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COMPOSITES
THEORY AND
PRACTICE

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PRO-ADHESIVE SOL-GEL COATINGS FOR FIBERS IN EPOXY RESIN COMPOSITE MATERIALS

Inadequate adhesive strength of the reinforcing fibers to the matrix in composite materials causes their delamination, which reduces the bearing capacity and durability of the defected product, and in the case of pressure vessels or pipelines, may cause their depressurization. One of possible methods to improve the adhesive strength is to coat the reinforcing fibers by the sol-gel method with organosilica coatings. Silane coatings serve two purposes: 1) the film binds chemically to the surface of the glass fiber, 2) wetting is improved by an increased chemical affinity of the resin to the fiber. Carbon and aramid fibers are usually not coated in this manner, resulting in inferior adhesive properties. In this study, organosilica materials were obtained by the sol-gel method using various silica precursors: methyltrimethoxysilane (MtMOS), ethyltriethoxysilane (EtEOS) and tetramethoxysilane (TMOS). The materials were deposited on glass fiber and hybrid carbon/aramid fiber textiles, resulting in a change in the surface properties. The chemical structures were characterized by Raman spectroscopy, indicating the presence of groups characteristic for silica, as well as the presence of functional organic groups connected by silicon-carbon bonds. The surfaces of the coated fibers were observed by scanning electron microscopy (SEM), indicating undesirable fiber bonding by the coatings obtained using the MtMOS and TMOS precursors, while no such bonding was observed for the coating obtained using the EtEOS precursor. The wettability of the glass fibers by epoxy resin was measured using the electro-optical method, revealing that the coatings made of the MtMOS and TMOS mixture improved the wettability of the fibers with epoxy resin, facilitating adhesion.

Keywords: **sol-gel, organosilica coatings, glass fibers, carbon fibers, aramid fibers**

PROADHEZYJNE POKRYCIA ZOL-ŻELOWE NA WŁÓKNA W EPOKSYDOWYCH MATERIAŁACH KOMPOZYTOWYCH

Niedostateczna wytrzymałość adhezyjna połączenia włókien wzmacniających z matrycą (osnową) materiału kompozytowego prowadzi do delaminacji, powodujących redukcję zdolności do przenoszenia obciążeń oraz trwałości wyrobu, a w przypadku zbiorników ciśnieniowych i rurociągów może spowodować ich rozszczelnienie. Jedną z możliwych metod poprawy wytrzymałości adhezyjnej jest pokrywanie włókien wzmacniających metodą zol-żel powłokami organokrzemionkowymi. Warstwa silanowa wiąże się chemicznie (wiązaniami kowalencyjnymi Si-O) z powierzchnią włókien szklanych. Zwilżanie ulega poprawie dzięki większemu powinowactwu chemicznemu żywicy do włókien pokrytych niż niepokrytych. Lepsze zwilżanie poprawia powiązanie adhezyjne pomiędzy włóknami a matrycą (żywicą) ze względu na większą powierzchnię kontaktu pomiędzy żywicą a włóknami. Włókna węglowe i aramidowe zwykle nie są w ten sposób pokrywane, co skutkuje gorszymi właściwościami adhezyjnymi. W pracy materiały organokrzemionkowe zostały uzyskane metodą zol-żel z użyciem różnych prekursorów krzemionkowych: metylotrimetoksysilanu (MtMOS), etylotrietoksysilanu (EtEOS) oraz tetrametoksysilanu (TMOS). Materiały te zostały naniesione na tkaninę z włókien szklanych oraz hybrydową tkaninę węglowo/aramidową, powodując zmianę ich właściwości powierzchniowych. Struktury chemiczne zbadano z użyciem spektroskopii Ramana, wykazując obecność ugrupowań chemicznych charakterystycznych dla krzemionki, jak również obecność organicznych grup funkcyjnych połączonych wiązaniami krzem-węgiel. Powierzchnie pokrytych włókien obserwowano pod skaningowym mikroskopem elektronowym (SEM), wskazując niepożądane zlepienie włókien przez pokrycia z prekursorów MtMOS i TMOS, przy braku takiego zlepienia przez pokrycia z prekursora EtEOS. Zwilżalność włókien szklanych przez żywicę epoksydową zbadano metodą elektrooptyczną, wykazując, że pokrycia z MtMOS i TMOS poprawiają zwilżalność, promując tym samym adhezję.

Słowa kluczowe: **zol-żel, pokrycia organokrzemionkowe, włókna szklane, włókna węglowe, włókna aramidowe**

INTRODUCTION

Textiles made of synthetic fibers are widely used in the production of polymer matrix composite materials for applications in the automotive, aeronautics, and other industries, but also for the construction of pipelines and storage tanks, including high-pressure vessels [1-3]. Despite the numerous advantages of such structural composites, they are characterized by structural defects, which are manifested in insufficient adhesion of the reinforcing fibers to the matrix. The inadequate adhesive strength of composites causes their delamination [4]. This phenomenon is particularly observed in the case of composite materials reinforced with carbon and aramid fibers. Delamination of the composite reduces the bearing capacity and durability of the defected product, and in the case of pressure vessels or pipelines, may cause their depressurization [5]. One of the possible methods to improve the adhesive strength is to coat reinforcing fibers by the sol-gel method. The process leads to an increase in wettability by an epoxy resin [6-10]. Commercially used textiles are composed of glass, carbon, or aramid fibers, or their mixtures. Glass fibers are commonly coated with silane films that serve both as a wetting-improving agent and adhesion promoter. Such coatings are not commonly used with carbon or aramid fibers. The silane film chemically binds (with Si-O covalent bonds) to the surface of the glass fiber. Wetting is improved by an increased chemical affinity of the resin to coated fibers, compared to uncoated ones. Better wetting enhances the adhesive connection between the fibers and the matrix (resin) because of the larger contact surface between the resin and fibers. Adhesion is enhanced, however, also by introducing chemical bonding between the resin and the silane. For example, in fiber coatings intended for use with epoxy resins, amine groups in the silane film may react with the epoxy groups in the resin, or vice versa - the epoxy groups in the silane may react with the amine hardener mixed with the resin. The roving (i.e. untwisted strands of hundreds or thousands of individual fibers), is usually subjected to silane treatment that doubles as sizing - protection of the fibers during further processing, e.g. weaving [4].

In this paper, the authors describe the synthesis and measurement of sol-gel silica coatings that improve the wettability of synthetic fibers by epoxy resin.

EXPERIMENTAL PROCEDURE

Materials

Organosilica coatings were synthesized by the sol-gel method and deposited on synthetic fibers. Various silica precursors were used: methyltrimethoxysilane (MtMOS, AlfaAesar), ethyltriethoxysilane (EtEOS, Sigma-Aldrich) and tetramethoxysilane (TMOS, Sigma-Aldrich). Ethanol (EtOH, Stanlab Sp.J.) was used as the solvent. The reactions were catalyzed by concentrated hydrochloric acid (HCl). Two different sols were obtained. In the first one MtMOS and TMOS (MtMOS/TMOS molar ratio = 4.2) were used as the precursors. In the second one, EtEOS was the precursor. The ingredients were homogenized with a magnetic stirrer for 1.5 hours.

Each sol was deposited on two kinds of textiles: a textile made of glass fibers with a chemically active finish (type ST-60, Tkaniny Techniczne w Pabianicach - S.A.) and a hybrid textile made of carbon and aramid fibers (type PDL 9018, SGL TECHNIK). Before coating deposition the textiles were cleaned in acetone, then in demineralized water and at the end in ethanol, using an ultrasonic bath. To deposit the coating, the substrate, in form of a textile, was immersed in a particular sol, then sonicated and left immersed in the sol overnight. After the deposition process the textiles were rinsed in methanol (MeOH, Stanlab Sp.J.) by an ultrasonic washer to remove the excess coating material. After drying in air the materials were thermally stabilized for 12 hours at 60°C with a controlled temperature gradient.

Measurements

The physicochemical properties were characterized by Raman spectroscopy with a Horiba Jobin Yvon LabRAM HR800 at the Laboratory of Sol-Gel Materials and Nanotechnology, Wroclaw University of Technology, and scanning electron microscopy (SEM) with a Zeiss EVO LS 15 at the Laboratory of Electron Microscopy, Wroclaw University of Environmental and Life Science. Raman spectroscopy was performed for structural characterization. The surface morphology of the samples was analyzed by SEM.

Fiber wetting speed tests were carried out on a stand for measuring the wetting process by the electro-optical method (Fig. 1) [11]. The stand was inspired by test stands described by earlier authors [12-14].

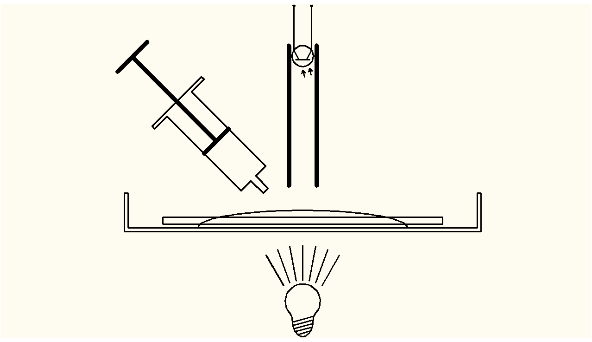

Fig. 1. Diagram of electrooptical method of investigating wetting process

Rys. 1. Schemat metody elektrooptycznego badania procesu zwilżania

A glass Petri dish with the examined piece of fabric is lit from the bottom by 8 LED. Above the Petri dish, in a collimating tube, a photodiode sensor is placed. The photodiode is connected to an electrical source and microammeter. The LED light is transmitted through the dish and the fabric in it, and induces current in the microammeter circuit. The induced current is proportional to the intensity of light reaching the photodiode, which in turn depends on the attenuation of light on the fabric. The attenuation weakens with progressing wetting, hence the stream of light reaching the photodiode intensifies. The measurement starts with injecting

10 mL of resin onto the fibers. The current is registered as a function of time. The wetting time is found on the graph as the time two tangents intersect [12]. The fiber wetting tests were performed using Araldite LY 1564 SP epoxy resin as the wetting agent. The measurements were carried out on glass fibers only - this is because the measurement method requires a sample which is at least partially translucent. However, the influence of the coating on the wettability properties should be similar also in case of other substrates because the coating properties determine the wettability of the coated fibers.

RESULTS AND DISCUSSION

Physicochemical properties

The SEM examinations show the surface morphology of the obtained coatings on the synthetic fibers. Figures 2 and 3 show two different coatings on glass fibers at 1000x magnification. Figures 4 and 5 show coating on carbon fibers and aramid fibers respectively, at 5000x magnification. Figure 2 clearly reveals the visible coating made using MtMOS and TMOS as precursors, which however, make the fibers stick together.

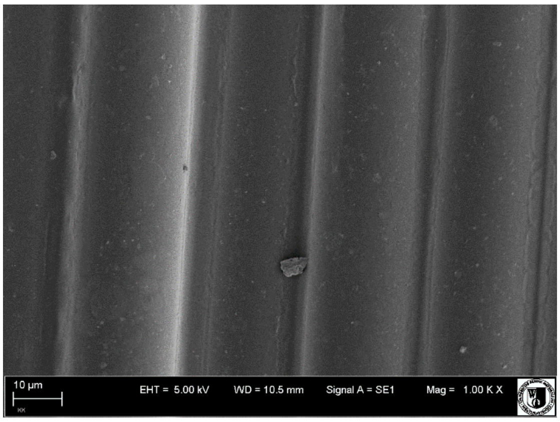

Fig. 2. SEM micrograph of glass fibers with coating made of MtMOS and TMOS as precursors

Rys. 2. Mikrografia SEM włókien szklanych z pokryciem z użyciem prekursorów MtMOS i TMOS

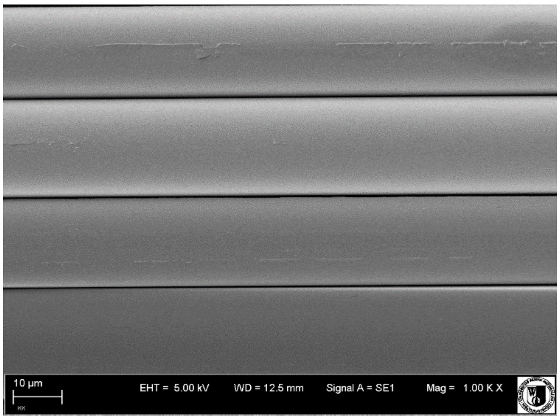

Fig. 3. SEM micrograph of glass fibers with coating made of EtEOS as precursor

Rys. 3. Mikrografia SEM włókien szklanych z pokryciem z użyciem prekursora EtEOS

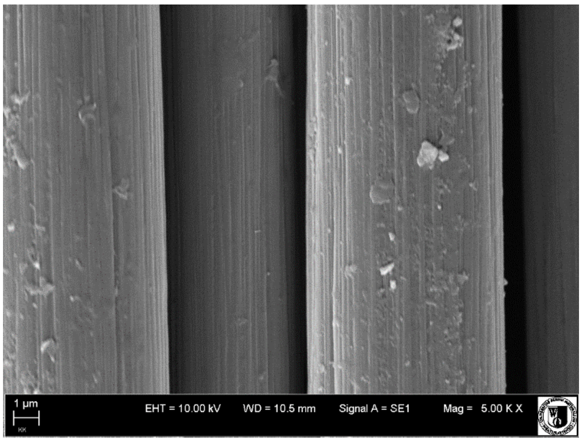

Fig. 4. SEM micrograph of carbon fibers with coating made of EtEOS as precursor

Rys. 4. Mikrografia SEM włókien węglowych z pokryciem z użyciem prekursora EtEOS

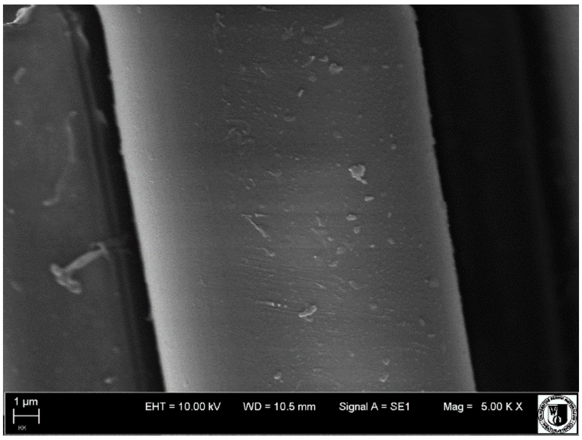

Fig. 5. SEM micrograph of aramid fibers with coating made of EtEOS as precursor

Rys. 5. Mikrografia SEM włókien aramidowych z pokryciem z użyciem prekursora EtEOS

The fiber bonding effect (the undesired phenomenon of binding of individual fibers by an excessive amount of coating material) does not occur in the sample with the coating obtained using EtEOS as the precursor, as presented in Figure 3. The SEM micrographs of the coated carbon fibers (Fig. 4) and coated aramid fibers (Fig. 5) also show an absence of fibers bonded by the coating. The lack of fiber bonding by the coatings may indicate that every fiber is individually coated.

The Raman spectra of uncoated and coated glass fibers, presented in Figure 6, show the similarity of structural characteristics of organosilica coatings and glass fibers used as the substrate, which correspond to the authors' expectations. Bands characteristic for the amorphous silica network are observed on the spectra.

Figure 7 shows the Raman spectra of uncoated and coated aramid fibers, which indicates the presence of the coating made of MtMOS and TMOS as the precursors. In the spectrum of this sample, the low intensity band characteristic of Si-OH groups (995 cm^{-1}) appeared. Bands characteristic of functional organic groups connected by silicon-carbon bonds (2205 cm^{-1}, 2413 cm^{-1}, 2574 cm^{-1}) also appeared. Identification of the chemical groups, carried out based on literature [15, 16], are presented in Table 1.

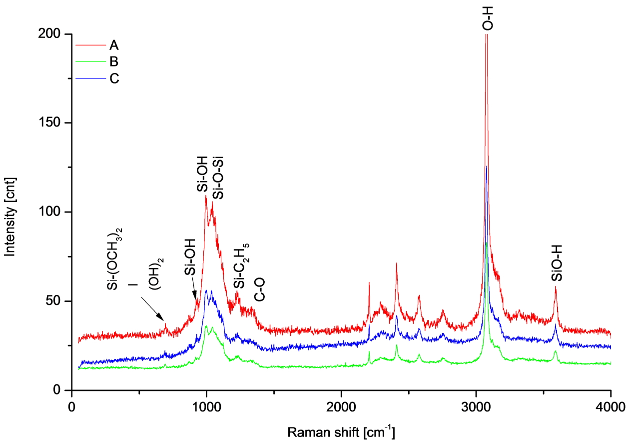

Fig. 6. Raman spectra of uncoated and coated glass fibers. A - uncoated glass fibers, B - glass fibers with coating made of MtMOS and TMOS as precursors, C - glass fibers with coating made of EtEOS as precursor

Rys. 6. Widmo Ramana niepokrytych oraz pokrytych włókien szklanych. A - niepokryte włókno szklane, B - włókno szklane z pokryciem wykonanym z użyciem MtMOS i TMOS jako prekursorów, C - włókno szklane z pokryciem wykonanym z użyciem EtEOS jako prekursora

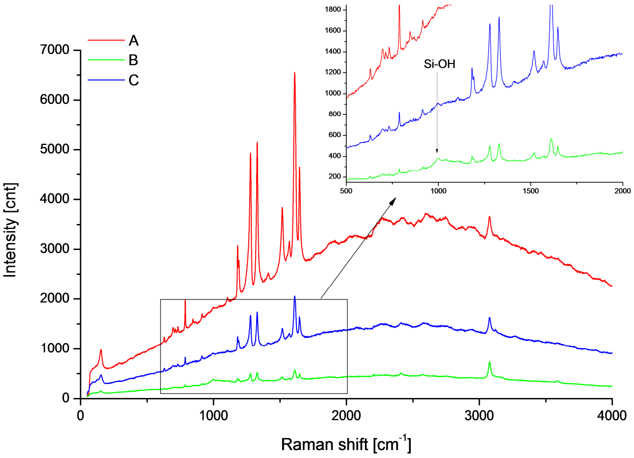

Fig. 7. Raman spectra of uncoated and coated aramid fibers. A - uncoated aramid fibers, B - aramid fibers with coating made of MtMOS and TMOS as precursors, C - aramid fibers with coating made of EtEOS as precursor

Rys. 7. Widmo Ramana niepokrytych oraz pokrytych włókien aramidowych. A - niepokryte włókno aramidowe, B - włókno aramidowe z pokryciem wykonanym z użyciem MtMOS i TMOS jako prekursorów, C - włókno aramidowe z pokryciem wykonanym z użyciem EtEOS jako prekursora

Literature data suggest that the amount and length of alkyl chains contained in the inorganic network would have effects on the solid surface energy, manifesting in the surface wettability [17, 18]. The alkyl groups of the precursor linked directly to the silicon are not reactive to hydrolysis reactions and they remain within the inorganic network formed by hydrolysis-condensation reactions, influencing the flexibility of the obtained materials [19]. In the case of the described materials, the aforementioned groups (methyl: -CH$_3$ and ethyl: -CH$_2$CH$_3$) are nonpolar and they can mask the polar and dispersive energy of the oxide film. A decrease in the solid surface energy is related to an increase in the number of remaining alkyl groups and the length of their chains. In accordance with the differences in surface energy, the surface wettability should also be different.

TABLE 1. **Identified chemical units and their Raman shifts [15, 16]**

TABELA 1. **Zidentyfikowane ugrupowania chemiczne i ich przesunięcia Ramanowskie [15, 16]**

Value read from the spectra [cm^{-1}]	Referenced Raman shift [cm^{-1}]	Structural unit
694 (Figure 6)	697	Si-(OCH$_3$)$_2$ (OH)$_2$
928 (Figure 6) 994 (Figure 6) 995 (Figure 7)	955÷830, 980	Si-OH
1047 (Figure 6)	1090÷1010	Si-O-Si
1216 (Figure 6)	1250÷1175	Si-CH$_2$R
1298 (Figure 6)	1300	C-O
2207 (Figure 6) 2205 (Figure 7) 2409 (Figure 6) 2413 (Figure 7) 2570 (Figure 6) 2574 (Figure 7) 2757 (Figure 6)	~2210, ~2410, ~2580, ~2750	not hydrolysable organic moieties
3070 (Figure 6)	3000÷3800	O-H
3594 (Figure 6)	3595	SiO-H

Wetting process

In Figure 8 the graph of the glass fiber wetting process (uncoated and coated) by epoxy resin is presented. Analysis of the current intensity changes in the sensor circuit during the fiber wetting process indicate an increased speed of the process for the fibers modified by the coating made of MtMOS and TMOS as precursors. This fact reveals improvement in the wetting process after fiber modification. It indicates that the material applied on the fibers has a greater affinity to the resin than uncoated fibers. In the case of fibers modified by the coating made of EtEOS as the precursor, the speed of the fiber wetting process decreased, which may indicate a low affinity of this material, caused by the relatively high amount of nonpolar ethyl groups, to the epoxy resin or the absence of coating.

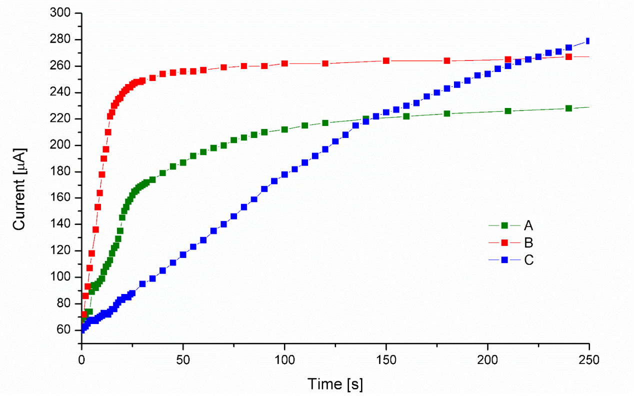

Fig. 8. Graph of glass fiber (uncoated and coated) wetting process by epoxy resin. A - uncoated glass fibers, B - glass fibers with coating made of MtMOS and TMOS as precursors, C - glass fibers with coating made of EtEOS as precursor

Rys. 8. Wykres procesu zwilżania włókien szklanych (niepokrytych oraz pokrytych) przez żywicę epoksydową. A - niepokryte włókna szklane, B - włókna szklane z pokryciem wykonanym z użyciem MtMOS i TMOS jako prekursorami, C - włókno szklane z pokryciem wykonanym z użyciem EtEOS jako prekursora

CONCLUSIONS

This work describes a method of modifying the surface of synthetic fibers by the sol-gel method. It was observed that different kinds of fibers have a different affinity to the applied materials, resulting from the physicochemical structure of the fibers.

Based on SEM analysis, it was noticed that the undesired fiber bonding effect depended on the precursor used. For the materials synthesized using a combination of MtMOS and TMOS as the precursor, this undesirable effect occurs, but for the obtained sol-gel materials based on the EtEOS precursor, the fiber bonding effect did not occur.

It was also found, however, that the coatings made of MtMOS and TMOS as precursors perform better in improving the wettability of the fibers by epoxy resin. Improvement in the glass fiber wettability was obtained to an extent even greater than that achieved during the production of glass fiber fabrics (pre-applied preparations). This may indicate that it is possible to improve carbon and aramid fiber wettability using the same coatings.

Acknowledgements

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