COMPOSITE NANOFIBERS: POLYMER – WOOD DUST (GREEN COMPOSITES)

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Abstract

The paper describes preparation of nano fiber composites made of polyvinyl butyrate (PVB) and wood dusts. The used wood dusts of nano- and micro-dimensions were obtained by grinding of exotic woods - garapa and teak.

Electrostatic spinning technology Nanospider was used to prepare nanoparticles from the following mixtures:
- Polymer PVB (10 wt\%) + ethanol
- Polymer PVB (10 wt\%) + ethanol + 20 wt. \% dust from teak
- Polymer PVB (10 wt\%) + ethanol + 20 wt. \% dust from garapa
- Polymer PVB (10 wt\%) + ethanol + 20 wt. \% mixture dust from garapa and teak in the ratio 2:1.

The prepared composites PVB – garapa, PVB – teak, PVB – garapa + teak were examined by means of FTIR analysis and their thermal stability and morphology of fibers were determined by TGA, DSC and SEM resp.

The composites belong to the category of “green composites” in which reinforcement occurs by biological decomposition of the components.

The results have shown an increase of thermal resistance of composites prepared from different kinds of woods in the course of their pyrolysis.

Another variant of the composite was prepared by application of wood dust from teak and garapa between layers of nano fibers – the sandwich structure. A layer of wood dust was sputtered on a nano fiber layer of polycaprolactone and it was homogenized by ultrasound. Subsequently, the material was covered with another layer of nano fibers to enclose the powder material in the composite.

In this case very good sorption properties were demonstrated in respect to oil products on water surface.

Keywords: nanofiber, composite, wood dust, garapa, teak

1. INTRODUCTION

Composites (composite materials) are generally defined as heterogeneous systems made up of at least two phases with different properties. The new substance (material) created by their combination usually features additional new properties - as a result of synergy.

We have focused our attention on composite materials with a polymer matrix where the particles (reinforcement) in the composite are made of a natural, easily biodegradable material. The composites have been called “green composites” [1]. They contain cellulose-lignin materials, i.e. wood dust, wood sawdust, cellulose, nano cellulose, bamboo fibers, coconut fibers, leather etc. [2] Materials used as polymer matrix are usually epoxides [3], polypropylene (also modified) [4-9] polyethylene (also modified) [5,10,6], polyvinyl alcohol [1], polyvinyl butyral [2], polycaprolactone [11,14], polymethyl metacrylate [12], polypropylene – ethyl vinyl acetate copolymer [13].
Most of the quoted works indicate changes in mechanical properties of the prepared composites, such as hardness, tensile strength, bending strength, tensile modulus of elasticity etc., in relation to the employed polymer or its modification [4,3,10].

For our experiments we prepared composites from nanofibers formed by electrostatic spinning of polyvinyl butyral (PVB) matrix and wood dust from teak and garapa wood and their mixtures.

The prepared composites were analyzed by FTIR and we determined their thermal stability (TGA, DSC) and morphology of the fibers (SEM). Also a sandwich composite was prepared (polymer-dust-polymer) from polycaprolaktone (PCL) and garapa wood dust and its sorption capacity was tested.

2. COMPOSITE NANO FIBERS PVB – WOOD DUST

2.1. Preparation of composite nano fibers and measuring technology

Exotic woods - teak (*Tescona Graundis*) and garapa (*Apuleia Leiocarpa*) - were ground on a grinding machine with an abrasive-band, type Houdek PBH 300B Basset, grinding belt speed 17m/s, the abrasive grain was 100. The grinding was originally performed in order to measure the quantity and distribution of nano- and micro- aerosol particles. The composite was prepared from the dust that sedimented on the surface at the grinder.

From macroscopic viewpoint the sedimented dust of the teak wood had a coarse structure, minimum dustiness and it was cohesive with aggregation tendency. The garapa dust consisted mostly of smaller particles with medium dustiness and good powderiness. Examples of microscopic structure of the employed teak and garapa dusts are shown in Figs 1 and 2.

Polyvinyl butyral (PVB) polymer made by Kurakay, molecule weight 60 thousand, was used as 10% percent solution in ethanol. Electrostatic spinning technology Nanospider was used to prepare nano fibers from the following mixtures:

- PVB polymer (10 wt.%) + ethanol
- Polymer PVB (10 wt.%) + ethanol + 20 wt.% teak dust
- Polymer PVB (10 wt.%) + ethanol + 20 wt.% garapa dust
- Polymer PVB (10 wt.%) + ethanol + 20 wt.% mixture of garapa and teak dust, 2:1

The preparation was performed at various winding speeds 60, 50, 40, 30 mm/min. The underlying textile was Spunbond. The photos were made in TWIST Flexible Digital Microscope, by Learning Resources, Inc., USA. ATR analysis (FTIR spectrometry) used the Brucker Alpha/FT-IR, ATR crystal (identified platinum Diamond 1 Refl), software OPUS 6.5, source IR SiC Globar. Measuring parameters: number of spectrum scans 24, resolution 4 cm⁻¹, spectrum range 375 - 4000 cm. The measurement was performed on solid samples and
ATR crystal was covered with an thin optical layer. The thin layer formation on the crystal was ensured by pressing the tip with force set up by the manufacturer.

The thermal analyses TGA and DSC of the prepared nano fibers were also performed on STA 1500 Instrument Specialists Incorporated-THASS, analytical scale SUMMIT, SI 234-4, air flow: 20 ml/min., heating speed: 10°C/min., ceramic crucible, diameter: 5 mm, height: 8 mm, degradation medium: air.

Mechanical properties of the composites were tested on a single column INSTRON mod. 5544. The scanning electron microscope (SEM) was Hitachi FE SEM S-4800.

2.2. Thermal stability of the prepared PVB – wood dust composites

We tested thermal stability of the prepared composites and of the initial polymer, depending on the type of wood and partly also on the winding speed during the preparation.

TGA curves of samples No. 1 through 5 (see Figs. 3 - 7) can be divided into several sections with different slopes, i.e. weight loss rates. The thermal effect (ΔH) of the process was determined as the area of the peak of the respective thermal process, i.e. the area outlined with the DSC curve and the line between the beginning and the end of the thermal process. The area of the peak is directly proportional to the heat released or consumed by the reaction and the height of the peak (H_H) is directly proportional to the reaction rate.

When heating samples No. 1 through 5, the DSC the curves (see Figs. 3 - 7) demonstrated three to five thermal processes. At temperatures from 25 °C to ca, 100 °C samples No. 1 through 4 demonstrated endothermic processes, with the exception of the composite PVB-garapa + teak. At temperatures 414.8°C to 480.8 °C all samples underwent significant exothermic processes with the peak area on the DSC curve corresponding to ca. 1000 kJ/kg for the samples No. 1 and 4, over 1800 kJ/kg for the samples No. 2 and 5 and over 2000 kJ/kg for the sample No. 3.

![Fig. 3 STA of the sample No. 1 – PVB, winding speed 30 mm/min. (weighted sample 9.1 mg)](image1)

![Fig. 4 STA sample No. 2 – PVB – garapa, winding speed 30 mm/min (weighted sample 9.2 mg)](image2)
The biggest overall thermal effect during decomposition of the tested composites was found for PVB – garapa, prepared at the winding speed 40 mm/min (2545 kJ/kg). The value was ca. one half of the thermal effect of the garapa dust alone (5535 KJ/kg) and essentially the double of that of PVB alone (1321 kJ/kg). Also TGA and DSC curves of garapa wood dust were different from those of the composites (compare Figures No. 3-7 and Fig. No. 8). The decomposition of garapa occured with two separate exothermic effects with the same maximum height on the DSC curve.

The first pronounced exothermic effect started as early as at 233°C, which is a much lower temperature than temperatures for composites containing garapa. A similar decomposition curve has been described for teak wood dust [15] and also in this case the beginning of the first exothermic effect occurred at a much lower temperature than for the composite PVB – teak.
2.3. Infrared spectrums of the prepared composites PVB – wood dust

Examples of IR spectrums of PVB alone and the composite PVB-garapa+teak (2:1) are provided in Figures No. 9 and 10. The spectrums show differences in ratios of the strongest absorbance values in the range 1200-900 cm\(^{-1}\) as indicated in the framed parts of the spectrums.

![Fig. 9 IR-spectrum of PVB](image)

![Fig. 10 IR-spectrum of PVB+ garapa + teak (2:1) composite](image)

This spectrum shows the strongest absorbance on the bond C-O-C in the wood (garapa 1030.1 cm\(^{-1}\) and teak 1027.68 cm\(^{-1}\)). The absorbance values in the IR spectrum are also influenced by the speed of the winding band during electrostatic spinning, i.e. stratification of nano fibers and thus their different crystallinity. Even here, however, we have demonstrated the role of the wood type from which the composite was made.

2.4. Determination of strength characteristics of the prepared PVB – wood dust composites

The prepared material (layers of nano fibers) can be essentially described as a non-woven textile or a foil containing wooden composite. Therefore the laboratory of the Institute of Food Conservation and Meat Technology tested strength characteristics using the same procedures as for packaging foils. The tested samples of the foil were 100 mm long and 15 mm wide.

**Foil thickness:**
- PVB: 14.3 µm
- PVB-garapa: 36.2 µm
- PVB-teak: 10 µm
- PVB – garapa + teak: 21 µm

The measured strength characteristics, such as maximum tear strength, tensile strength, tensile modulus of elasticity and rigidity, i.e. energy necessary to tear the samples, are shown in Figure No. 11.

The diagram indicates that the tensile strength is lower for the composite – see **Fig. 11c)** - it is more than half of that of the foil prepared only from PVB and it is comparable for the individual composites – see **Fig. 11c)**. Differences between individual types of composites are in tensile modulus of elasticity which characterizes resistance of material against deformation - see **Fig. 11a)** and material rigidity – see **Fig. 11b)**. The differences were found between composites containing garapa and teak, while for composites containing a mixture of garapa and teak the values were between the values of the individual woods - for comparison see **Figs. 11a) and 11b)**. This fact has confirmed the assumption that mechanical properties are affected by the wood type, or rather by the chemical and physicochemical properties of its micro- and nano sawdust.
a) Resistance of composite foils against deformation (y: tensile module of elasticity)

b) Rigidity – energy needed to tear the composite foils (y: energy)

c) Tensile strength of composite foils (y: tensile strength)

d) Maximum tear strength of the composite foils

**Fig. 11** Measured strength characteristics of PVB alone and PVB composites with the indicated wood dust (x: slepy = blank)

### 2.5. Morphology of the prepared PVB composites

Morphological differences between PVB alone and the prepared composites are illustrated with electron microscope images (SEM) in **Fig. 12**. The images show characteristic “bulges”, while no such formations were observed in PVB alone. The number of “bulges” was affected by the winding speed during the preparation. The nano fibers used in the composite with teak were thinner than in the composite with garapa and the large-volume formations were not found so often in them, as they were probably caused by bigger dust particles.

**Fig. 12** Comparison of SEM images: PVB and composites containing PVB. The left pictures are 50 µm, the right pictures are 5 µm.
3. PREPARATION OF SANDWICH MATERIAL PCL – GARAPA DUST – PCL AND ITS IDENTIFICATION

The employed polymer was polycaprolactone (PCL) made by Sigma Aldrich with the molecule weight 45,000. The polymer was dissolved in a solution of chloroform/ethanol (8:2) to the resulting concentration of 19 wt. %. Spinning of polymer solution was performed with a rotary spinning electrode of an elongated shape under the patent WO 2008028428. Voltage of +15kV was applied to the electrode rotating at 25 rev/min. Voltage of -38kV was applied to a moving band (collector) made of Spunbond material. A layer of nano fibers was created on the moving band and garapa dust was subsequently applied on the nano fibers by sputtering. A special sputtering device was used to apply the dust and the layer was homogenized with ultrasound. Subsequently, another layer of nano fibers was applied to enclose the powder inside the composite.

It should be noted that when we applied the garapa dust on the first layer of nano fibers we were not able to achieve its full homogeneity. This shortcoming can be eliminated by improvement of the technology, however we used the inhomogeneous layer of dust to evaluate the effect of concentration of wood dust between the PCL layers on physicochemical properties of the sandwich material. We split the sandwich material into two sections, one with the minimum content of garapa wood dust and one with a high content of dust. Then we examined the sections with a microscope, TGA and DSC analyses, FTIR and SEM analyses. The basic comparison of the results is shown in Fig. 13 (a – d versus a* - d*).

![Fig. 13 Basic comparison of results of analyses of the sandwich material PCL–garapa dust–PCL](image)

The difference in the content of wood dust in the material is obvious from the comparison of microscope images (magnification 150x in Fig. 13 a – a*). Thermograms in Fig. 13 b – b* indicate the difference of up to 163 °C in the temperature at which decomposition starts with an exothermic effect. The garapa wood alone decomposes with an exothermic effect 30 – 40 °C later than the sandwich material with a high content of wood.[15] The overall thermal effect of the decomposition is also different: it is 1 871 kJ.kg⁻¹ for the material with the minimum dust content and 6 063 kJ.kg⁻¹ for the material with a high dust content.

The IR spectrum of PCL–garapa dust–PCL with a high dust content demonstrated one half of the absorbance value, with new vibrations of O-H group at 3 265 cm⁻¹, shift of C-H vibrations by 10 cm⁻¹ and penetration of deformation vibrations of ether and glycoside bonds C-O-C with the strongest vibration at 1 045 cm⁻¹ and multivibrations in the range 702 – 412 cm⁻¹ characteristic for the wood spectrum (Fig. 13 c – c*).
SEM images (Fig. 13 d – d*) indicate two types of fibers in both the samples, regardless of the content of wood dust: thinner fibers up to 500 nm thick and thicker fibers over 500 nm thick. The representation of thicker fibers and uneven distribution of both the types of fibers is higher in the material with high content of wood dust.

3.1. Sorption capacity (absorbability) of sandwich material PCL–garapa dust–PCL

The sandwich material was prepared mainly in order to have a material which has suitable sorption properties and is biologically degradable. The test of sorption capacity was based on gravimetric measurement of the ability to absorb water, oil and water + oil during surface contact. The average absorbability (increase of weight) of the material for water was 299 – 336 %, for oil 397 – 419 % and for water + oil 456 – 505 %. A positive dependence of absorbability on the quantity of wood dust has not been demonstrated.

4. CONCLUSION

Results of the experiments have shown effects of wood material used as composite reinforcement and of method of composite preparation on the physicochemical and mechanical properties of the composites. At the same time, the experiments have raised a number of questions about factors that influence properties of nanocomposites. Preparation of nanocomposites offers numerous variants of different combinations of polymer type, wood type and size of wood dust particles, methods of preparation etc. A combination of such variants might enable to prepare composites with desired properties.

LITERATURE


