WATER GLASS AS HYDROPHOBIC AND FLAME RETARDANT ADDITIVE FOR NATURAL FIBER REINFORCED COMPOSITES

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ABSTRACT

Within this research work natural fiber reinforced composites with high natural fiber content between 70 wt.-% and 80 wt.-% and a thermoset polymer system on acrylic basis will be treated with environment-friendly sodium silicates (water glass). Water glass is applied in other fields as binder, hydrophobic system, and flame retardant system. The new matrix system will be applied by binder dispersion in a dipping process on the natural fiber mats. Processing conditions such as curing temperatures and times of this system should be comparable to those of a standard acrylic resin system. Mechanical characteristics and the water absorption of manufactured components were examined. The effectiveness of the flame retardant effect of water glass was also tested. This paper describes the first results of the research project.

1 INTRODUCTION

Natural fiber reinforced composites have established themselves due to their good mechanical properties, their low production costs, and the good environmental properties. Due to their low density (approx. 1.5 g/cm³), natural fibers have a very good lightweight potential [1]. Other features of natural fiber composites are the very good process related and acoustic properties. Additional advantages like good life cycle assessment and easier processability compared to glass fiber materials can also be taken into account. Nevertheless, their potential use is greatly reduced because of their high hydrophility and their low chemical compatibility with hydrophobic polymers. This leads to elevated water absorption of natural fiber reinforced composites that can have a significant effect on the mechanical properties of the composites [2, 3]. Tensile properties of natural fiber composites with a high fiber fraction can decrease up to 65 % after a water immersion of 24 hours. In order to improve the adhesion between the fiber and the matrix for both thermoplastic and thermoset compounds and to reduce the water absorption coupling agents like silane can be added [4, 5].

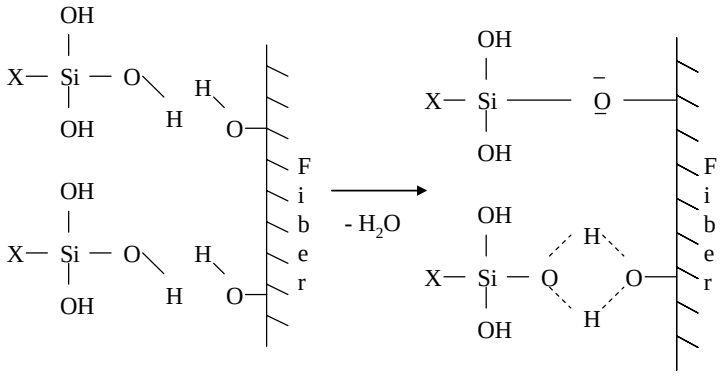


Figure 1: Bonds between natural fibers and silane groups

One other big disadvantage of natural fiber reinforced composites is their high flammability that limits their application in many fields.

The goal of this project is to reduce both the water absorption and high flammability of natural fiber reinforced composites with high natural fiber contents between 70 wt.-% and 80 wt% by a treatment of the matrix (polymer system on acrylic basis) with environment-friendly sodium silicates (water glass) in an economical processing method.

2 WATER GLASS

Sodium silicates belong to the family of soluble silicates, also known as water glasses that represent one of the most versatile inorganic chemicals available. Sodium silicates are manufactured by melting a mixture of soda and quartz sand. Soluble silicate (water glass) is a viscous liquid with about 21 to 34 wt.-% SiO_2 and 6 to 18 wt.-% Na_2O [6, 7]. Water glass reacts in aqueous solutions to polysilicates (Figure 2).

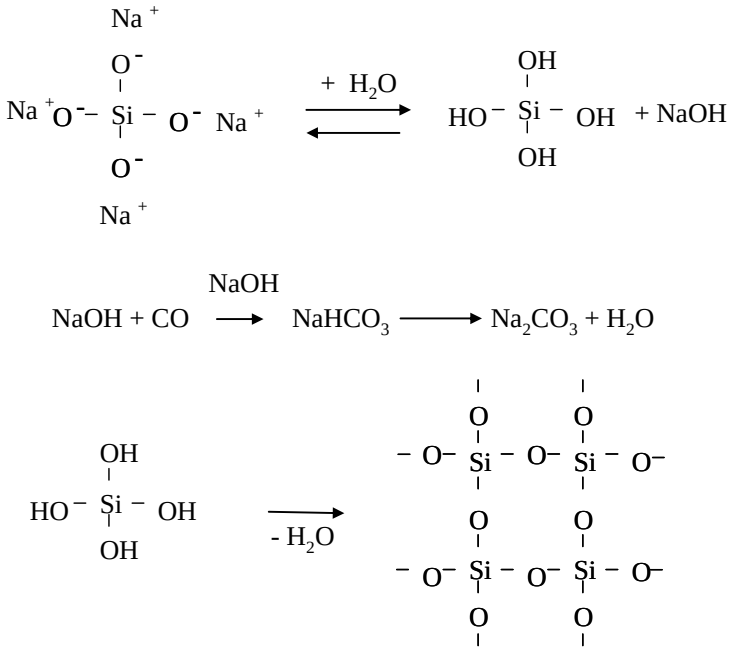


Figure 2: Polycondensation of water glass

Due to the similarity between silane and polycondensated water glass, it can be assumed that the polymerized water glass can act as a coupling agent between the fibers and the matrix (Fig. 3).

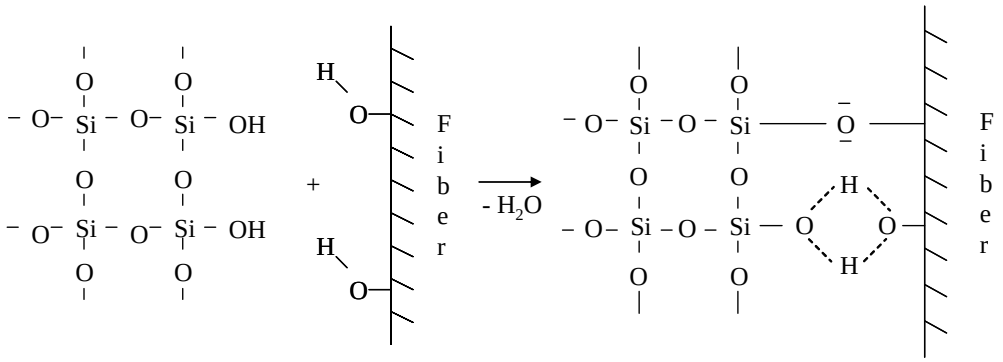


Figure 3: Theoretical model for the surface between water glass and natural fibers

Sodium silicates are used as cement for glass, pottery, and stoneware; for fireproofing paper, wood, cement, and other substances; for fixing pigments in paintings and cloth printing, flux binder for welding rods, etc.

3 COMPATIBILTY OF THE BINDER SYSTEMS

As polymeric system a thermoset polymer system on acrylic basis was used. The binder is based on a polycarboxylic acid and a polyalcohol. At temperatures above 130 °C, the modified polycarboxylic acid reacts with the polyalcohol to form polyester. After the curing process, the material has thermoset properties.

Different percentage of sodium water glass was added to the thermoset matrix to prove the compatibility of the polymeric system with water glass. The stability check of the modified systems was carried out through viscosity measurements. While for a mixture ratio up to 30 wt.-% of water glass the viscosity increases from 10 up to 50 Pa*s, the mixture system with 40 wt.-% water glass reaches a viscosity of approx. 1000 Pa*s at the end of the test time. Mixtures with 50 wt.-% water glass reach very quickly high viscosities up to approx. 25000 Pa*s (Fig. 4) impeding an adequate impregnation of the fiber mats with the matrix system.

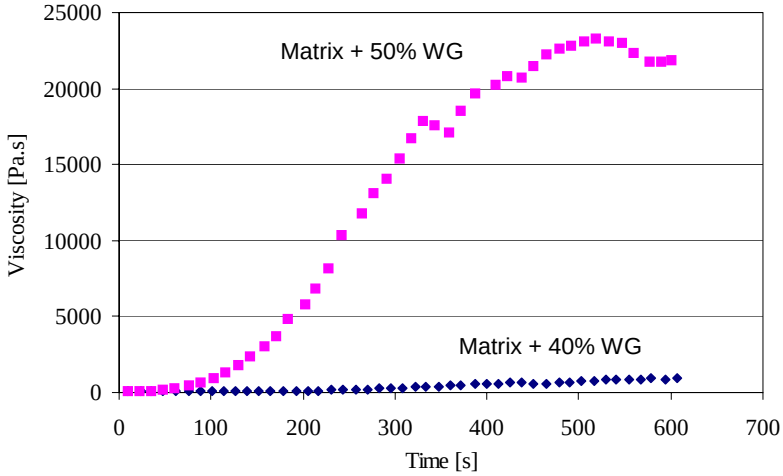


Figure 4: Viscosity of the matrix system mixed with water glass

Therefore, impregnation tests of the natural fiber with the modified matrix systems were carried out with maximal 30 wt.-% water glass mixed in the thermoset system.

4 IMPREGNATION, PRESS PROCESS, AND TESTING

Needled natural fiber mats were impregnated with the modified matrix systems in a dipping process. Within this process natural fiber mats were immersed in the matrix in a fluid form. Afterwards the excess of the absorbed matrix was compressed between two rollers under pressure. Then the impregnated mats were dried in a drying chamber until a rest humidity in prepreg of approx. 15% was reached.

For these trials, kenaf-hemp fiber (70:30) mats with an area weight of approx. 1380 g/m^2 were used. The thermoset matrix system was modified with 10 wt.-%, 20 wt.-%, and 30 wt.-% sodium water glass (Table 1). The natural fiber mats were therewith impregnated. The dipping process was so far optimized that the polymer quantity could be adjusted to approx. 30 wt.-%. The impregnated mats were press molded in a conventional hot press without any additional conditioning at 160 °C for 100 sec at 20 bar.

As it appears in Table 1 the matrix quantity in the composite decreases by increasing the water glass amount. This tendency can be probably explained by an interference of the reaction between polycarboxylic acid and the polyalcohol to form polyester with a reaction of one or even both matrix components with water glass inhibiting the generation of the polyester system. Alcohols and acids upon other molecules that do not react to polyester will be evaporated under the high press temperature. It must also be indicated

that the pressed plates with a water glass content of 30 wt.-% exhibited almost no rigidity.

Table 1: Modified matrix systems

Material	Polymer matrix [%]	Sodium water glass [%]	Composite's matrix quantity [%]
1	100	0	32 ± 2
2	90	10	27 ± 2
3	80	20	26 ± 2
4	70	30	24 ± 1
5	0	100	30 ± 2

After curing tensile tests were carried out at room temperature to determine the mechanical properties of the composites. Furthermore water absorption tests were performance to analyze the flame retardant effect of water glass on the natural fiber composites fire testing categorization according to DIN 53438. The used European standards and the test parameters are specified in Table 2.

Table 2: Test procedures

Test	Standard	Geometry	Parameter
Tensile test	DIN EN ISO 527-4	Type 2	Velocity: 2 mm/min
Water absorption	DIN EN ISO	50 x 50 mm	24 h under water
Fire testing	DIN 53438, part 2	190 x 90 mm	15 s flame, test ends after 20 s

5 RESULTS OF THE CHARACTERIZATION

5.1 Mechanical characterization and water absorption

To characterize the mechanical properties of the components' tensile tests were carried out (Fig. 5). The results of the mechanical tests show that tensile properties decrease by increasing the sodium water glass percent in the matrix system.

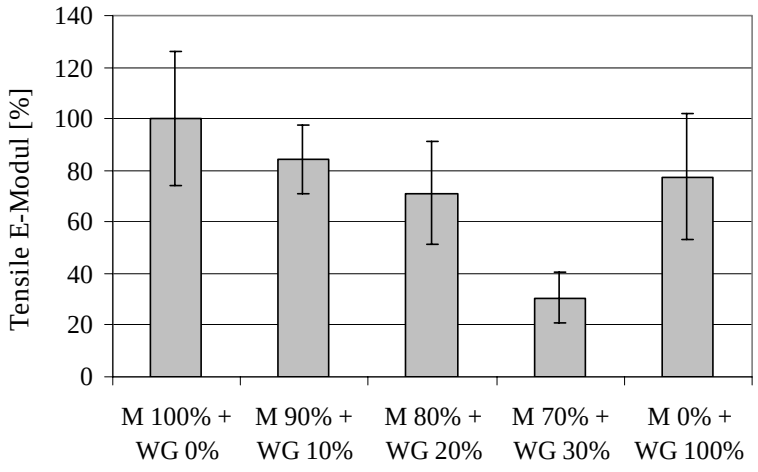


Figure 5: Dependence of the tensile properties of the composites with the water glass content

For the water absorption tests a new water glass type specially developed as hydrophobic additive for acrylic systems was tested. This water glass was mixed with the matrix system and applied on the natural fiber mats in the same way as yet. The amount of water glass represents 5 wt.-% of the matrix which means approx. 1.5 wt.-% related to the composite. The water absorption shows a clearly dependence of the water glass amount in the compound and it increases the higher the water glass fraction in the matrix system (Fig. 6).

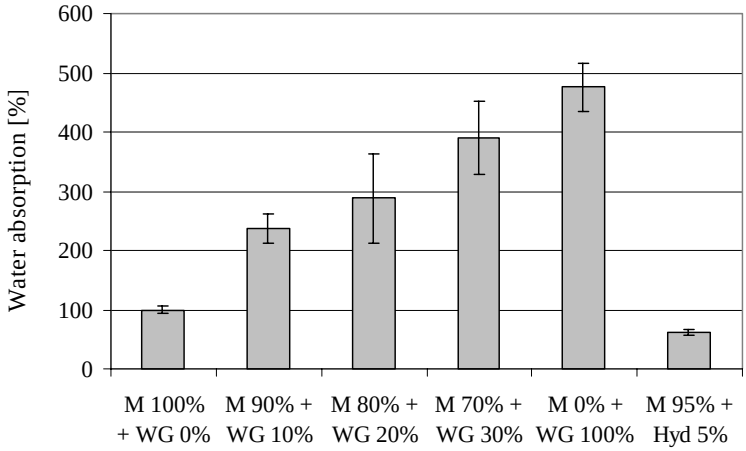


Figure 6: Dependence of the water absorption of the composites with the water glass content

While composites with just thermoset matrix show a water absorption value of approx. 50 wt.-%, the compounds with water glass exhibit water absorption up to 190 wt.-%. Press plates that were impregnated just with sodium water glass show water absorption values between 200 wt.-% and 250 wt.-%. Just the mixture between the thermoset matrix and the water glass especially developed as hydrophobic system in acrylic systems reduce considerable the water absorption of the composites.

5.2 Morphologically analysis

The scanning electron microscopic (SEM) analysis of the composites surfaces shows that water glass posses a very brittle structure (Fig. 7a). A very open surface can be also perceived (Fig. 7b), which explains the high water absorption in the composite.

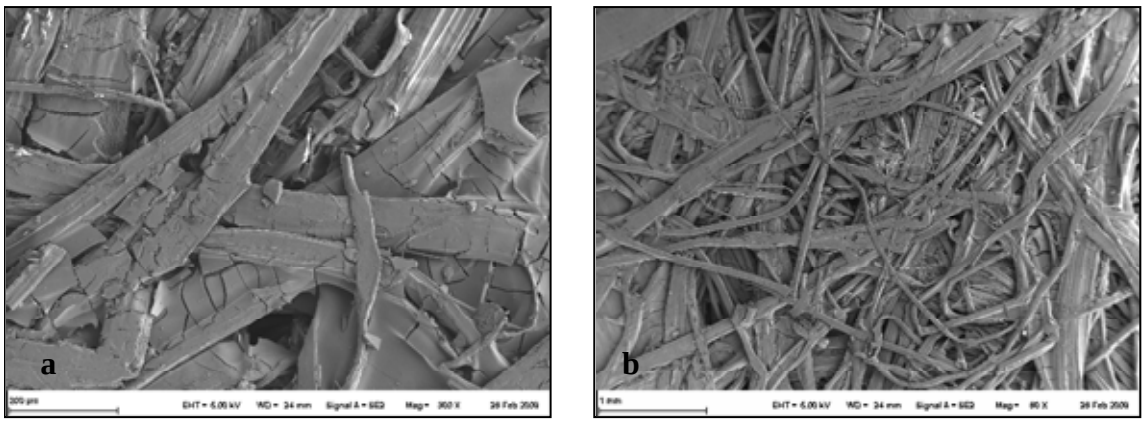


Figure 7: SEM-pictures of the natural fiber mats impregnated with sodium water glass

An explication for the decreasing of the mechanical properties of the composites can be explained considering the SEM analysis of the samples. Figure 8 shows the surface of the natural fiber mats that were impregnated just with the thermoset matrix system and with thermoset and sodium water glass modified matrix. By increasing the amount of

water glass in the matrix system less polymer can be observed in the composite's surface. This is also a sign that water glass probably interferes in the curing process of the polyester and components like alcohols and acids evaporate due to the high temperature during the press process.

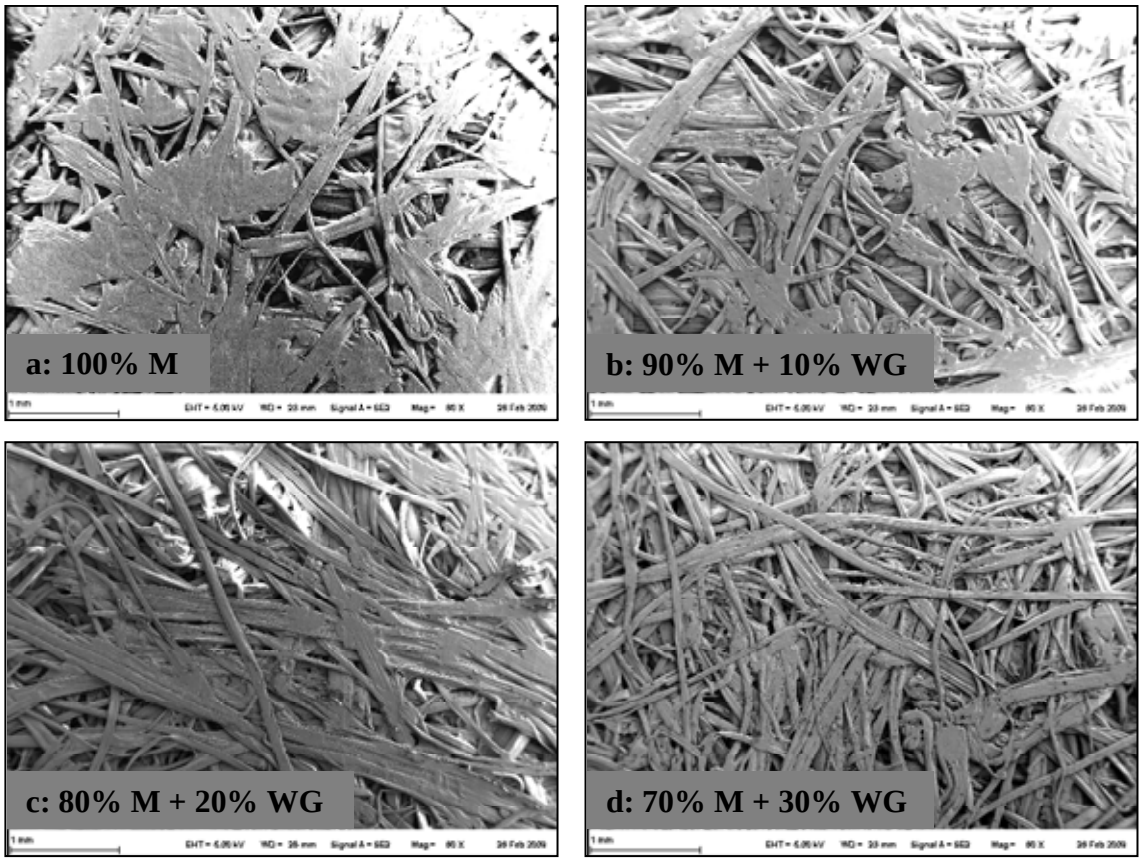


Figure 8: SEM-pictures of the composites' surface: (a) 100 % matrix; (b) 90 % matrix + 10 % water glass; (c) 80 % matrix + 20 % water glass; (d) 70 % matrix + 30 % water glass

A change on the polymer's structure is also visible within the SEM-analysis. While the thermoset polymer shows a smooth, homogeneous surface (Fig. 9a), the compound with 30 wt.-% water glass exhibits an irregular structure with many air gaps (Fig. 9b).

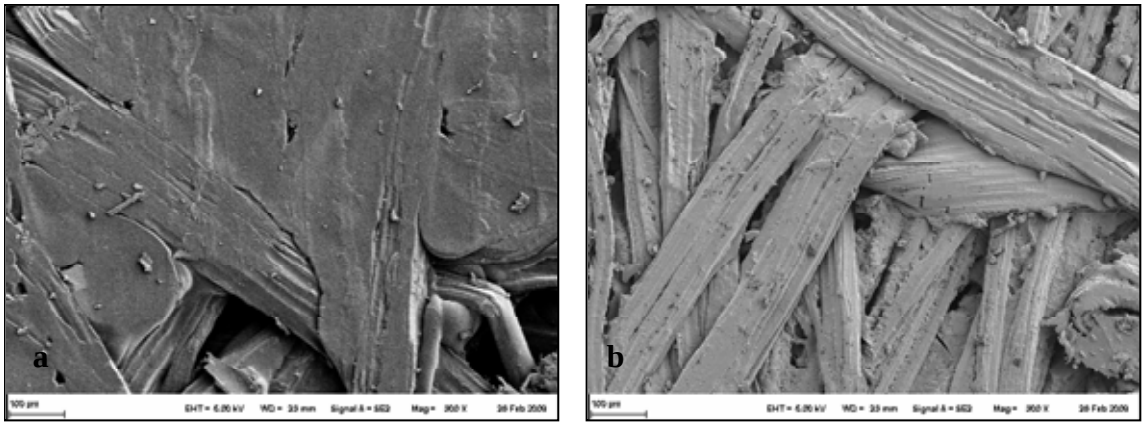


Figure 9: Details of the composites' surfaces; (a) 100 % matrix; (b) 70 % matrix + 30 % water glass

This affects negatively the fiber matrix bonding and therefore the properties of the natural fiber composite.

5.3 Flame retardant efficiency of water glass

According to DIN 53438, part one, 190 x 90 mm test plates with a measuring flame front of 150 mm were burnt at the rough edge for 15 s (Fig. 10). After this time the flame was removed from the testing plate. The test ran 5 more seconds and after 20 seconds in total it was stopped and the specimens evaluated.

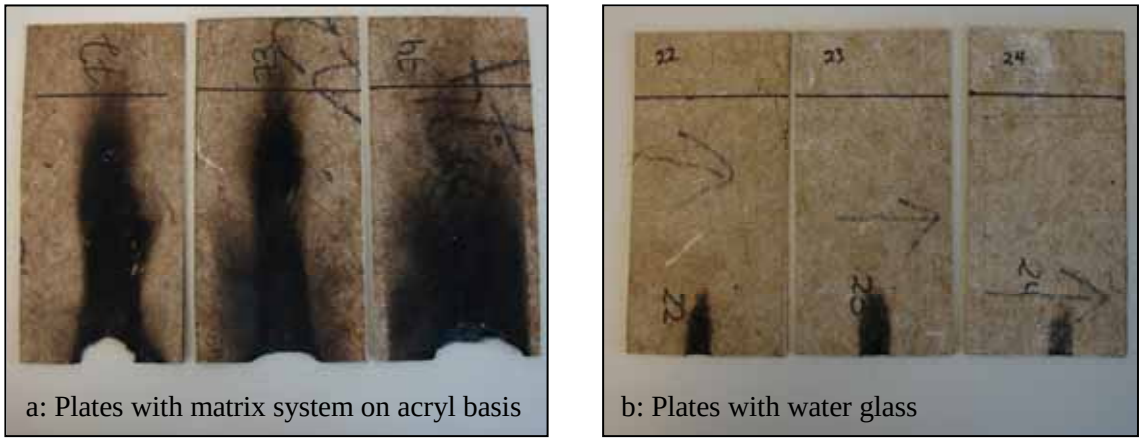
Figure 10: Natural fiber composite by fire testing

The characterization takes place following the next categories specified in Table 3.

Table 3: Fire testing categories according to DIN 53438 part 2

Category	Specifications
K1	The measuring line will not be reached. The flame extinguishes by itself
K2	The flame front reaches the measuring line after 20 and more seconds
K3	The flame front reaches the measuring line within 20 seconds

The flame front of the composite impregnated with the thermoset system reaches within 20 seconds the measure line of 150 mm (Fig. 11a) and is therefore classified in the last category K3. By contrast the composites impregnated just with water glass fall in the best category K1 because the flame extinguishes by itself when the flame is taken away from the specimens (Fig. 11b).



a: Plates with matrix system on acryl basis

b: Plates with water glass

Figure 11: Test plates with thermoset matrix (a) and water glass (b) after 20 seconds burning time

All other tested variations with water glass show a positive trend and fall in the middle category K2. The flame front does not reach the measure line of 150 mm within the

testing 20 seconds showing a clearly smaller flame than with just the thermoset material. The more water glass amount in the compound the better the flame retardant efficiency and the lower the flame front reached within the test time (Fig. 12).

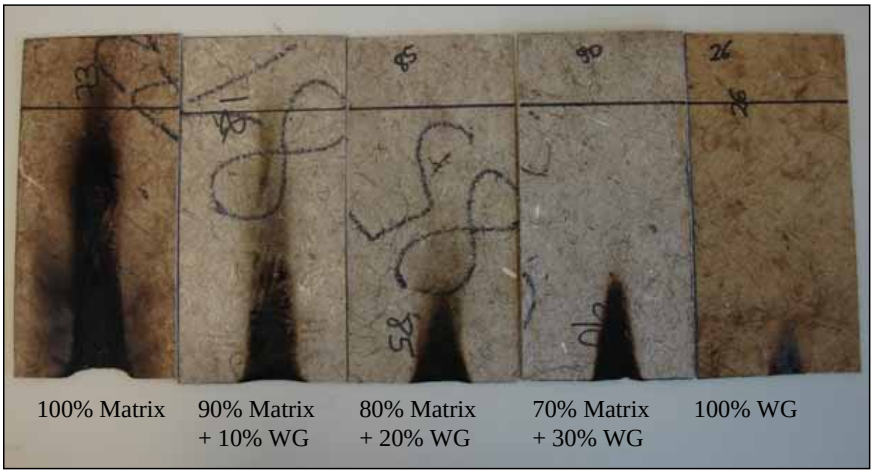


Figure 12: Test results of the fire testing after 20 s burning time

The compound impregnated with matrix and hydrophobic system (the only tested material which reduced the water absorption) shows during the fire testing a similar behavior like the natural fiber mats impregnated with a pure thermoset system and burnt during the 20 second test time.

5.4 EDX analysis

EDX analysis (Energy Dispersive X-Ray Analysis) is a technique used for identifying the elemental composition of a sample. The EDX analysis system works as an integrated feature of a scanning electron microscope (SEM). During EDX analysis an electron beam strikes the surface of the sample inside the scanning electron microscope. The energy of the beam is 120 keV. This causes X-rays to be emitted. The energy of the X-rays emitted depends on the material under examination. The bombarding electrons collide with the specimen atoms' own electrons, knocking some of them off in the process. A position vacated by an ejected inner shell electron is eventually occupied by a higher-energy electron from an outer shell.

Within this research work EDX analysis was applied on the surfaces of the SEM-samples. By using this technique the composition of the compounds could be detected. Samples impregnated just with thermoset matrix showed only carbon and oxygen signals, the samples impregnated with sodium water glass showed a small peak for carbon and sodium, a middle signal for oxygen, and a significant signal for silicon (Fig. 13).

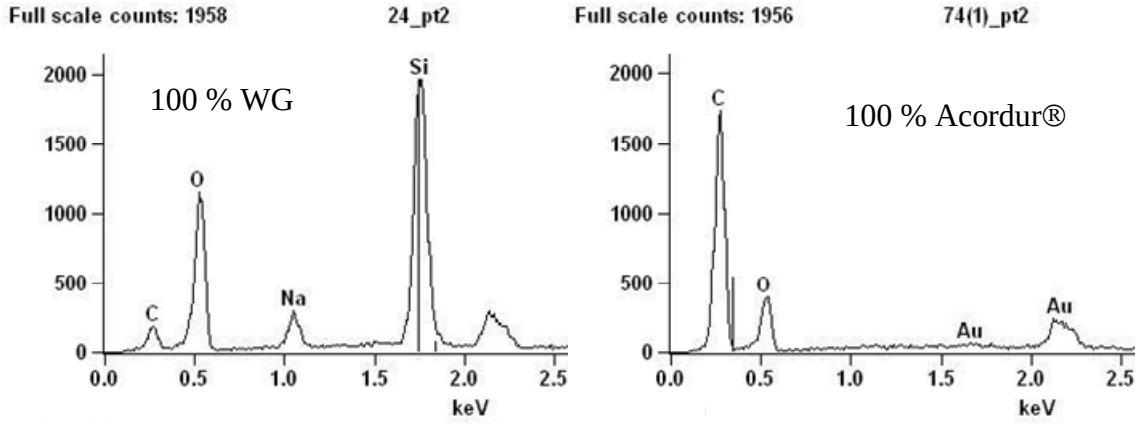


Figure 13: EDX analysis of natural fiber mats impregnated with pure Acrodur and pure water glass

It could be detected on the 10 wt.-%, 20 wt.-%, and 30 wt.-% water glass samples that water glass is evenly distributed on the entire sample (fiber and matrix) even on the fiber surfaces having apparently no polymer (Fig. 14). The presence of water glass on the complete surface explains the good behavior of the composite during the flame test.

It can also be perceived that the decreasing of the carbon signal takes place by increasing the water glass amount on the composite. This could again be a sign of the decreasing of the thermoset polymer amount in the composite due to the interference of water glass on the curing reaction of the polyester system.

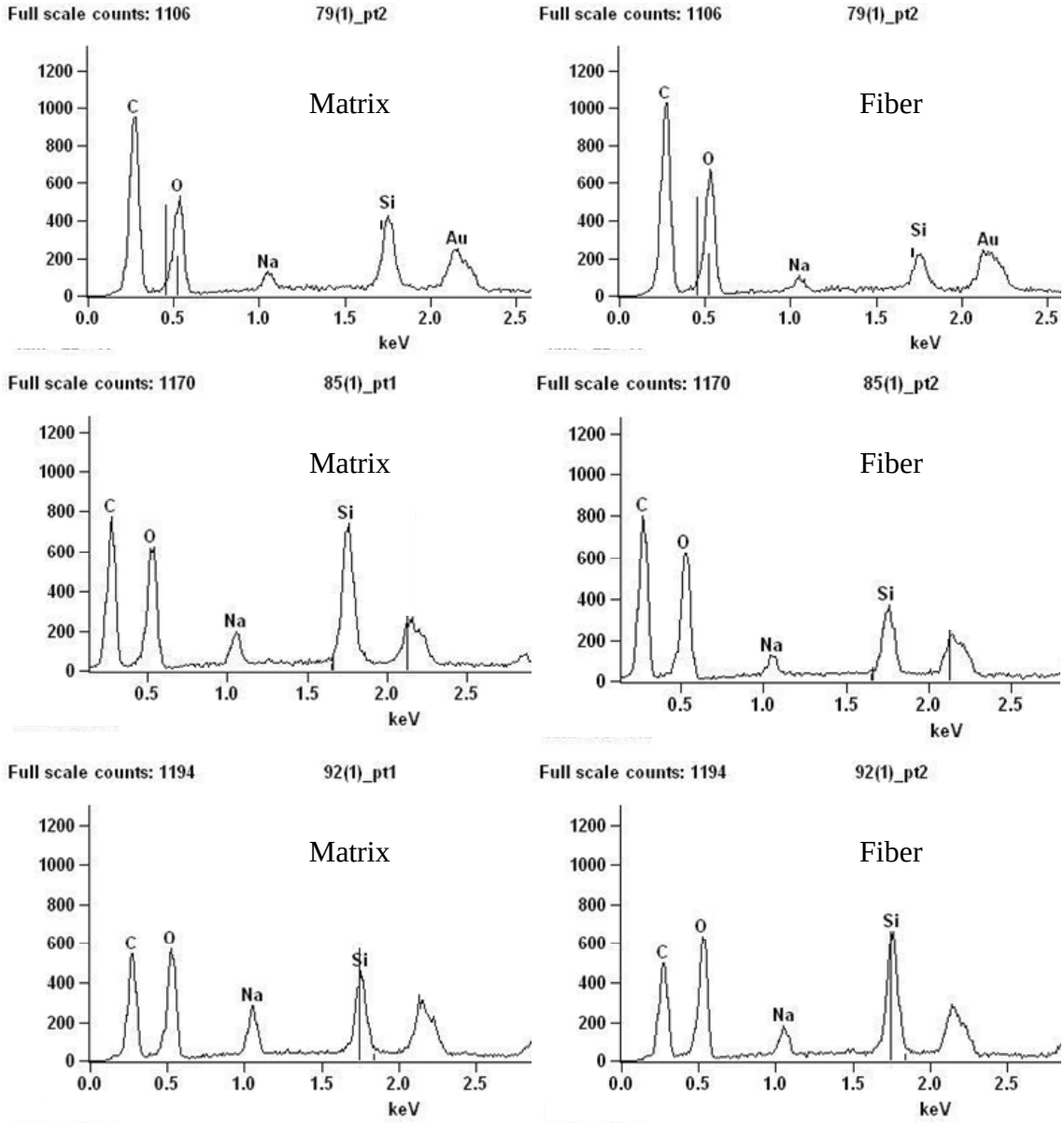


Figure 14: EDX analysis of natural fiber mats impregnated with a mixture of thermoset matrix and 10 wt.-%, 20 wt.-%, and 30 wt.-% water glass

6 CONCLUSIONS

Within this research work sodium water glass was used as environment friendly inorganic additive in a thermoset matrix system. Water glass should act in the composite as a binder as well as a hydrophobic system and a flame retardant system. Due to the chemical incompatibility of both systems an increasing of the mechanical properties or the water absorption of the systems could not be reached. By contrast these properties decrease by increasing the amount of water glass in compound probably due to the interference of water glass on the curing reaction of the polymer avoiding the generation

of the polyester. Just the adding of a water glass hydrophobic system showing a high compatibility with acrylic systems reduces the water absorption of the material up to 60 %. Very promising is therefore the flame retardant effectiveness of water glass on the natural fibers. The flame extinguished by itself during the fire testing when the flame was taken away from the tested plates at needled natural fiber mats impregnated with sodium water glass.

7 ACKNOWLEGMENTS

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