings, 1224. 88 and 1168. 96 sm–1 C – O bonds, the peaks between 969. 86 – 657. 42 sm–1 CH = CH, and are the absorption lines of CH oscillations in (CH2)n groups . It should be noted that, as far as approximately all of the spectra are similar, the IR – spectra analysis of biopolymer samples poses some difficulties. However, it is known that chemical modification of cellulose, above all, at the 3700 – 3100 sm–1 area leads to the changes, so that the broad absorption lines correspond to the valence occilation of hydroxyl groups attached to the hydrogen bonds.

## Mechanical proporties of the biocomposition

Having studied the basic properties of the components, the composite based on biopolymer was prepared and major indices of the composition were investigated. The major indices of the composite obtained on the basis of phenol – formaldehyde oligomer filled and modified with biopolymers are given in table 4. Table 4 The major indices of the composite filled with biopolymers Indices BCSolidification rate,% 98, 9 Stickiness strength, Mpa 7, 163 Heat resistance, ° 181The obtained composition was thermally solidified at temperature 90°C. The results of the research have proved that composition filled with biopolymer sample is more durable, of high physical- chemical properties, as well as environmentally more friendly. The compositions obtained from them can be applied as varnish – paint cover in construction, furniture manufacturing, automobile industry and in lots of various areas.

## Conclusion

The phenol – formaldehyde oligomer was modified with nitrogen-containing carbamid . The main parameters of the obtained oligomer have been studied. For comparison, the main indices of the unmodified oligomer have been researched. An environmentally friendly coating was obtained using a carbamid – phenol – formaldehyde oligomer as binder and nut shell as a filler.