Calcium lignosulfonate as eco-friendly additive for crosslinking fibrous composites with phenol-formaldehyde resin matrix

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DOI: dx.doi.org/10.14314/polimery.2018.2.3

Abstract: The possibility of application of calcium lignosulfonate (CLS) as an eco-friendly additive for crosslinking fibrous composites with phenol-formaldehyde resin matrix was investigated. CLS has been characterized in detail in terms of its physicochemical and dispersive-morphological properties. The compositions of phenol-formaldehyde resin with CLS or with bentonite modified with trimethyl-2-hydroxypropyl ammonium chloride were prepared. Such compositions were used to impregnate fiberglass meshes. Mechanical properties of the prepared samples were determined, and their morphology as well as surface properties were assessed. A pronounced effect of the type of applied filler on the mechanical properties was observed. The best results were obtained for fiberglass meshes impregnated using phenol-formaldehyde resin with 1 wt % modified bentonite and 1 wt % CLS.

Keywords: calcium lignosulfonate, composite, phenol-formaldehyde resin.

Lignosulfonian wapnia jako przyjazny środowisku dodatek do sieciowania kompozytów włóknistych na bazie żywicy fenolowo-formaldehydowej

Streszczenie: Badano możliwości zastosowania lignosulfonianu wapnia (CLS) jako przyjaznego środowisku dodatku stosowanego do sieciowania kompozytów włóknistych, których osnowę stanowiła żywica fenolowo-formaldehydowa. Na wstępie szczegółowo scharakteryzowano CLS określając jego najważniejsze właściwości fizykochemiczne i dyspersyjno-morfologiczne. Następnie wytworzono kompozycje żywicy fenolowo-formaldehydowej z CLS lub z bentonitem modyfikowanym chlorkiem trimetylo-2-hydroksypropyloamoniowym. Tak przygotowanych kompozycji użyto do impregnacji siatek z włókna szklanego. Zbadano właściwości mechaniczne oraz oceniono morfologię i właściwości powierzchniowe sporządzonych próbek. Stwierdzono wyraźny wpływ rodzaju zastosowanego napełniacza na parametry wytrzymałościowe próbek. Najlepsze rezultaty uzyskano w przypadku siatek szklanych impregnowanych żywicą fenolowo-formaldehydową z dodatkiem 1 % mas. modyfikowanego bentonitu i 1 % mas. CLS.

Słowa kluczowe: lignosulfonian wapnia, kompozyt, żywica fenolowo-formaldehydowa.

Phenolic resins are among of the most widespread organic resin systems. High popularity of this group of resins is associated with sensational performance/price ratio. Phenolic binders are mainly used as permanent bonding (wood composites, insulation materials, laminates), temporary bonding (abrasives, friction linings) and complementary bonding (coatings and surface protection) [1].

A wide variety of applications requires the use of different fillers and additives. Plywood composites use rye flour, wheat flour, coconut shell flour and $CaCO_3$ in order to adjust wetting and obtain uniform joint thickness [2, 3]. Manufacturing of high density phenolic foam insulators requires the use of graphite, aluminum hydroxide, ammonium polyphosphate, calcium silicate and calcium carbonate as fillers [4]. Fillers in paper-based and fabric-based laminates are used for another purpose, *e.g.*, antimony trioxide or zinc borate increase flame retardancy [5, 6].

The role of fillers is even more important in case of abrasive and friction materials. Abrasive manufacturing industry mostly uses high performance composites based on phenol-formaldehyde continuous phase. Abrasive composites are often exposed to high mechanical stresses, extremely high temperatures and machine cool-

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ants [7]. Aside from abrasive grain and phenolic binder, such demanding environment enforces the use of fillers as additives. Most common fillers, such as cryolite, iron sulfide, zinc sulfide, calcium sulfate and calcium chloride, are used in order to improve grinding efficiency and to help protect the grain [4]. Calcium carbonate or wollastonite can be used to increase the durability, heat resistance or toughness. High density grinding tools may also employ alkaline metal oxides for faster resin cure and water absorption [4].

Due to the high level of chemical resistance after curing, phenolic resins are often used in the preparation of coatings and anticorrosive layers. In order to achieve high quality surface protection, preparation of coatings employs both inactive and active fillers. Inactive fibers, silicates and sulfates strengthen the coating layer, while active pigments, such as chromates, provide color effect and anticorrosive properties [8].

To date, the innovative additives are being sought as components of phenol-formaldehyde resins in order to improve the mechanical properties of the final products (among other lignin and its derivatives) [9]. Thus, in the framework of this study, calcium lignosulfonate was used as an additive to the phenol-formaldehyde resin. The newly created compositions were subjected to evaluation of mechanical properties, in addition, images were taken using a scanning electron microscope as well as atomic force microscopy. Additionally, calcium lignosulfonate has been characterized in detail in terms of its physicochemical and dispersive-morphological properties.

EXPERIMENTAL PART

Materials

Calcium lignosulfonate (CLS) with average molecular weight $\overline{M}_w \approx 18\ 000$ and $\overline{M}_n \approx 2500$ (Sigma-Aldrich, Germany) was used as a filler. In addition, bentonite (Sigma-Aldrich, Germany) was used, which was modified using trimethyl-2-hydroxypropyl ammonium chloride (BQAS, Sigma-Aldrich, Germany). Fenoplast DS-05 (LERG, Poland) was selected as the phenol-formaldehyde resin. Furthermore, fiberglass meshes with a weight of 195, 265 and 464 g/m^2 manufactured by Rymatex Sp. z o.o. (Poland) were used.

Preparation of the phenol-formaldehyde resin composition with the addition of fillers

Modified bentonite or CLS were added in a quantity of 1.0 wt % to a liquid phenol-formaldehyde resin using a multi-step homogenization consisting of premixing by means of a slow rotating mechanical stirrer at room temperature, then the mixture was heated to 50 °C and stirred with an ultrasonic homogenizer. The next homogenization step was carried out in a high-speed turbine agitator in a vacuum vessel at 50 °C at a stirring speed of 4000 rpm. The final homogenization was carried out in a 0.5 mm deep cylinder-cylinder grinder providing intensive shear due to the high rotational speed of the cylinder moving at 6000 rpm.

Preparation of composites enhanced with fibers of fiberglass using phenol-formaldehyde resin matrix composition

Prepared phenol-formaldehyde resin with 1.0 wt % of modified bentonite or 1.0 wt % of CLS was used to impregnate fiberglass meshes of different weights: 195, 265 or 464 g/m^2 by means of the grooved roll and then subjected to a drying process in the temperature range from 90 to 140 °C. The 229 x 23 mm discs were cut from the meshes obtained from the dies for the dynamic strength test as well as the 250 mm squares which were cross-linked at 160 °C for 4 h.

Determination of physicochemical properties of calcium lignosulfonate

CLS was subjected to a comprehensive characterization using the most advanced analytical methods and techniques. The dispersive properties were evaluated based on the particle size distributions determined using a Zetasizer Nano ZS and a Mastersizer 2000 (Malvern Instruments Ltd., UK) operating based on non-invasive back scatter and laser diffraction techniques, respectively.

CLS was also subjected to morphological and microstructural analysis using a scanning electron microscope (Zeiss EVO40, Germany).

The presence of the expected functional groups was confirmed by attenuated total reflectance (ATR) spectroscopy, using a Vertex 70 spectrophotometer (Bruker, Germany). The tests were performed at a resolution of 0.5 cm^{-1} in the wavenumber range 4000–400 cm^{-1}.

The elemental contents of CLS were determined using a Vario EL Cube instrument (Elementar Analysensysteme GmbH, Germany), which is capable of registering the percentage content of carbon, hydrogen, nitrogen, and sulfur in samples after high-temperature combustion. A properly weighed sample was placed in an 80-position autosampler and subjected to combustion. The decomposed sample was transferred in a stream of inert gas into an adsorption column. The results are given with an accuracy of ± 0.01 %, and each result was obtained by calculating a mean from three measurements.

In order to characterize porous structure of CLS, nitrogen adsorption/desorption isotherms at 77 K and parameters such as surface area (A_{BET}), pore volume (V_p) and average pore size (S_p) were determined using an ASAP 2020 instrument (Micromeritics Instrument Co., USA). The sample was degassed at 120 °C for 4 h prior to measurement. The A_{BET} value was determined by the multipoint BET (Brunauer–Emmett–Teller) method using the adsorption data in the relative pressure (p/p_0). The BJH

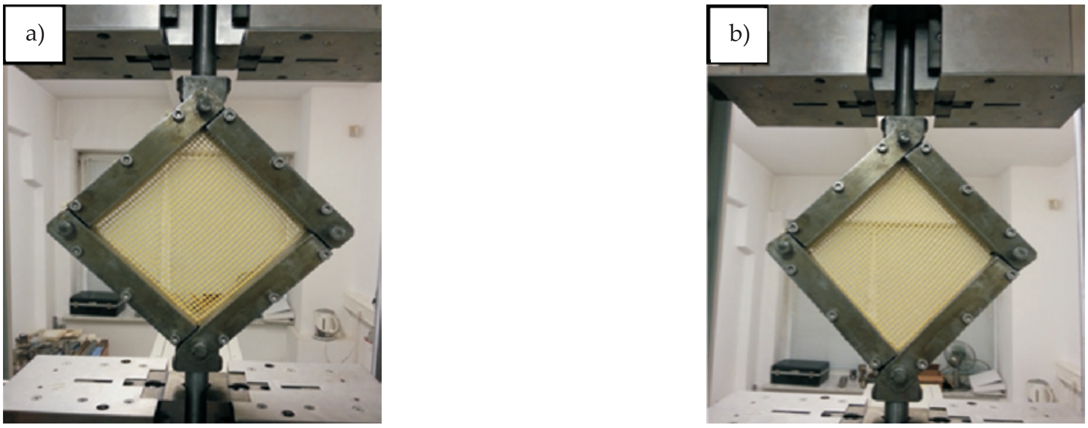

Fig. 1. Appearance of the sample fixed in the handles before (a) and after (b) the shear test

(Barrett–Joyner–Halenda) method was applied to determine the V_p and the S_p values.

Thermogravimetric analysis was performed using a Jupiter STA 449 F3 (Netzsch GmbH, Germany). The sample (approximately 10.0 mg) was placed in an Al_2O_3 crucible and heated at a rate of 10 °C/min from 30 to 1000 °C in nitrogen atmosphere.

Methods of testing of prepared compositions

Mechanical properties

Measurement of dynamic strength of the abrasive wheel at break was conducted in accordance with the EN 12413:2007 standard. The tests were carried out in a wheel diameter of 230 mm and a thickness of 2 mm, at 25 °C. The shear strength was determined using a shear frame test at a tensile speed of 2 mm/min on a Zwick/Roell strength crosslinked 250 mm squared machine as it is shown in Fig. 1. The shear stress (τ) was determined according to the following equation:

$$\tau = \frac{P}{\sqrt{2} \cdot a \cdot b} \tag{1}$$

where: P – maximal force, a – thickness of the sample, b – side length of the sample.

Morphology

Morphology of fragile breakthroughs of hardened fibrous composites was analyzed using the JEOL JSM-5500 LV scanning electron microscope (Japan). The composite breakthroughs were obtained after the ice-cold moulds and their impact fracture. Before sample measurement, gold was sprayed.

Mesh surface topography

Atomic force microscopy (AFM) was used to visualize the mesh surface using the tapping mode technique. The tests were performed using a Nanoscope V microscope (Bruker, Germany) equipped with a RTESPA scanning needle with a constant $k = 5$ N/m. Images were recorded at 1 kHz scanning speed and 512 lines resolution and then analyzed using Nanoscope Analysis.

RESULTS AND DISCUSSION

Physicochemical characterization of calcium lignosulfonate

The aim of the first stage of the study was to characterize the microstructure properties of calcium lignosulfonate. The results are presented in Table 1 and Fig. 2. The dispersive analysis of this product confirmed its monomodal particle size distribution, corresponding to primary and secondary agglomerates with diameters in the range of 2.30–6.64 μm. The data acquired from Mastersizer 2000 also indicated that the product has a tendency to agglomerate. In the sample, 10 % of the volume is occupied by particles smaller than 5.1 μm, while 50 % and 90 % of the sample volume are attributed to the presence

T a b l e 1. Physicochemical characteristic of calcium lignosulfonate

Sample	Elemental content, %				Porous structure properties		
Calcium lignosulfonate	N	C	H	S	A_{BET}, m^2/g	V_p, cm^3/g	S_p, nm
	0.1	39.2	5.0	4.2	0.9	0.001	29.8
	Dispersive properties						
	Range of particle size distributions by volume μm			Particle diameter from Mastersizer 2000 μm			
	2.30–6.64			d (0.1)	d (0.5)	d (0.9)	D [4.3]
				5.1	18.3	46.8	18.6

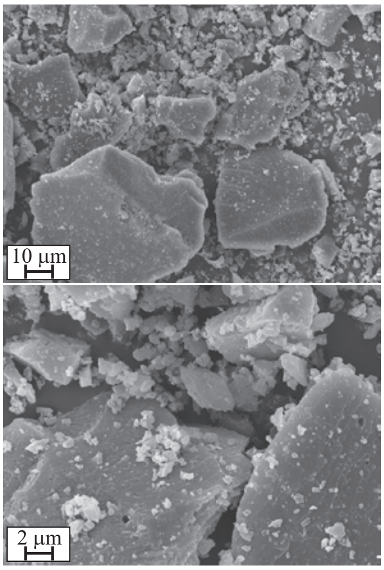

Fig. 2. SEM images of calcium lignosulfonate (two different magnifications)

of particles smaller than 18.3 and 46.8 µm, respectively. These observations are in agreement with the SEM analysis. The SEM microimages show the presence of individual particles with an average size of 5–8 µm (Fig. 2). The particles exhibit the ability to connect with each other, forming an agglomerate structure.

The FT-IR spectrum of CLS, shown in Fig. 3, was taken and analyzed to identify the functional groups in the structure of the CLS. The medium intensity band in the range 3550–3250 cm^{-1}, characteristic for the stretching vibrations of hydroxyl groups was found. Important bands in this spectrum include those peaking at 2915 cm^{-1} (attributed to stretching vibrations of C-H from CH_3 and CH_2 groups). The band in the range of 1710–1600 cm^{-1} is attributed to unconjugated and conjugated stretching vibrations of C=O groups. CLS contains aromatic rings, the presence of which is manifested by the characteristic bands peaking at 1598 cm^{-1}, 1512 cm^{-1}, 1420 cm^{-1} and 650 cm^{-1}. The appearance of bands in the range of 1500–1000 cm^{-1} indicates the presence of many groups, including the C-H groups (bending vibrations of methyl and methylene groups as well as groups from aromatic rings), ether groups (C-O-C), C-C bonds and C-O groups typical for secondary alcohols, among others. These results are in full agreement with previous reports [11, 12].

The results obtained for CLS confirmed the diversity of the elemental composition of the product (see Table 1). The CLS system largely consists of carbon (39.2 %) and hydrogen (5.0 %). The presence of sulfur (4.2 %) can be explained by the process of separation of cellulose from lignin *via* sulfuric wood digestion.

The next stage of physicochemical evaluation involved the analysis of the porous structure parameters of the used product. This structure is characterized by $A_{BET} = 0.9\ m^2/g$, $V_p = 0.001\ cm^3/g$ and $S_p = 29.8$ nm.

Thermal stability of CLS was low as confirmed by 66 % mass loss during its heating up to 1000 °C what is presented in Fig. 4. The first mass loss of 10 % was noted in the temperature range of 25–200 °C. This was related to the elimination of water physically bound in the biopolymer structure [13]. Second mass loss of 46 % concerns degradation of bonds in the lignosulfonate structure due to thermal treatment as well as further elimination of water constitutionally bound to the biopolymer. Heat treatment realized beyond 600 °C resulted in a partial elimination of fragments of lignosulfonate related to carbon. The fragmentation process of the lignosulfonate molecule takes place as a result of unknown chemical reactions [13, 14].

Evaluation of mechanical properties of hybrid composites based on calcium lignosulfonate

In order to evaluate the influence of the used fillers, including CLS, on the mechanical properties of the studied hybrid fibrous composites, the dynamic strength of the abrasive wheel at break as well as shear stress were determined, and the obtained results are presented in Table 2. Based on the results it can be observed that the

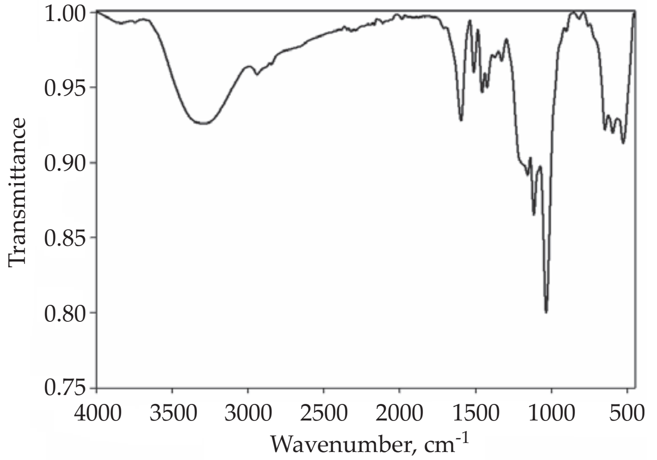

Fig. 3. FT-IR spectrum of calcium lignosulfonate

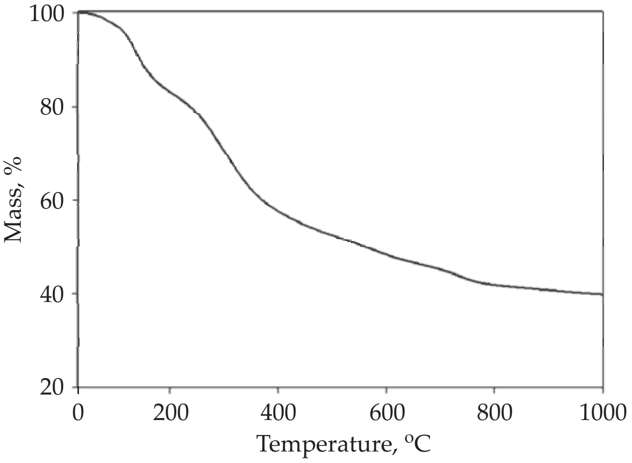

Fig. 4. Thermogravimetric curve for calcium lignosulfonate

Table 2. Results of determination of mechanical properties of tested composites

Mechanical properties	Phenol-formaldehyde resin	Phenol-formaldehyde resin + 1 wt % of CLS	Phenol-formaldehyde resin + 1 wt % of BQAS	Phenol-formaldehyde resin + 1 wt % of BQAS + 1 wt % of CLS
Mesh with basis weight of 195 g/m^2				
Shear stress, MPa	0.52 ± 0.05	0.57 ± 0.04	0.60 ± 0.04	0.78 ± 0.02
Dynamic strength of the abrasive wheel at break, rpm	10 430	10 640	10 920	11 270
Mesh with basis weight of 265 g/m^2				
Shear stress, MPa	0.74 ± 0.06	0.81 ± 0.04	0.85 ± 0.02	1.11 ± 0.02
Dynamic strength of the abrasive wheel at break, rpm	14 900	15 200	15 600	16 100
Mesh with basis weight of 464 g/m^2				
Shear stress, MPa	1.04 ± 0.04	1.13 ± 0.06	1.17 ± 0.03	1.55 ± 0.04
Dynamic strength of the abrasive wheel at break, rpm	20 860	21 280	21 840	22 540

fillers had a notable influence on the enhancement of the studied mechanical properties. The best results were obtained for fiberglass meshes impregnated with the phenol-formaldehyde resin with the addition of 1 wt % of BQAS and 1 wt % of CLS, in case of which a notable increase of the studied traits was achieved: the dynamic durability was increased by approximately 15 % and the shear stress by 66 % compared to composites based on non-modified phenol-formaldehyde resin. In case of the remaining layer composites with the addition of 1 wt % of CLS an increase of dynamic durability by 10 % and shear stress by approximately 44 % was noted.

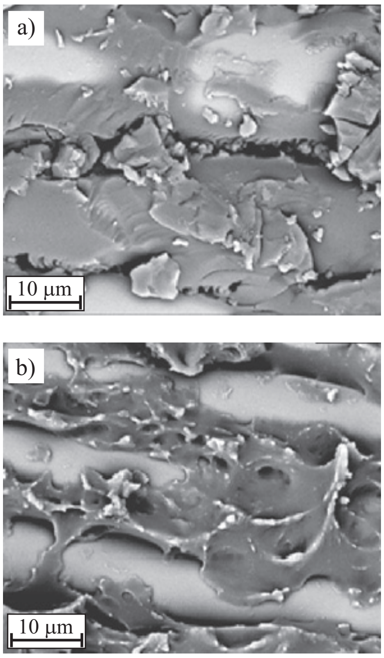

Fig. 5. SEM images of brittle fractures in the composites based on: a) unmodified phenol-formaldehyde resin, b) resin + 1 wt % BQAS and 1 wt % CLS

SEM analysis of brittle fractures in the studied composites

Studies with the use of SEM were conducted for brittle fractures of the fibrous composite samples in the direction parallel to the fibers. The aim of these studies was to evaluate the influence of the used fillers on the microstructure of the composites.

The morphology of the brittle fractures in glass laminates based on the resin with 1 wt % of BQAS and 1 wt % of CLS differed notably compared to the morphology of composites based on the unmodified resin as it can be seen in Fig. 5. In the case of the unmodified composition, the surface of the fracture is smooth, which indicates an easier propagation of the formed cracks (Fig. 5a). Upon the addition of the modified bentonite and CLS, the surface of the fracture became irregular, rough and included numerous furrows, which limited the formation of cracks (Fig. 5b).

AFM analysis

Based on the conducted AFM microscopic studies, images of the topography and difference of phase on the surface of meshes impregnated with unmodified and modified polymer compositions were obtained. The analysis of the obtained images, shown in Fig. 6, indicates that the addition of the calcium lignosulfonate filler notably changes the surface of the composite. This is also confirmed by the roughness value *Ra* (mean standard deviation of the profile from the base line), which were increased by 10.5 nm compared to the composite with the unmodified resin. Notable differences are also visible on the phase image. In the case of surface of the composite with the unmodified resin the image is uniform, whereas in the case of the phase image of the composite with the modified resin two separate phases may be distin-

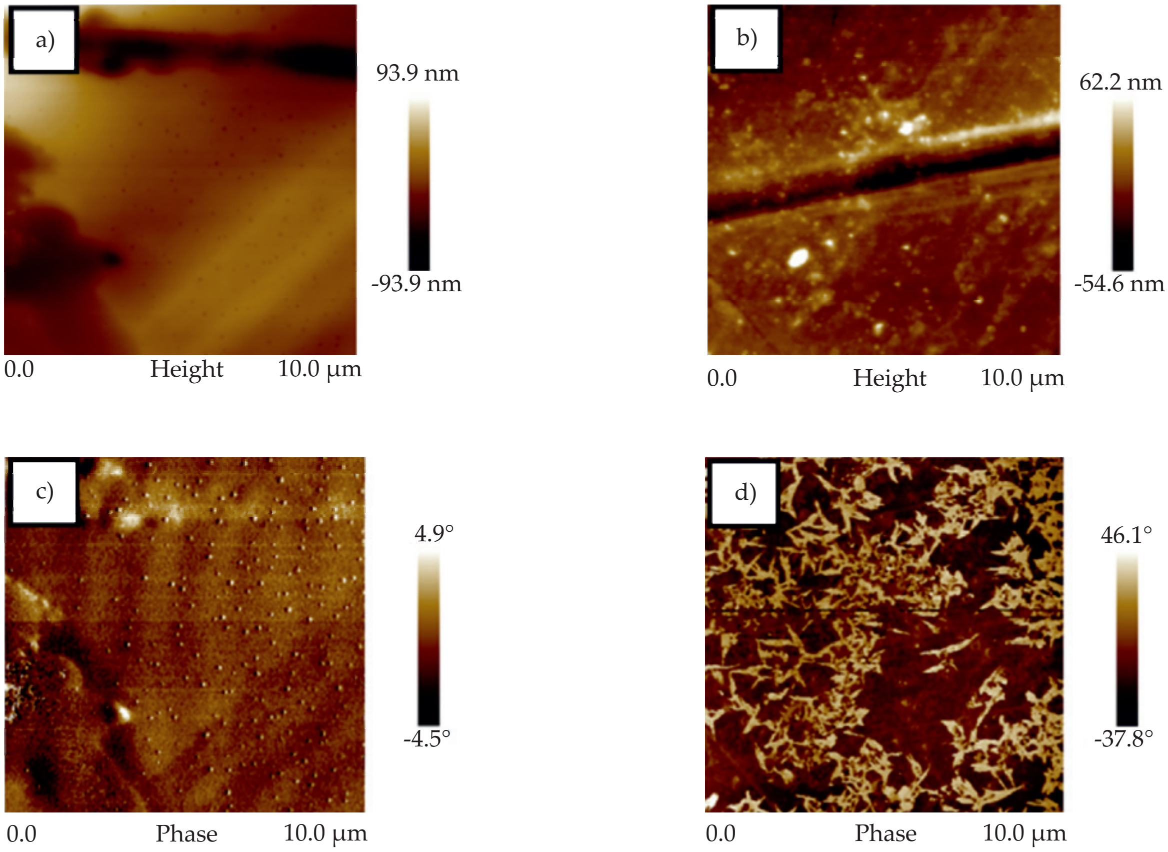

Fig. 6. AFM images showing the topography and phase difference of the mesh surfaces of unmodified (a, c) and modified (b, d) polymer composition

guished, *i.e.*, dark-brown regions which originate from the polymer composition and light-brown regions which originate from the dispersed additives, characterized by regular shapes. The analysis of the cross-section indicates that the width of the composite fibers ranges from 0.10 to 0.20 μm. Furthermore, small agglomerates of combined fibers are also visible in the phase image with transverse dimension below 0.45 μm. On this basis, it can be confirmed that the applied homogenization process and the technology of obtaining impregnated meshes with the addition of CLS allow for their equal distribution in the polymer composition.

CONCLUSIONS

In the framework of this study, CLS was used as an addition for crosslinking of fibrous composites with a phenol-formaldehyde resin. On the basis of the physicochemical studies, it can be conducted that the average particle size of the used biopolymer was 18.6 μm. It is also characterized by 66 % mass loss during heating up to 1000 °C as well as a small BET surface area value of 0.9 m^2/g. The use of CLS as an environmentally friendly additive in phenol-formaldehyde resins contributed to the enhancement of mechanical properties of the final product. A notable increase of dynamic strength by approximately 15 % and shear stress by approximately 66 % compared to composites with unmodified resin was achieved. Additionally, based on the scanning electron microscopy and atomic force microscopy results, it has been established that the used process of homogenization and the technology of obtaining impregnated meshes with the addition of calcium lignosulfonate allow for their equal distribution in the polymer composition.

This work was supported by the National Science Centre Poland under research project No. DEC-2014/15/B/ST8/02321.

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Received 2 X 2017.

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