

**WATER ASSISTED INTERACTION BETWEEN  
NANOSILICA, NANOSILVER AND WOOD FIBER**

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**ABSTRACT**

The interactions between wood and nano-ceramic and nano-metallic particles was examined in the microscopic scale. The particles observed differed in their shapes and physicochemical structures. They were spherical amorphous nano-SiO<sub>2</sub> and Ag nano-crystallites, wood was in the form of crystalline-amorphous micron-sized pine wood fibers. It appeared that the small component of the system, which in our experiments was H<sub>2</sub>O, may play a substantial role in the binding processes, in particular the adhesion of SiO<sub>2</sub> to wood. It may be explained as a result of a surface termination of nano-SiO<sub>2</sub> and hydrogen bond formation with cellulose what occurred only in the presence of H<sub>2</sub>O. The SiO<sub>2</sub> particles, mixed with wood fibers in water, covered tightly wood cell walls and during heating formed a vitreous protective shell. Preliminary investigations of fire resistance proved diminished total heat release for wood fibers – nano SiO<sub>2</sub> blends.

**KEYWORDS:** Nanosilica, nanosilver, wood fiber, fire resistance.

**INTRODUCTION**

Wood as a selfassembling nano-sized molecular structure is very interesting for nano-technological applications. At the international Technology Summit II, held in the USA in 2004,

an idea arose that wood industry ought to be modernized by taking advantage of nano-technology and the document “Nanotechnology for the Forest Products Industry-Vision and Technology Road Map” was produced (Wegner and Jones 2005, Moon et al. 2006). One of the six areas prioritized in this road map consists of modifying nanoscale surfaces and developing inorganic-organic nanocomposites. Wood-organic polymer composites have long been known and used. A new trend concerns particle- composites i.e. wood nano-particles and mineral nano-particles (clay, silica) bonded with a polymer or cement (Tetsuo 1996). New trends concerning composites made of wood-fibres and mineral nano particles (clay, silic.) bonded with a polymer or cement (Tetsuo 1996) and modification of wood with nano-silicon compound have been also earlier published (Mai and Militz 2004). Experiments with introducing SiO<sub>2</sub> nano-particles into wood by the in-statu-nascendi method during a sol-gel process has shown that these particles crystallize on the surfaces of the wood cells giving them good anti-flammable properties (Furuno et al. 1997, Miyafuji and Saka 2001).

In view of the specific properties of nano-sized matter, the interactions taking place between and with the nano-particles may differ essentially from those observed between bulk materials. The objective of this study was to examine the interactions that occur between the nano-particles of materials of the different types: a metal and a non-organic oxide and ligno-cellulose (wood fiber), without the participation of an external mechanical force that is active in Scanning Force Microscope, or electrical force that is occurring in electrophoresis.

## MATERIAL AND METHODS

The materials under examination were prepared from nano-Ag powder (Amepox-Microelectronics Ltd. Łódź, Poland) produced by silvercompounds – thermal decomposition, nano SiO<sub>2</sub> powder (Orisil Ltd., Kalush, Ukraine) produced by SiCl<sub>4</sub> hydrolysis in flame and pine wood fibers (Pfleiderer SA Poland) industrial produced fibers with defibrator at T = 175–193 °C. The electron properties of the materials in bulk form are given in Tab. 1.

*Tab. 1. Electron properties of the materials in the bulk form*

Solid	Bandgap (eV)	Electron work function (eV)	Ionisation energy (eV)
Ag	-	4.4	7.5
SiO <sub>2</sub>	8.9	9.0	11.7

The Zeta potentials of investigated particles in H<sub>2</sub>O were measured using Laser Doppler Electrophoresis method (Malvern Instruments, Herrenberg Germany).

The sizes and shapes of the particles and their blends were observed in an ultra-high resolution scanning electron microscope Hitachi S5500 operated in the reflected and transmission modes. While wood and SiO<sub>2</sub> are dielectric the samples were evaporated with Os to a thickness small enough to create continuous electric conducting layer.

The particles composition samples were produced by mixing the particles in water in weight proportions up to 1:1 and subjecting them to an ultrasonic treatment in a VCX 750 Sonic disintegrator at the temperature T ≤ 25 °C for 15 min. The mixture was afterwards dried freely in air so it formed plates of thickness d ≈ 2mm.

The chemical composition of the pine wood fibers, nano-SiO<sub>2</sub> and their mixtures with and without participation of H<sub>2</sub>O was analysed by FTIR spectroscopy (Genesis Mattson) using the KBr pellet method.

The preliminary tests of fire resistance of the produced composites were performed with Cone Calorimeter in air at the thermal radiation flow of the intensity 50 kW.m<sup>-2</sup>. The influence of high temperature impulse heating on the composites microstructure was examined with the use of defocused CO<sub>2</sub> Synrad laser beam of  $\lambda$  10,64  $\mu$ m, of power 240 W and of frequency 20 kHz.

## RESULTS AND DISCUSSION

The size distribution of nano-SiO<sub>2</sub> and nano-Ag is shown in Fig. 1.

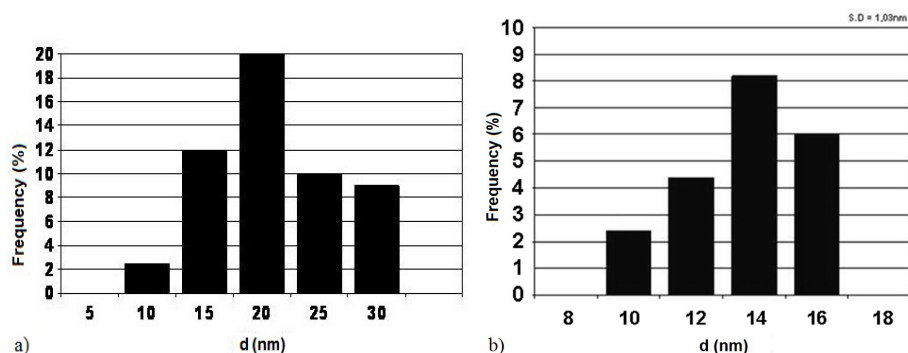


Fig. 1: Size distribution a) nano-Ag, b) nano-SiO<sub>2</sub>

The appearances of the nano-particles are shown in Figs. 2, 3. They were deposited on the SEM/TEM mesh from a hydrosol droplet. As can be seen, the nano-Ag particles were the smallest and not linked with one another. The SiO<sub>2</sub> nano-particles were mutually linked with stable bridges. This was confirmed by the observed fact that it was only SiO<sub>2</sub> particles which were able to form hydro-gels. The wood fiber in “pristine” state is shown in Fig. 4.

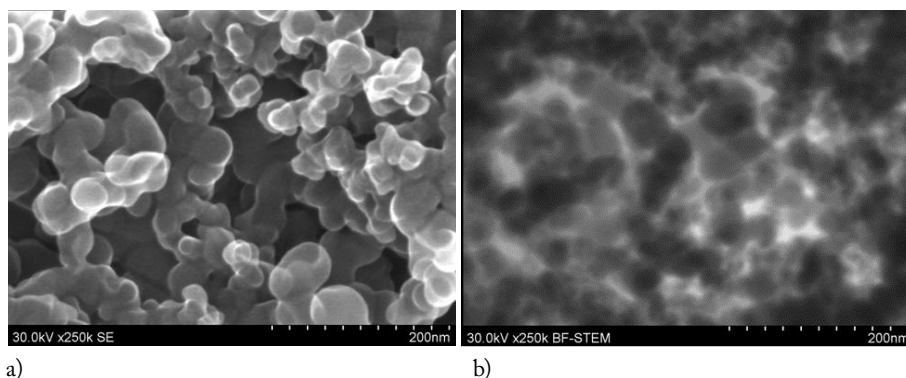


Fig. 2: SiO<sub>2</sub> particles a) scanning image b) transmission image

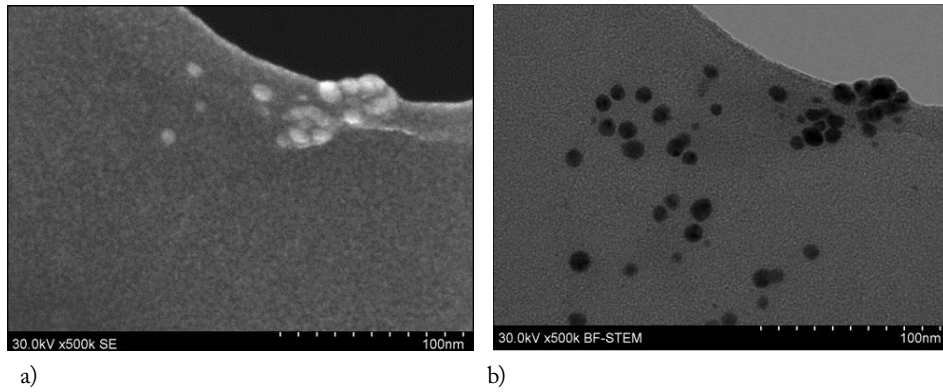


Fig. 3: Ag particles a) scanning image b) transmission image

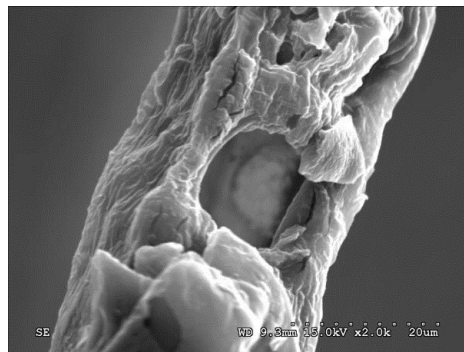


Fig. 4: Pine wood fiber

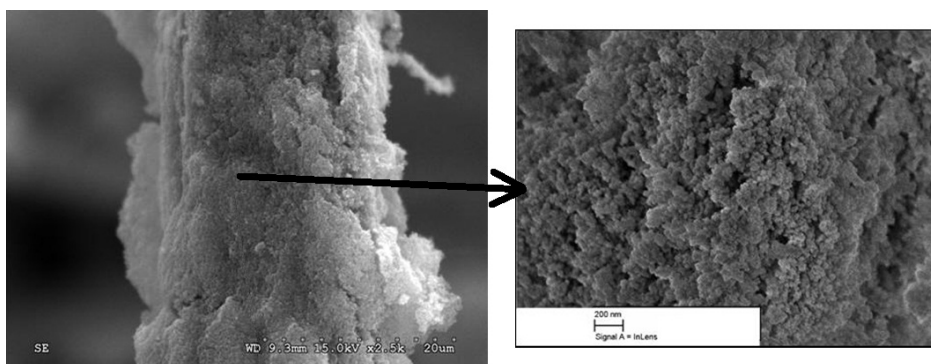


Fig. 5: Wood fibers with SiO<sub>2</sub> particles (5:1) in water mixed

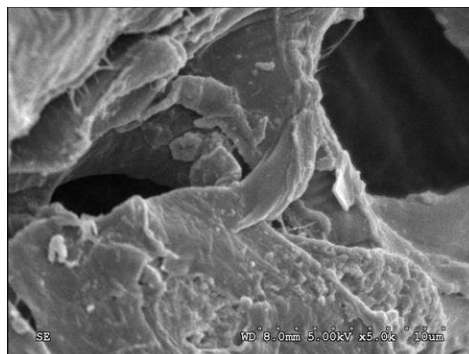


Fig. 6: Wood fibers with Ag particles (5:1) in water mixed

The results of in water-mixing the nano-non-organic particles and the wood fiber are shown in Fig. 5, 6, 7 successively: wood with SiO<sub>2</sub>, wood with Ag, SiO<sub>2</sub> with Ag. We can see diametrical differences between SiO<sub>2</sub> and Ag. The SiO<sub>2</sub> nano-particles clung to the surface of the wood cell walls which evidenced good adhesion between these two materials. The nano-Ag particles did not adhere at all to the ligno-cellulose and hence it was even difficult to prepare a sample with these particles present on the wood cell surface. The nano-Ag and nano-SiO<sub>2</sub> particles showed no mutual adhesion.

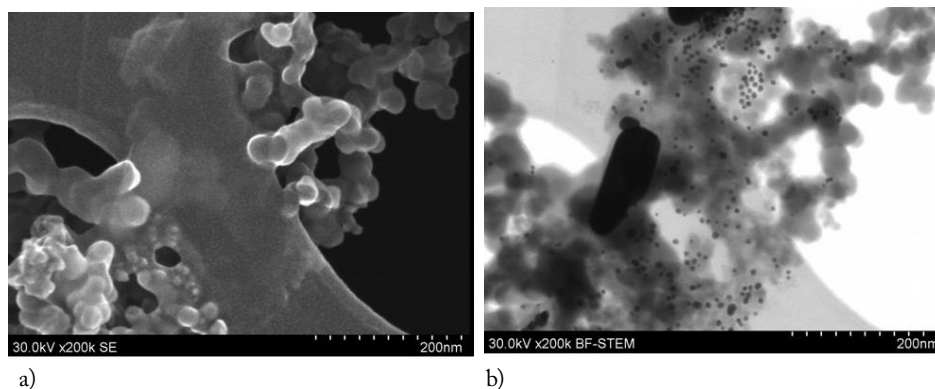


Fig. 7: SiO<sub>2</sub> with Ag particles in water mixed a) scanning image b) transmission image

In order to bring better the role of water into prominence a dry-mixed nano-SiO<sub>2</sub> with wood fibers was also investigated in a form of composition sample. The comparison of dry-mixed and in water mixed products are presented in Fig. 5 and Fig. 8. As can be seen the adhesion of SiO<sub>2</sub> to ligno-cellulose is much weaker when mixed without water.

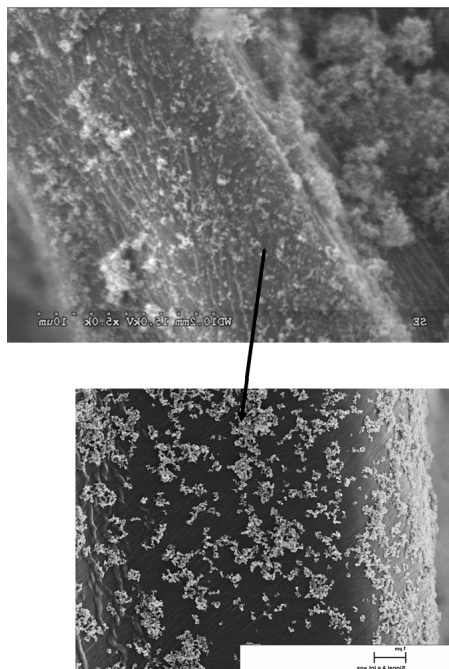
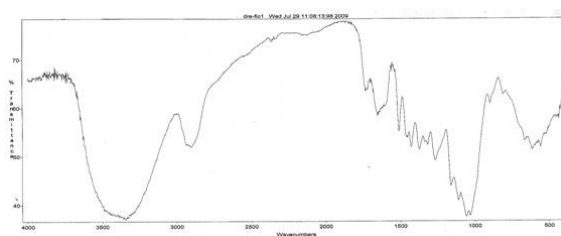


Fig. 8: Wood fibers with SiO<sub>2</sub> particles (5:1) dry mixed

The infra red spectra for silica, wood fiber, both particles dry-mixed and in water mixed in the same quantities are presented in Fig. 9. The spectrum for dry-mixed products represented only an additive sum of the spectra for both ingredients. In the spectrum of in-water-mixed ingredients, the peak about 800 cm<sup>-1</sup>, derived from Si-O bending mode and the peak about 1120 cm<sup>-1</sup>, derived from Si-O asymmetric stretching mode were strongly decreased. Only the peak about 480 cm<sup>-1</sup>, derived from rocking mode was unchanged. This observation may indicate the chemisorption of SiO<sub>2</sub> influenced by water.



a)

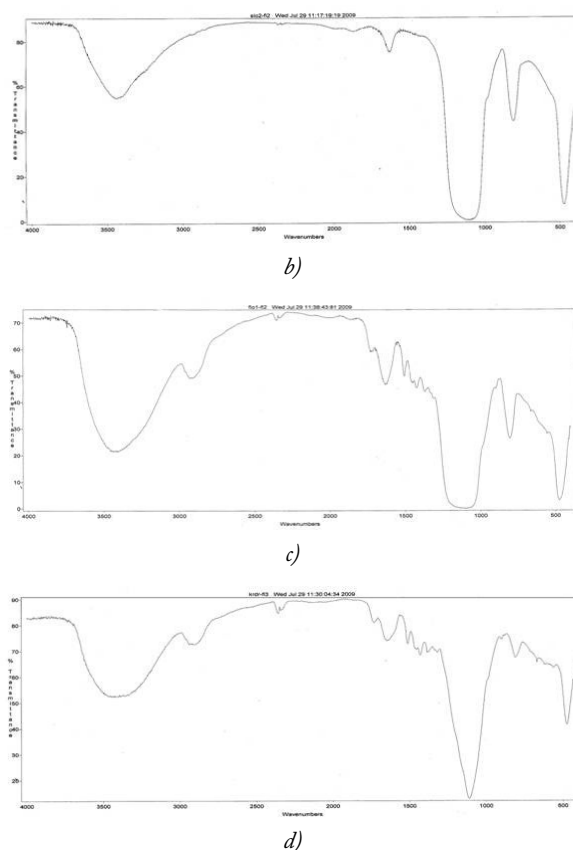


Fig. 9: I.R. spectra a) silica b) silica with wood fiber dry mixed c) silica with wood fiber in water mixed d) wood fibers

The Zeta potentials of examined particles in  $H_2O$  presented in Tab. 2 suggest that the interaction between wood and nano Ag should be stronger than with nano-  $SiO_2$ . The electron properties of the materials examined (Tab. 1) also suggest that the adhesion of nano-Ag, irrespective of whether mutual, to  $SiO_2$  or to ligno-cellulose, should be strong. Significantly the examinations reported in ref. (Ohmae 1997) have shown that between nano-Au (tip) and an Au surface there is a strong bond, which however is markedly weakened after contact with oxygen.

Tab. 2: Zeta potentials in water

Particel	Ag	$SiO_2$	Wood fiber
Z (mV)	-9.2	-17.6	-16.3

The only explanation of the water influence is that the surfaces of all the nano-particles in a state of a hydrosol were terminated with H or OH which had to alter totally their electron affinity. This created conditions favorable for the chemisorption of  $SiO_2$  with cellulose and the 'repulsion' of Ag. The "Coulomb" interactions between the quasi-free conduction electrons in

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solids (Lifschitz 1956, Inglesfield 1976) were surpassed in strength by the energy of chemical bonds between the atoms of the surface. For example the bonds could be hydrogen bonds as illustrated in Fig. 10.

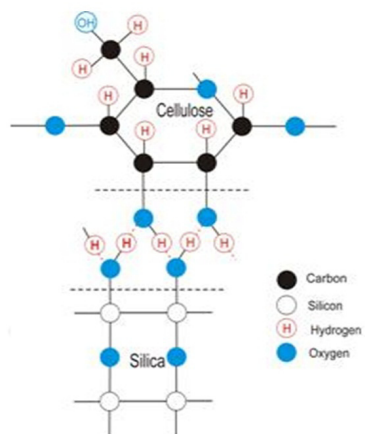


Fig. 10: Cellulose-silica-water bonds

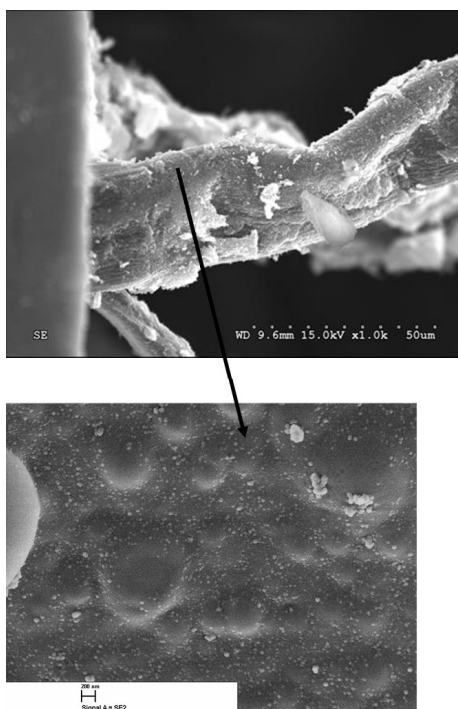


Fig. 11: Wood fiber with SiO<sub>2</sub> coated after heating by a CO<sub>2</sub> laser beam



The excellent adhesion – chemisorption – of nano-SiO<sub>2</sub> to the walls of the wood cells can well explain the anti-flammable properties of silica reported in (Miyafuji and Saka 2001). In order to examine this effect, a dried and pressed together product of in water mixing nano-SiO<sub>2</sub> with wood cells at a weight ratio of 1:5 was subjected to heating by a laser beam. As can be seen in Fig. 11, silica present on the surfaces of the ligno-cellulosic walls has been vitrified forming inflammable armour that protects the wooden cells. The results of preliminary tests of fire retardance of nano-SiO<sub>2</sub>-wood cell composite are presented in Tab. 3. As can be seen the total heat release is diminished due to nano SiO<sub>2</sub> addition to the wooden material.

Tab. 3: Fire testing results

Specimen	Total heat release (MJ.m <sup>-2</sup> )	Time to ignition (s)	Time to flameout (s)
A-wood fibers	42.64	22	340
B-wood fibers + nano SiO <sub>2</sub>	36.57	22	310

## CONCLUSIONS

In the system examined, which was composed of SiO<sub>2</sub> nano-particles, Ag nano-particles and sub-micron wood fibers (ligno-cellulose) particles, SiO<sub>2</sub> showed strong adhesion to the wood particles whereas Ag particles did not adhere to any of the system components. The spontaneous binding of some components of the particle mixture, which resulted in the formation of a common structure that constituted the origin of a new composite material, can be regarded as a kind of self-assembly. In the system examined this only applies to SiO<sub>2</sub> and only in the presence of H<sub>2</sub>O.

The water-induced surface termination seems to be the main determinant of the interactions between the SiO<sub>2</sub> nano-particles and wood. The small, molecular component of the system, which in our case is H<sub>2</sub>O, may therefore play a substantial role in all the binding processes that proceed with participation of the nano-particles.

## ACKNOWLEDGMENTS

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